UNIVERSIDADE ESTADUAL DE CAMPINAS
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ÁDINA LIMA DE SANTANA

Application of supercritical and pressurized liquid technologies for the valorization of turmeric wastes: obtaining of bioactives, cost of manufacture, phase equilibrium and encapsulation of extracts

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Supervisor/Orientadora: Prof^{a}. Dr^{a}. Maria Angela de Almeida Meireles Petenate

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A ata de Defesa, assinada pelos membros da Comissão examinadora, consta no processo de vida acadêmica do aluno

´´Faça o seu melhor na condição que tem, enquanto não tem condições melhores para fazer melhor ainda´´

(Mario Sergio Cortella)

´´Não importa se você faz certo ou errado. As pessoas sempre vão encontrar um motivo para te criticar´´

(Clarice Lispector)

´´Seja menos curioso sobre as pessoas e mais curioso sobre as ideias´´

(Marie Curie)

´´Todos estes que aí estão
Atravancando o meu caminho,
Eles passarão...
Eu passarinho!´´

(Mario Quintana)

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RESUMO

Além de ser uma perspectiva atual, a obtenção de compostos bioativos a partir de rejeitos agroindustriais é uma alternativa viável para o aproveitamento destes materiais, o que resulta na formação de produtos com características diferenciadas e alto valor agregado. No caso da cúrcuma (*Curcuma longa* L.), que possui vasta aplicação como corante natural, a quantidade de rejeito sólido gerado a partir dos processos de extração de óleos voláteis e curcuminóides (pigmentos amarelos) é elevada, e chega a atingir aproximadamente a quantidade de matéria-prima bruta utilizada para se realizar os procedimentos; por exemplo, para se obter óleo volátil por hidrodestilação, 98% de rejeito sólido é gerado para se obter da matéria-prima bruta apenas 2% de extrato. Esses resíduos possuem composição atrativa em termos de carboidratos que lhe conferem aplicação para a formulação de novos produtos, seja na forma de amido isolado, seja para produção de biofilmes ou açúcares simples e etanol a partir de hidrólise. Além de carboidratos, esses rejeitos possuem curcuminóides, que lhe conferem poder corante e efeitos antioxidantes. Diante disso, esta tese propõe alternativas sustentáveis para a valorização dos rejeitos de cúrcuma gerados a partir de processos que empregam fluidos supercríticos e líquidos pressurizados. Inicialmente foi investigado o cenário promissor da utilização de fontes não convencionais de amido para fins comerciais, além das tendências e perspectivas futuras para inclusão dos resíduos de cúrcuma como fonte complementar para o mercado de amidos. Posteriormente, foram investigadas duas alternativas para o aproveitamento dos rejeitos de cúrcuma, que consistem na realização de ensaios de hidrólise parcial com o uso de água pressurizada e na investigação do impacto das tecnologias de extração com dióxido de carbono supercrítico e etanol pressurizado na modificação física dos rejeitos de cúrcuma e nos subsequentes amidos isolados. A partir da reação de hidrólise foram estudados dois produtos, um extrato líquido e o rejeito sólido, ambos constituídos de curcuminóides e carboidratos. Não fugindo dessa questão do aproveitamento, o comportamento a altas pressões do rejeito parcialmente hidrolisado e dos óleos voláteis de cúrcuma foi estudado a partir do levantamento de dados de equilíbrio de fases empregando-se o método sintético-visual sem retirada de amostra, cujo aparato experimental foi construído e validado nesta tese. Diante da baixa estabilidade e pobre absorção dos compostos bioativos da cúrcuma no organismo humano, foram realizados ensaios de encapsulação dos extratos de curcuminóides e óleos voláteis em polietilenoglicol com o intuito de oferecer um novo produto de maior estabilidade em termos de biocompostos com efeitos antioxidantes.

Palavras-chave: Resíduos agroindustriais, cromatografia em camada fina, equilíbrio de fase, hidrólise parcial, micropartículas.

ABSTRACT

In addition to being a current perspective, obtaining bioactive compounds from agroindustrial wastes is a viable alternative for the use of these materials, which results in the formation of products with differentiated characteristics and high added value. In the case of turmeric (*Curcuma longa* L.), which has a wide application as a natural dye, the amount of solid waste generated by the extraction of volatile oil and curcuminoids (yellow pigments) is elevated and reaches approximately the amount of the raw material used to carry out the procedures, i.e., to obtain volatile oil using hydrodistillation, 98% solid waste is generated to obtain only 2% crude extract from raw material. These residues have attractive composition in terms of carbohydrates that give it application for the formulation of new products, either as an isolated starch or for the production of biofilms or simple sugars and ethanol from hydrolysis. In addition to carbohydrates, these materials have curcuminoids, which attribute it colorant power and antioxidant effects. In this context, this thesis proposes sustainable alternatives for the valorization of the turmeric wastes generated from processes that use supercritical fluids and pressurized liquids. We initially investigated the promising scenario of the use of unconventional sources of starch for commercial purposes, as well as future trends and perspectives for inclusion of turmeric residues as a complementary source for the starch market. Afterwards, we investigated two alternatives aimed for the reuse of turmeric wastes, which consists of application of partial hydrolysis using pressurized hot water and the investigation of the impact generated by extraction technologies using supercritical carbon dioxide and pressurized liquid ethanol in the physical modification of turmeric wastes and the subsequently isolated starches. From the hydrolysis reaction, two products, i.e., a liquid extract and the solid waste, both consisting of curcuminoids and carbohydrates, were studied. High-pressure phase behavior of the turmeric partial hydrolyzed waste and volatile oils was studied through acquisition of phase equilibrium data using the synthetic-visual method without sample withdrawal, which experimental apparatus was constructed and validated in this thesis. In view of the low stability and poor absorption of turmeric bioactive compounds in the human body, encapsulation tests of curcuminoids ethanolic extract and volatile oils in polyethylene glycol were carried out in order to provide a new product with greater stability in terms of bioactives with antioxidant effects.

Keywords: Agro-industrial wastes, thin-layer chromatography, phase equilibrium, partial hydrolysis, microparticles.

SUMÁRIO

- CAPÍTULO 1 –

Introdução e objetivos

Este capítulo aborda as circunstâncias que encadearam o desenvolvimento desta tese, uma singela continuação do ciclo de pesquisas realizado pelo grupo de pesquisas Lasefi, cujo alvo está em atingir o máximo aproveitamento dos rizomas de cúrcuma (*Curcuma longa* L.). Nesta etapa foi feita uma breve revisão das tecnologias de fluidos supercríticos e líquidos pressurizados usadas nesta tese para estudar o aproveitamento dos rejeitos de cúrcuma, o comportamento termodinâmico dos extratos e posterior formação de partículas.

1 INTRODUÇÃO

Cúrcuma (*Curcuma longa L.)* é uma planta que possui utilidade histórica para fins medicinais, datada de aproximadamente 4000 anos (Prasad e Aggarwal, 2011). Além disso, possui propriedades de conservação e atribuição de cor, que lhe permitiram aplicação nas indústrias de alimentos, têxtil, farmacêutica e cosmética (Ching et al., 2014). O Brasil é o décimo quarto produtor desta matéria prima, cuja produção mundial está estimada entre 800.000-1100.000 toneladas anuais (Aaditya, 2014).

Os compostos bioativos majoritários desta matéria-prima são os curcuminóides e o óleo volátil. Os curcuminóides são a curcumina (60-80 g/100g), a demetoxicurcumina (15-30 g/100g) e a bisdemetoxicurcumina (2-6 g/100g) (Rohman, 2012), enquanto que os principais constituintes do óleo volátil deste material são os terpenos, dentre eles a ar-turmerona ou turmerona aromática (Carvalho et al., 2014, Braga e Meireles, 2007). A literatura aborda que os níveis em base seca dos curcuminóides na cúrcuma cultivada no Brasil variam de 1,4 a 6,1 g/100g, enquanto que os níveis da fração volátil variam de 1 a 7,6 mL/100g (Rosso e Mercadante, 2009).

Estudos focados na aplicabilidade dos compostos bioativos presentes nesta matéria-prima (Leonel et al., 2003, Kuttigounder et al., 2011, Braga et al., 2006a) comprovam sua atuação promissora para o preparo de massas, molhos, iogurtes e hambúrgueres de coelho (Park et al., 2012, Mancini et al., 2015, Lim et al., 2011) no que diz respeito ao aumento da vida de prateleira, além da atribuição de cores e sabores diferenciados dos produtos convencionais.

Processos de extração de óleos voláteis e curcuminóides a partir dos rizomas de cúrcuma geram elevada quantidade de rejeitos, que geralmente são descartados e não se tem registro de aplicação, salvo para alimentação de caldeiras (Abraham et al., 2013) ou componente para formulação de filmes comestíveis (Maniglia et al., 2014). Por exemplo, hidrodestilação contribui para se gerar 98% de rejeito sólido para se obter apenas o rendimento de 2% em extrato (Braga et al., 2003), enquanto que o processo de extração com líquidos pressurizados (*Pressurized liquid extraction*, PLE) a produção de rejeito sólido varia de 87-91% (Osorio-Tobón et al., 2014).

Além de ser uma fonte de amido não-convencional, a cúrcuma também pode ser aproveitada na forma de substrato para posterior reação de hidrólise, resultando na obtenção de açúcares de cadeias menores para formulação de novos produtos (Moreschi et al., 2004, Leonel et al., 2003).

A extração com fluido supercrítico (*Supercritical fluid extraction*, SFE) é uma operação unitária que explora as propriedades dos solventes acima de seus pontos críticos para extrair ou separar componentes de uma mistura (Brunner, 1994). A intensificação de processos visando a máxima obtenção de compostos bioativos através da associação das tecnologias SFE e PLE foi usada com sucesso para extração de carotenoides da fibra de palma prensada (Cardenas-Toro et al., 2015), de curcuminóides da cúrcuma desaromatizada (Osorio-Tobón et al., 2014), polifenóis do alecrim (Zabot et al., 2015), de beta-ecdisona do ginseng brasileiro (Debien et al., 2015), cafeína e catequinas das folhas de chá verde (Bermejo et al., 2015), entre outros. A principal vantagem deste método está no curto tempo de extração e baixo consumo de solvente (Suchan et al., 2004).

O estudo do equilíbrio de fases a altas pressões e temperaturas de misturas fluidas fornece informações de interesse para aplicações práticas e científicas para desenvolvimento e otimização de processos de separação. Esta metodologia é aplicada em substancias de interesse para os setores de alimentos, produtos farmacêuticos, químicos, entre outros, a fim de auxiliar a recuperação destas substancias em posteriores etaps de separação como os de extração com fluido supercrítico, absorção de gases ácido, destilação e assim por diante (Bogatu et al., 2006, Sandler, 2006, Avdeev et al., 2004, Richon, 2009).

Os curcuminóides, apesar da vasta atribuição de efeitos funcionais à saúde humana, possuem baixa estabilidade e absorção pelo organismo humano (Gómez-Estaca et al., 2015). Diante desta questão o processo de coprecipitação possui relevância na indústria alimentícia em virtude de sua habilidade em proteger compostos sensíveis presentes nos alimentos contra reações de degradação e perda de voláteis (Chranioti et al., 2015). Cocristalização ou coprecipitação é uma forma de encapsulação que envolve cristalização ou precipitação espontânea em que o composto de interesse é retido no material de parede (Zuisam e Nedoviċ, 2010).

A coprecipitação com aplicação de fluido supercrítico (SAS, Supercritical Antisolvent) ou líquido comprimido como antisolvente favorece o controle do tamanho de partículas coprecipitadas a partir do ajuste dos parâmetros do processo, tais como pressão, temperatura, e vazão de solvente e antisolvente. Este processo tem sido aplicado para a encapsulação dos mais variados compostos bioativos, como os carotenoides luteína (Miguel et al., 2008) e bixina (Santos e Meireles, 2013).

Muitas variáveis contribuem para a qualidade dos produtos precipitados. Altas concentrações de soluto podem contribuir com o aumento do tamanho da partícula Com o aumento da vazão de CO_2, o diâmetro da gota inicial e o tempo de evaporação são reduzidos, e o tamanho médio de partícula poderá diminuir (Guha et al., 2011, Kalani e Yunus, 2011, Sanguansri e Augustin, 2006)

A aplicação da tecnologia supercrítica para estudo de extratos vegetais visando cenários promissores de comercialização é objeto das linhas de pesquisa do LAboratório de Tecnologia Supercrítica: Extração, Fracionamento e Identificação de extratos vegetais - LASEFI (DEA/FEA/UNICAMP). No referido laboratório, com cerca de 30 anos de existência, são desenvolvidas pesquisas com diferentes matrizes vegetais com destaque à aplicação da tecnologia de fluidos supercríticos e líquidos pressurizados.

A partir das considerações supracitadas, esta tese conclui um ciclo de trabalhos realizados por nosso grupo de pesquisa, no que se refere à combinação/intensificação de processos aplicados aos rizomas de cúrcuma, que se iniciou com extração do óleo volátil dos rizomas através da extração supercrítica com CO_2 (Carvalho et al., 2014), seguido pela extração dos curcuminóides através da extração com líquidos pressurizados (PLE) cujo solvente foi o etanol (Osorio-Tobón et al., 2014).

Nesta tese foram investigadas duas alternativas de aproveitamento do rejeito desaromatizado e despigmentado (ou seja, pós SFE e PLE) para a recuperação dos compostos bioativos presentes nessas matrizes, que consistiram na submissão desse material a ensaios de hidrólise hidrotérmica parcial (executada em aparato que emprega o processo PLE) a partir da utilização de condições brandas de temperatura e pressão, e no isolamento dos amidos dos materiais submetidos individualmente às etapas de SFE e PLE.

Também foi estudado o comportamento termodinâmico do rejeito parcialmente hidrolisado e dos óleos voláteis através da coleta de informações referentes ao equilíbrio de fases destes materiais na presença de diferentes solventes. Essas informações foram coletadas em um aparato experimental que foi construído e validado nesta tese. O aparato experimental emprega o método puramente visual, em que não há quantificação das composições durante os estágios de equilíbrio.

O rejeito parcialmente hidrolisado teve seu comportamento termodinâmico estudado pois se acreditava que pelo fato de possuir mais de 80% de carboidratos em sua composição esse material fosse um polímero promissor para ensaios de encapsulação realizados em aparato experimental que emprega o processo SAS (Supercritical Antisolvent).

Infelizmente isso não ocorreu, por mais que se variassem os tipos de solvente, concentração de sólidos na solução e as condições de temperatura, pressão ou vazão de antissolvente, todo esforço foi inútil por resultar em entupimentos no sistema injetor, na bomba e no filtro de linha, além de não ocorrer nenhuma precipitação de particulados. Testes com amido modificado também foram realizados, porém resultaram no mesmo efeito. A adoção do polietilenoglicol fez com que houvesse êxito nos experimentos, sem acontecer problemas com os equipamentos.

Diante da baixa estabilidade e pobre absorção dos compostos bioativos de cúrcuma no organismo humano, foram realizados ensaios de coprecipitação dos óleos voláteis e dos extratos de curcuminoides e polietilenoglicol a fim de oferecer produtos de maior estabilidade. Este estudo finaliza a tese.

1.2 JUSTIFICATIVA

Atualmente é crescente a demanda por compostos bioativos, substâncias de alto interesse comercial, e por técnicas de separação que sejam ecologicamente corretas, que não degradem o extrato ou deixem resíduos poluentes.

Neste contexto, esta tese estuda o aproveitamento dos rejeitos de cúrcuma através dos usos das tecnologias SFE e PLE, visando a máxima utilização da matéria-prima para a recuperação de curcuminóides e carboidratos.

1.3 OBJETIVOS

1.3.1 Objetivo geral

Valorização dos rejeitos de cúrcuma para obtenção de compostos bioativos a partir das tecnologias PLE e SFE.

1.3.2 Objetivos específicos

1. Investigar o estado da arte referente a funcionalidade das fontes não-convencionais de amido para atuação como fontes alternativas às matérias-primas convencionais;
2. Realizar dos ensaios de hidrólise hidrotérmica parcial e isolamento dos amidos da cúrcuma residual dos processos SFE e PLE;
3. Estudar a composição química e viabilidade econômica dos produtos obtidos com ensaios de hidrólise parcial;
4. Estudar o impacto da SFE e PLE nos rejeitos de cúrcuma e seus amidos isolados;
5. Analisar o estado da arte das metodologias experimentais utilizadas para estudo do comportamento de fases a altas pressões de substâncias de interesse para a indústria alimentícia;
6. Construir e validar de uma unidade de equilíbrio de fases a altas pressões que emprega o método sintético-visual;
7. Estudar o comportamento de fases do óleos voláteis e do rejeito sólido de cúrcuma na presença de dióxido de carbono, etanol e dimetilsulfóxido;
8. Formar partículas dos extratos de curcuminóides e dos óleos voláteis de cúrcuma através da coprecipitação dos mesmos em polietilenoglicol.

1.4 ESTRUTURA DO TRABALHO

A tese está dividida em 10 capítulos, nos quais estão registrados os resultados obtidos das distintas etapas. Nestes capítulos estão inclusos o levantamento bibliográfico, artigos publicados e artigos submetidos para publicação. No **Capítulo 1 – Introdução e objetivos** – são apresentados sucintamente os objetivos pretendidos neste trabalho e as etapas envolvidas para a sua realização. As atividades cumpridas neste trabalho estão exibidas na Figura 1.

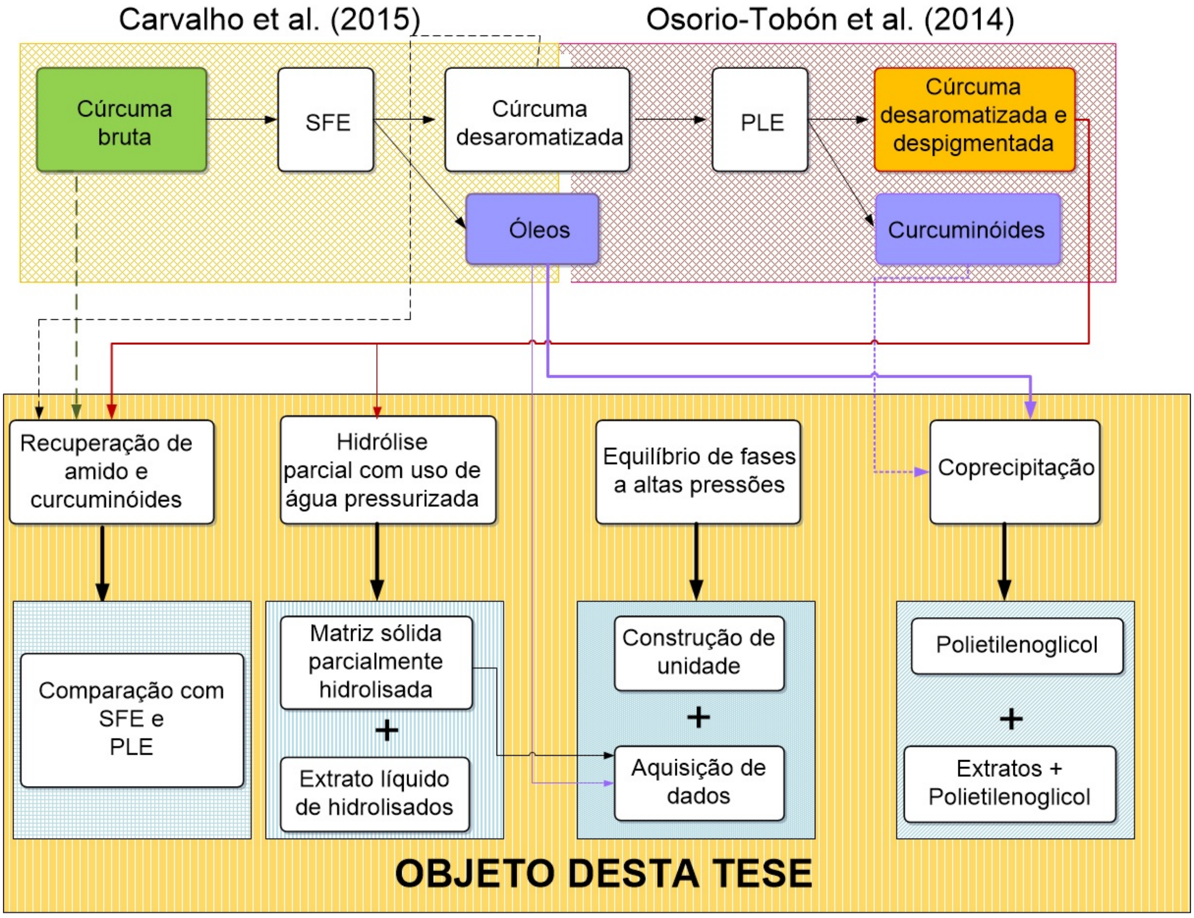

Figura 1. Fluxograma das atividades realizadas nesta tese.

O **Capítulo 2 – New starches are the trend for industry applications: a review** – mostra características e aplicações práticas de fontes não-convencionais de amido.

No **Capítulo 3 – Thin-layer chromatography profile of turmeric (*Curcuma longa* L.) non-commercial products obtained after hydrothermal hydrolysis** – está relatada a composição química da porção não comercial (resíduos) da cúrcuma através de uma abordagem qualitativa por cromatografia de camada delgada.

O **Capítulo 4 - Partial-hydrothermal hydrolysis is an effective way to recover bioactives from turmeric wastes** – detalha o procedimento experimental para hidrólise parcial da cúrcuma desaromatizada e despigmentada sob uso de água pressurizada em condições brandas para a obtenção de um extrato líquido composto e de uma fração sólida residual. Ambos os produtos possuem qualidade relevante no que diz respeito aos níveis de curcuminóides e carboidratos. Além disso, foi investigada a viabilidade econômica do processo para a obtenção destes dois produtos.

O **Capítulo 5 – Starch recovery from turmeric wastes using supercritical technology** – investiga o reaproveitamento da cúrcuma residual dos processos de extração que empregam fluidos supercríticos e líquidos pressurizados: a parte experimental retrata o efeito dos processos de extração nas características dos resíduos e a parte econômica avalia a viabilidade econômica de reaproveitamento desses rejeitos na forma de amido isolado.

O **Capítulo 6 – High-pressure phase equilibrium methodologies applied for food systems -** contextualiza a aplicação de métodos experimentais para aquisição de dados de equilíbrio de fases a altas pressões, aplicado a sistemas em que substâncias de interesse para a indústria alimentícia estão envolvidas.

O **Capítulo 7 – High-pressure phase behavior of turmeric waste and extracts in the presence of carbon dioxide, ethanol and dimethylsulfoxide** – mostra as etapas de construção, validação do aparato de equilíbrio de fases e sua aplicação para obtenção de dados para sistemas que envolvem os óleos voláteis e o rejeito sólido de cúrcuma.

O **Capítulo 8 - Coprecipitation of turmeric extracts and polyethylene glycol with compressed carbon dioxide –** finaliza este ciclo de trabalhos com a análise dos coprecipitados dos extratos de cúrcuma (extrato etanólico de curcuminóides e óleos voláteis) a partir do uso do polietileno glicol como material de parede.

O **Capítulo 9 – Discussão geral** – mostra discussões generalizadas referentes aos resultados obtidos nos capítulos desta tese.

No **Capítulo 10 - Conclusões gerais e sugestões para trabalhos futuros** – está apresentada uma conclusão resumida dos resultados obtidos em cada capítulo, e sugestões de novos trabalhos, que motivem a continuidade desse ciclo de estudos.

1.5 REFERÊNCIAS BILIOGRÁFICAS

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- CAPÍTULO 2 –

New starches are the trend for industry applications: a review

A versatilidade do uso de matérias-primas amiláceas não-convencionais foi investigada neste capítulo. Além de serem fontes renováveis de energia, os novos amidos têm potencial de aplicação comercial, cuja incorporação em formulações de produtos proporciona redução de custo do produto final.

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New Starches are the Trend for Industry Applications: A Review

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Abstract Starch is widely consumed by humans as an inexpensive and stable available carbohydrate source, and much work has been performed on the structure, functionality and applicability of starches. Although conventional sources of starch, such as corn and potato, other sources with improved properties are becoming significant to allow simpler and more robust processes. The feasibility of the use of new starches, i.e., legume, seed and palm, as renewable materials for commercial application may provide cost reduction of raw material in industries. Little information is available on the structure, properties and practical applicability of non-conventional sources of starch. Thus, it is necessary that these starches be studied to obtain and report their structural parameters, information that is required to gain competitiveness in an international-scale industry. A review of properties, applications, future trends and perspectives of some new starches is presented in this review.

Keywords New starches, Non-conventional starches, Turmeric, Annatto

1. Introduction

Most foods are multi-component systems that contain complex mixtures of water, carbohydrates, proteins, lipids and numerous minor constituents. Starch is a macro-constituent of many foods, and its properties and interactions with other constituents are of interest to the food industry and for human nutrition.

Sales of starches and derivatives were $51,2 billion in 2012 and are expected to reach $77,4 billion by 2018, a compound annual growth rate (CAGR) of 7,1% between 2012 and 2018 [1]. Indeed, the starch derivative market is expected to growth extensively at a rate of 6,2% from 2014 to 2019 because of the technological advancements occurring in the industry [2].

Starch application in industrial-related products dates back to ancient times [3]. For industrial uses, the selection of a starch is made by considering its availability and also its physicochemical characteristics, which vary depending on the source [4].

The inherent functional diversity of materials extracted from different biological sources adds to the range of applications. Currently, some uses of starch include the following: as a food additive to control the consistency and texture of sauces and soups, to resist the breakdown of gel during processing and to increase shelf life of an end product in the food industry; in the laundry sizing of fine fabrics and skin cosmetics in the textile and cosmetic industry; for enhancing paper strength and printing properties in the paper industry; as drug fillers in the pharmaceutical industry; as binders in the packaging industry [3].

Globally, intensive efforts have been channeled toward producing polysaccharide derivatives of different types of starch for diverse applications in different industries [5]. The widespread use of starch is justified because it is inexpensive and available in large quantities. In addition, it is relatively pure and does not require intense purification, as is often the case with other natural polymers such as cellulose and gums [6].

Commercial starches are obtained from cereals, such as corn, wheat and various types of rice, and from tubers or roots, such as potato and cassava (or tapioca) [7].

The main botanical source of starch is maize, accounting for about 80% of the world market. Maize starch is an important ingredient in the production of foodstuffs, and has been widely used as a thickener, stabiliser, colloidal gelling agent, water retention agent and as an adhesive [8].

The use of new starches, i.e., starches from non-conventional sources such as those isolated from roots and tubers could provide options for extending the spectrum of desired functional properties, which are needed for added-value food product development [7].

With the industry demand for new technological properties, several non-conventional starch sources, with different properties have been studied due to interest in using native starches for food production instead of using chemically modified starches [9]. Currently, these native

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starches are usually ignored and wasted during the isolation and separation of small molecule bioactive ingredients [10].

A large number of scientific investigations concerned with the use of starch have been published to date. Table 1 shows the literature searched in the "Scopus" and "Web of Knowledge" databases using the keywords "starch", "food" and "processing".

Table 1. Number and type of documents published in the Scopus and Web of Knowledge databases between 2010 and 2014

Year	**Database**	
	Scopus	Web of Science
2014	85	112
2013	153	185
2012	154	189
2011	154	205
2010	147	183
Document type		
Article	512	710
Review	72	108
Book chapter	44	3
Conference paper	32	75

A comprehensive study on the relationship between the structural characteristics and functional properties of starches from different sources could provide important information for optimizing industrial applications.

Much work was done for a better understanding of the new starches characteristics. This review summarises some of several non-conventional sources of starch, in terms of properties, applications, future trends and perspectives, to provide a greater range of options for increasing the use of these new starches.

2. Classification

Starch can be divided into three categories based on its nutritional classification: rapidly digestible starch, slowly digestible starch and resistant starch. Resistant starch is not digested in the small intestine and enters the colon for fermentation [11].

The starch molecule can be extracted and sold as such (native starch), but it can also undergo several processing operations to improve its proprieties and enlarge the range of its uses (modified and hydrolyzed starches).

Native starch is the starch chain extracted from raw material in its original form. Modified starches are starches that are modified by a chemical, physical or enzymatic process. Hydrolyzed starch is the starch chain broken into smaller glucose chains via a hydrolysis reaction.

Native starches has limited application in industry because it exhibits some disadvantages such as a low shear resistance, high retrogradation and syneresis, and it is often modified by physical, chemical or enzymatic processes or a combination thereof to provide desirable functional properties for determined uses.

Physically modified starch can be considered as a natural material and a highly safe ingredient [12]. Nevertheless, the commonly used ways of obtaining modified starch are complex, expensive and time consuming [13, 14] and frequently employ treatments with hazardous chemicals.

Many industrial applications require the modification of native starches, including oxidation, esterification, hydro-xymethylation, dextrinization and cross-linking. These modifications overcome the limitations of native starch properties (e.g., stabilizing the polymers against severe heating, shear, freezing or storage).

Such modified starches have innumerable applications in the food industry, particularly in confectionery and bakery processes for thickening and emulsification, and in non-food sectors as adhesive gums, biodegradable materials and sizing agents in the textile and paper industries [15].

3. Properties of Starch

Starch is composed of two different glucan chains, amylose (a linear polymer of a-D-glucose units linked by a-1,4 glycosidic linkages) and amylopectin (a branched polymer of a-D-glucose units linked by a-1,4 and a-1,6 glycosidic linkages), representing approximately 98–99% of the dry weight [16]. These polymers have the same basic structure but differ in their length and degree of branching, which ultimately affects their physicochemical properties [13].

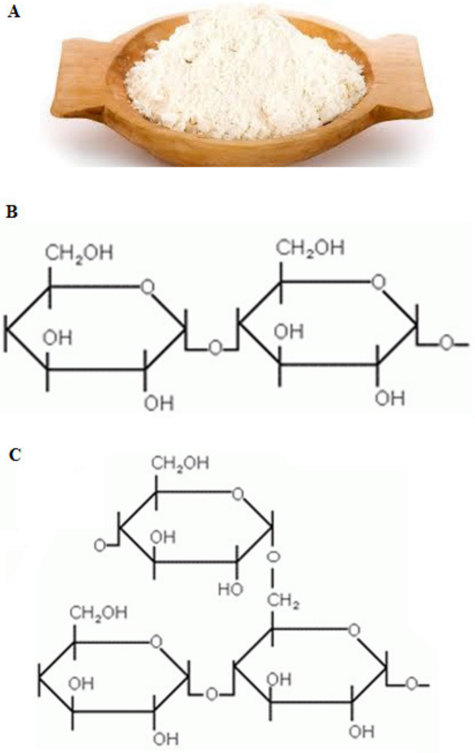

Figure 1. Starch as it such (A) [17], and chemical structure of amylose (B) and amylopectin molecules (C) [18]

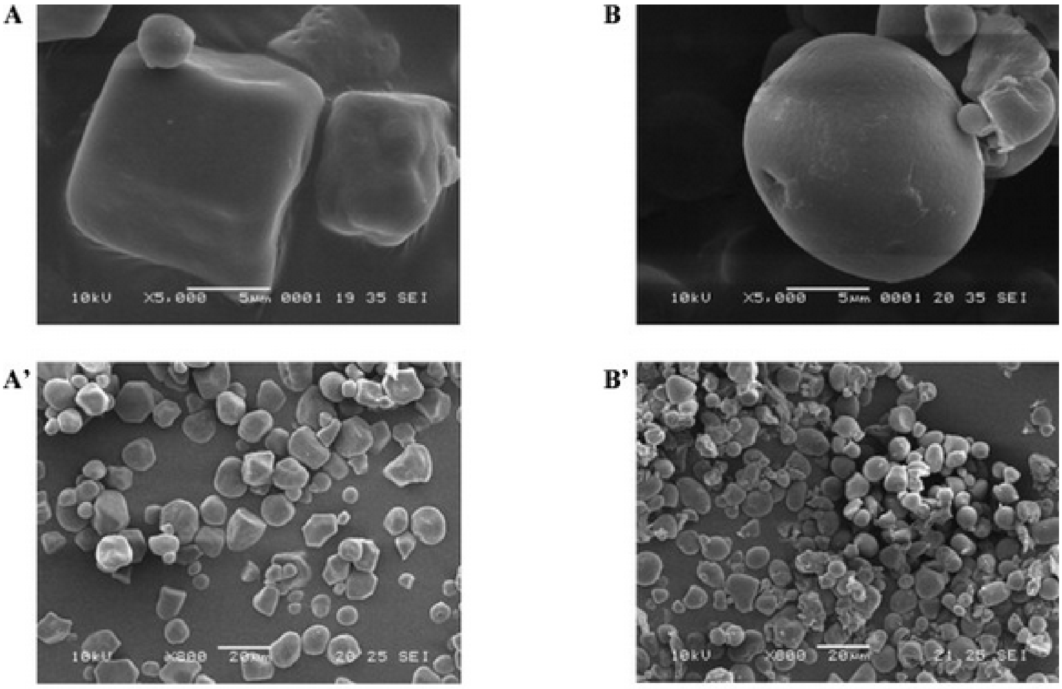

Figure 2. Scanning electron microscopy (SEM) images of_corn (A and A'), and ramon (B and B') granules [7]

Starch varies greatly in form and functionality between and within botanical species and even from the same plant cultivar grown under different conditions. This variability provides starches of different properties, but it can also cause problems in processing due to inconsistency of the raw materials [19].

Figures 2 and 3 deal with structure and whole raw material between two plants that represent common and uncommon sources of starch, respectively.

Figure 3. Corn (A) [20] and ramon (B) [7] plants

Physicochemical (e.g., gelatinization and retrogradation) and functional (e.g., solubility, swelling, water absorption, syneresis and rheological behavior of pastes and gels) properties determine the potential uses of starches in food systems and other industrial applications.

These properties depend on the molecular structural composition of amylose and amylopectin; how they are arranged in starch granules plays an important role in formulations. In food products, the functional roles of starch could be as a thickener, binding agent, emulsifier, clouding agent or gelling agent.

Another important material property of starch is its glass transition, in which the molecules in the amorphous fraction of starch transform from a frozen to a mobile state. Glass transitions of starch have been measured using, e.g., differential scanning calorimetry (DSC) [21]. DSC is one of the most suitable techniques that enable accurate determination of the temperature at which state changes occur in biopolymer systems [22].

The most important physical changes that occur during the industrial processing of native starches are the swelling of the granules upon heating in an excess of water and the subsequent solubilization of amylose and amylopectin ('gelatinization'). Amylose diffuses out of the swollen granule and, upon cooling, forms a continuous gel phase. Swollen amylopectin-enriched granules aggregate into gel particles, generating a viscous solution. This two-phase structure, called starch paste, is desirable for many applications in which processed starches are used as thickeners or binders. Native starches have few other uses because the polymers are relatively inert [15].

Starch hydrolysis has been used in the food industry to convert starches, starch derivatives and starch saccharification products, which have several applications in food processing. The products from starch hydrolysis are certainly highly versatile ingredients used in the food industry and are used in a wide range of food products due to both their functional and nutritional properties [23].

4. Applicability

With wide applications in the food, textile, pharmaceutical, paper and, recently, synthetic polymer industries, starch plays prominent a role even in technological developments [24]. In addition, it is purified in the shape of micro-granules and widely used as a solid matrix for the encapsulation of food ingredients [25].

Starch has been investigated widely for its use in the potential manufacture of products, including water-soluble pouches for detergents and insecticides, flushable liners and bags and medical delivery systems and devices [26]. In ceramic technology, starch is a frequently used as pore-forming agent [27].

Novel approaches in polymer manufacture imply the use of composites; for example, polypropylene carbonate (PPC) is being doped with starch to create ecofriendly, naturally degrading materials, thus reducing the negative effect of polymeric waste production. Starch also shows very interesting optical properties; for example, the second-harmonic generation of light can be achieved on starch granules [28].

The use of edible films in the food industry has been constantly increasing, and starch-based films play a key role in the food industry because starch is abundant, inexpensive, naturally renewable, biodegradable polysaccharide industries especially food products and more readily available worldwide than other natural resources, in applicability part [29].

One way of increasing the usefulness of starch for industrial applications is by treating it with acid at elevated temperature. It is mainly the amorphous part of the native starch that is subjected to acid hydrolysis, and this method is used as a pretreatment in various industrial applications (e.g., for gums, pastilles, jellies) to decrease viscosity and increase gel strength. Acid hydrolysis is also used to determine the degree of crystallinity of native starches and to prepare starch nanocrystals [21].

In addition to physical modifications, blending different native starches is another way to obtain new starch properties. It may also offer an economic advantage when a more expensive starch can be partially replaced by a cheaper alternative without affecting product quality [30]. Jackfruit, a source of new starch; the structure of its starch in formulation with sodium alginate is illustrated in Figure 4. Table 2 lists some general applications of starch.

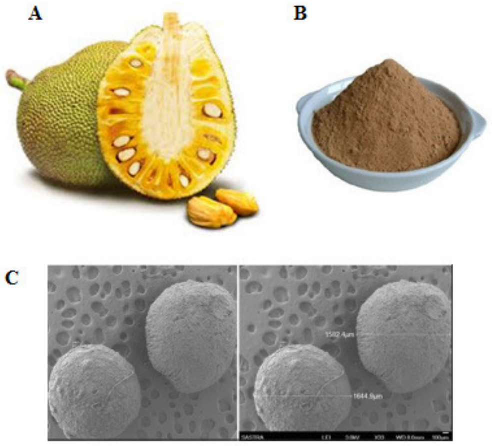

Figure 4. Whole jackfruit (A) [31], jackfruit seed powder (B) [32] and Scanning electron microscopy (SEM) of jackfruit seed starch-sodium alginate optimized formulation (C) [33]

Table 2. Applications of starches

Type of starch	Applications	References
Native starches	Paper, Textile food, cardboard and potable alcohol production (FI) industry	[34]
Hydrolyzed starches		
Maltodextrins:	- Food preparation (bulking agent)	[35]
	- Pharmaceutical (excipient)	[6]
	- Ingredient in ice cream industry	[36]
Glucose syrup:	- Dextrose Equivalent of between 40 and 60: food industry	[37]
	- Beverage and confectionary industry	[38]
	- Used directly as a substrate for the manufacture of fermentation products (such as citric acid, lysine or ethanol or glutamic acid)	[39]
	- Processed into other major starch derivatives, such as isoglucose, fructose syrup	[37]
Modified starches		
Substituted starches (starch esters, ethers, cross-linked starch):	- Textiles	[40]
	- Paper	[41]
	Water treatment (flocculation)	[42]
	Oil industry (fluid loss reducer)	[43]
Degraded/Converted starches:	- Dextrins: Adhesives (gummed paper, bag adhesives, bottle labeling);	[35]
	- Textiles (textile fabric finishing, printing);	[44]
Roast dextrin, oxidized starch, thin-boiled starch:	- Acid-modified starches: Food industry (sweets) and Pharmaceuticals	[45]
	- Oxidized starches: Food and paper industry (surface sizing, coating);	[46]
	- Textile industry (fabric finishing, warp sizing)	[47]
	- Enzymatically converted starch: paper industry and fermentation industry	[48]
Cross-linked starches:	- Food industry (desserts, bakery products, soups, sauces)	[49]
	- Textile industry (printing)	[50]
	- Adhesives	[51]
	- Pharmaceuticals	[6]

Source: Adapted from [52].

5. Non-Conventional Sources

Starch accounts for a significant fraction of a large range of crops. Cereals (e.g., corn, wheat, rice, oat, barley) contain from 60% to 80% of this carbohydrate, legumes (e.g., chickpea, bean, pea) from 25% to 50%, tubers (e.g., potato, cassava, cocoyam, arrowroot) from 60% to 90% and some green or immature fruit (e.g., banana, mango) as much as 70% of the dry weight [53]. Table 3 shows the starch content of some conventional and non-conventional sources.

Starch is frequently isolated and is used in food industries to impart the desirable functional properties, and modify food texture and consistency [54].

New starch preparation is done for each raw material before further analyses and application. There is a huge variety of methods to isolate, or prepare, starch and to evaluate its total content in products.

Among these methods authors take the liberty of using validated methods available in literature [55, 56], or their own method [13], or modified methodologies [7, 57] to isolate the starches from their studied raw materials.

To quantify starch some references use a total starch quantification kit according to the American Association of Cereal Chemists (AACC) [58], or the methodology of Association of Official Agricultural Chemists (AOAC) [59] or those validated and available in literature [60].

The source used for starch production varies worldwide depending on local traditions and climatic conditions, but more or less only starch and starch derivatives of maize and potato are of commercial interest [24].

Starches from different botanical sources vary in size, composition and the fine structure of amylopectin, and these factors influence the physical properties and end-uses for different natural starches [15]. The development of products and characterization of native starches from different botanical sources has been widely studied by several authors [99, 104, 114, 90].

The physicochemical and morphological characteristics of pine nut starch demonstrated its applicability as a pharmaceutical excipient due to the presence of phenolic compounds [6].

Sugar cane provides starches with very attractive properties that are completely different from those of cassava [115].

The addition of cellulose and cellulose nanoparticles to chayote tuber starch films was found to improve some of the mechanical, barrier and functional properties, solving the problems of plastic waste to obtain environmentally friendly materials [26].

The understanding of the gelling behavior of lentil starch and protein in composite gel is helpful for the structure formation of these two biopolymers in mixtures and will help their application in new product development [116].

After minor physical or chemical modification, chickpea starch from different cultivars is suitable for incorporation into foods subjected to high temperature processing, high shear and frozen storage due to its higher crystallinity, higher thermal stability and lower set-back [78].

Native chestnut starch presents a pasting profile similar to corn starch, making it a potential technological alternative to corn starch [76].

Velvet bean appears to be suitable in its native state for incorporation into thermally processed and frozen foods due to its higher thermal stability, higher resistance to shear and lower extent of set-back [90].

The properties of breadfruit starch indicate that it would require modification to reduce retrogradation [71].

A starch-rich fraction from the pulp of cupuassu fruit is described as being rheologically similar to the starches of tapioca (cassava) and corn [79]. The properties of sweetsop starch indicate that it has a potential for application as a thickener in frozen foods [56]. Kamo Kamo (*Cucurbita pepo*) starch exhibits behavior similar to that of potato starch [88].

Mango ginger (*Curcuma amada Roxb.*), a unique species with rhizomes that have a mango flavor, has high medicinal importance and occupies a position between turmeric and ginger starch [97].

Jack fruit seed starch is considered a useful stabilizer in a high-acid sauce [87] and could be used as an alternative for modified starches in a system needing starch with a high thermal and/or mechanical shear stability [117].

Pyrodextrinized lima bean starch is potentially useful in the manufacture of dressings and instant beverages, juices, jelly and soft candy, and it can be used as a stabilizer in sausages [118].

Table 4 briefly shows some of the application of these new starches.

The main benefit of starch addition to dairy products is cost reduction; however, starch does contribute important attributes that can improve the product functionality and performance. Starches are now readily added to yoghurts, cheese, custards etc. and thus, understanding their role within a specific product is extremely important. For example, syneresis can be inhibited or greatly reduced by starch addition; the counter effect could be a grainy texture. Thus, by manipulation the formulation and/or the processing conditions the desired outcome can be achieved [121].

There is strong interest in biologically based and/or biodegradable polymers. The reasons for this include the reduced cost, the abundance of the biomass and biodegradability of the materials, combined to the reduced disposal of non-degradable waste into the environment [122].

Although conventional sources of starch, such as corn, potato, other sources with improved properties are becoming significant to allow simpler and more robust processes. The feasibility of new starches as a renewable material for commercial application may provide cost reduction of raw material.

Industry continually aims to improve on existing products and/or explore solutions for cost reduction. Moreover, finding applications for new or existing ingredients continues to be at the forefront of their research [121].

Table 3. Conventional and non-conventional sources of starch (% dry basis)

Source	Popular name	Specie	Type	Method of obtaining	Content of starch (%)	Reference
Non-conventional						
	Amaranthus	Amaranthus cruentus	Cereal	[61]	57,5	[62]
	Annatto	Bixa orellana L.	Seed	NI *	40	[63]
	Apple	Malus domestica Borkh	Fruit	[64]	45,8	[65]
	Babassu	Orbignya phalerata Mart.	Palm	[66]	60,05	[67]
	Baby lima bean	Phaseolus lunatus	Legume	[68]	63	[68]
	Borassus aethiopum	Borassus aethiopum	Palm	[69]	24,73	[70]
	Breadfruit	Artocarpus altilis	Fruit	[69]	64,5	[71]
	Broad bean	Vicia faba L.	Legume	[72]	35	[14]
	Buckwheat	Fagopyrum tataricum Gaertn.	Pseudocereal	[73]	80,5	[29]
	Chayote	Sechium edule Sw	Tuber	[74]	60	[26]
	Cherimoya	Annona cherimola	Fruit	[75])	27,7	[60]
	Chestnut	Castanea sativa	Nut	[76]	93,2	[76]
	Chickpea	Cicer arietinum L.	Legume	[77]	34,75	[78]
	Cocoyam	Colocasia esculenta	Root	NI *	11,91	[3]
		Xanthosoma sagittifolium	Root	NI *	14,73	[3]
	Cupuassu	Theobroma grandiflorum	Fruit	[79]	15	[79]
	Edible cana	Canna edulis ker.	Grass	[80]	15,62	[81]
	Giginya	Borassus aethiopum	Palm	[50]	24,73	[70]
	Ginger	Zingiber officinale Roscoe	Rhizome	[72]	85	[82]
	Ginkgo biloba nut	Ginkgo biloba L.	Grass	[83]	32	[84]
	Grass pea	Lathyrus sativus L.	Legume	[80]	23,3	[85]
	Horse Chestnut	Aesculus indica	Nut	[72]	38,3	[13]
	Jack Bean	Canavalia ensiformis	Legume	[24]	18,42	[24]
	Jackfruit seed	Artocarpus heterophyllus L.	Fruit	[86]	32,14	[87]
	Kamo Kamo	Cucurbita pepo	Fruit	[72]	23,2	[88]
	Kudzu	Pueraria lobata	Root	[89]	99,5	[58]
	Lablab bean	Lablab purpureus	Legume	[80]	29,9	[90]
	Lentil	Lens culinaris	Legume	[91]	51,7	[92]
	Lima beans	Phaseolus lunatus	Legume	[93]	37,5	[94]
	Maca	Lepidium meyenii Walpers	Root	[95]	23,17	[96]
	Mango ginger	Curcuma amada Roxb.	Rhizome	[77]	43	[97]
	Millet	Panicum sumatrense	Cereal	[98]	70	[99]
	Navy bean	Phaseolus vulgaris	Legume	[80]	24,3	[90]
	Palmirah	Borassus flabellifer L.	Palm	[72]	38,34	[100]
	Pea	Pisum sativum L.	Legume	NI.	40	[101]
	Pehuen seeds	Araucaria araucana (Mol) K. Koch)	Pine	[72]	84	[102]
	Peruvian carrot	Arracacia xanthorrhiza, Bancroft	Root	[80]	80	[9]
	Pine nut	Araucaria angustifolia	Pine	[6]	72	[6]
	Ramon	Brosimum alicastrum Swartz	Fruit	[77]	92,57	[7]
	Soursop	Annona muricata	Fruit	[103]	27,3	[56]
	Sugar cane	Saccharum officinarum L.	Grass	[104]	99,1	[104]
	Sweet sorghum	Sorghum bicolor	Grass	[104]	98,9	[104]
	Sweetsop	Annona squamosal	Fruit	[103]	25,6	[56]
	Tef	Eragrostis tef (Zucc.) Trotter	Grain	[105]	75	[106]
	Tepary bean	Phaseolus acutifolius	Legume	[80]	27,6	[90]
	Turmeric	Curcuma longa L.	Rhizome	[72]	76	[82]
		Curcuma longa L.	Rhizome	[107]	86,62	[55]
		Curcuma zeodoaria	Rhizome	[107]	86,84	[55]
	Wolf Apple	Solanum lycocarpum	Fruit	[80]	51	[4]
	White yam	Dioscorea spp.	Tuber	NI *	83,93	[108]
	Velvet bean	Mucuna pruriens	Legume	[109]	25,2	[90]
Conventional						
	Banana	Musa paradisiaca	Fruit	[110]	26,3	[111]
	Barley	Hordeum vulgare	Cereal	[112]	60	[112]
	Corn	Zea mays	Cereal	[110]	31,3	[111]
	Potato	Solanum tuberosum	Tuber	[110]	23,65	[111]
	Rice	Oryza sativa	Grain	[105]	87,7	[106]
	Cassava	Manihot esculenta	Root	[72]	84	[113]
	Wheat	Triticum aestivum L.	Cereal	[110]	25,03	[111]

* NI – Not Identified

Table 4. Potential application for some new starches

Source	Application	Method of Obtaining	Starch (%)	References
Babassu	Biotechnological applications	[66]	60,05	[67]
Chayote	Biopolymer formation	[74]	60	[26]
Cherimoya	Food processing	[75]	27,7	[60]
Chestnut	Food processing	[76]	93.2	[76]
Edible cana	Biotechnological applications	[80]	15,62	[29]
Giginya	Food and non-food processing	[50]	24,73	[70]
Ginkgo biloba	Food processing	[83]	32	[84]
Jack fruit seeds	Food processing	[86]	32,14	[87]
Kamo Kamo	Food processing	[72]	23,2	[88]
Kudzu	Food processing	[89]	99,5	[58]
Lentil	Biopolymer formation	[91]	51,7	[116]
Lima beans	Food processing	[93]	37,5	[118]
Pea	Biotechnological applications	NI *	40	[119]
Peruvian carrot	Food processing	[6]	72	[9]
Pine nut	Biotechnological applications	[6]	72	[6]
Sweetsop	Food processing	[103]	25,6	[56]
Tef	Food processing	[105]	75	[106]
Turmeric	Biotechnological applications	[72]	76	[120]
Velvet bean	Food processing	[109]	25,2	[90]
White yam	Food processing	NI *	83,93	[71]
Wolf apple	Biotechnological applications	[80]	51	[4]

6. Future Trends and Perspectives: The Uses of Annatto and Turmeric Starches

Commercial extracts of annatto seeds and turmeric rhizomes are rich sources of the natural pigments bixin and curcumin, respectively, which are largely used for the coloring of various food products and for cosmetics and pharmaceutical applications [123, 82]. This has resulted in the increased demand for these compounds and consequently the number of studies published on obtaining these compounds. Nevertheless, there is a lack of research reporting the use of starch from these raw materials (usually contained in the residue).

Turmeric (*Curcuma longa*) and annatto (*Bixa orellana L.*), which are already used in industry to obtain food coloring and pharmaceutical products, may become commercially interesting as starch raw materials (Figures 5 and 6).

Figure 5. Whole form (A) [124], seeds (B) [125] and powder (C) [126] of annatto (*Bixa orellana L.*)

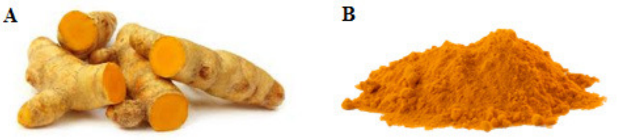

Figure 6. Rhizomes (A) [127] and powder (B) [128] of turmeric (*Curcuma longa L.*)

The main reserve carbohydrate on annatto seeds is starch [129]. Isolated starch from turmeric rhizomes after the extraction of its oil using supercritical fluid extraction (SFE) contains about 40% (w/w) starch [82].

Information on the unique characteristics of uncommon starches would be helpful for practical applications in food and non-food processing to improve the functionality of end-use products.

6.1. Methods of Value Addition to Turmeric and Annatto

6.1.1. New Product Development

The extraction of curcuminoids (pigments) from turmeric rhizomes generates a waste predominantly consisting of starch. This agroindustrial residue is considered to be a potential renewable material for ethanol and lactic acid production when subjected to acid hydrolysis [120].

Curcumin has been encapsulated in baker's yeast (*Saccharomyces cerevisiae*) cells, b-cyclodextrin (b-CD) and modified starch (MS) by various methods [130].

6.1.2. Extraction of Curcuminoids, Turmerones and Bixin Using Supercritical Technology

The starch from turmeric was analyzed before and after supercritical fluid extraction, showed in Figure 7, to obtain oleoresin and essential oil, revealing characteristics similar to commercial starches, indicating the potential for industrial applications [82].

Pressurized liquid extraction is a versatile technique that allows the extraction of natural bioactive compounds such as curcuminoids [131]. Supercritical technology has been employed for optimizing ar-turmerone extraction from turmeric volatile oil [132].

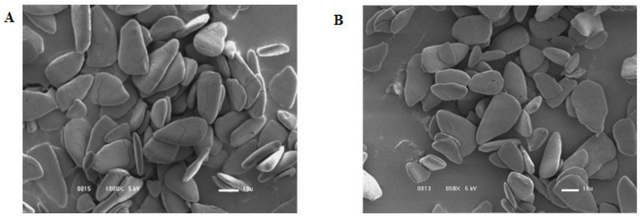

Figure 7. SEM images of turmeric starches before (A) and after (B) SFE [82]

Supercritical CO_2 extraction for the defatting of annatto seeds was studied as a pretreatment for the production of bixin [133]. Pressurized liquid extraction (PLE) and low-pressure solvent extraction (LPSE) methods have been used for the extraction of bixin from defatted annatto seeds [134].

The encapsulation of bixin in poly(3-hydroxybutirate-co-hydroxyvalerate) (PHBV) with dichloromethane as an organic solvent using the SEDS (solution-enhanced dispersion by supercritical fluids) technique was studied to evaluate the behavior of bixin release in different solvent media [135].

6.1.3. Spray-dried Turmeric Oleoresin

Turmeric extract have a commercial potential for obtaining spray-dried microparticles of poorly water-soluble phytochemicals [136].

6.1.4. Microwave and Ultrasound-assisted Extraction Technique for Curcuminoids and Bixin

A microwave-assisted extraction technique was more efficient in curcumin extraction from powdered *C. longa* rhizome in comparison with soxhlet, microwave, ultra-sonic and supercritical carbon dioxide-assisted extraction in terms of percent yield and the required extraction time [137].

Ultrasound-assisted extraction is an effective technique for annatto color extraction in comparison with conventional extraction methods, such as microwave-assisted extraction and supercritical fluid extraction [138].

Ultrasound-assisted curcumin emulsification was successfully used for the preparation of starch-stabilized nanoemulsions at lower temperatures (40–45 ℃) with reduced energy consumption [139].

7. Conclusions

Starch, a renewable biopolymer, is a versatile agricultural raw material for industrial purposes because it is inexpensive, relatively easy to handle, completely biodegradable and widely available in nature from sources such as cereals, roots, tubers, palms and seeds.

Developments in the industrial sector have increased interest in the identification of new starches with distinct properties and their potential for processing at large scales.

However, little information is available on the structure, properties and practical applicability of non-conventional sources of starch. Thus, it is necessary that these starches be studied to obtain and report their structural parameters, information that is required to gain competitiveness in an international-scale industry.

These starches show similarity or advantages with respect to some conventional sources, such as corn, potato and tapioca, making them attractive additives for food formulations in which the retrogradation process is undesirable; in addition, their aqueous suspension gelatinization requires less time and energy.

Legume, rhizome, grass, seed and palm starches can be used as ingredients in the same way as starches from cereals and tubers because of their similarity in physicochemical and functional attributes. These properties will allow the use of new starches with improved functionality, which can be employed to develop new processes and consequently new products.

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- CAPÍTULO 3 –

Thin-layer chromatography profiles of non-commercial turmeric (Curcuma longa L.) products obtained via partial hydrothermal hydrolysis

A composição química dos rejeitos de cúrcuma antes e após hidrólise hidrotérmica parcial é investigada através do uso de uma abordagem qualitativa, por cromatografia de camada delgada. A porção sólida residual mostra relevância em termos de fenólicos e voláteis, enquanto que a líquida de açúcares redutores.

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Thin-Layer Chromatography Profiles of Non-Commercial Turmeric (*Curcuma longa* L.) Products Obtained via Partial Hydrothermal Hydrolysis

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Abstract This study verifies an alternative use of waste turmeric from extraction processes via partial-hydrothermal hydrolysis, which provides partial hydrolyzed-deflavored and depigmented turmeric (PHDDT) and turmeric hydrolysates (TH). Thin-layer chromatography was used to fingerprint and evaluate the chemical compositions of these products in terms of phenolics, antioxidants, volatiles and sugars, which verified the possibility of adding value to these waste products. Reaction temperature variations influenced the quality of the analyzed compounds. Based on a qualitative approach, PHDDT provided a considerable source of bioactive compounds, while TH samples were determined to be a source of low-chain sugars. The production of various sugars and bioactive compounds from non-commercial turmeric represents a promising alternative for future methodologies that can diminish the quantity of agro-waste and improve economic profitability.

Keywords Turmeric, Partial Hydrolysis, Thin-Layer Chromatography, NP, DPPH, Vanillin, Alpha-naphthol

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1. Introduction

Turmeric (*Curcuma longa L.*) is an important medicinal plant and source of phenolic compounds, volatile oil, sugars, proteins and resins [1, 2]. The pigments in the colorant extracts obtained from turmeric are collectively known as curcuminoids, which are phenolic compounds. The major constituent is curcumin (60-80%) in addition to small amounts of demethoxycurcumin (15-30%) and bisdemethoxycurcumin (2-6%) [3].

Curcumin is widely used for foods and dyes, and possesses numerous biological benefits, including antioxidant, anti-inflammatory, antimicrobial, antiparasitic, antimutagenic, anticancer and antivirus properties [4].

Brazil possesses favorable turmeric cultivation conditions. The dry basis curcuminoid pigment levels in Brazilian turmeric range from 1.4 to 6.1 g/100 g, while the volatile oil fraction varies between 1.0 and 7.6 ml/100 g [5].

Several techniques have been used to qualitatively and quantitatively analyze turmeric species and byproducts. High-performance liquid chromatography (HPLC) was used to detect curcuminoid in extracts obtained via pressurized liquid extraction (PLE) [6]. The extracts were then used to standardize a beauty cream formulated with turmeric powder [7]. The curcumin contents of various *curcuma* varieties collected from different regions of India have been analyzed [2]. Random Amplified Polymorphic DNA was used to detect adulterants in the *Curcuma zeodoaria* and *Curcuma malabarica* species [1]. Thin Layer Chromatography (TLC) was used to identify curcumin in *curcuma* varieties [8], and turmeric extracts were obtained by supercritical fluid extraction (SFE), low-pressure solvent extraction (LPSE) and hydrodistillation [9].

TLC is one of the easiest and most versatile methods for identifying and separating compounds due to its low cost, simplicity, short development time, high sensitivity and good reproducibility [10].

TLC simultaneously separates substances in space. The R_F (retardation factor, ratio of fronts or retention index) value is the standard measure of retention. Given the general difficulty of controlling absolute R_F values, it is common to separate standards and samples in the same system for identification purposes [11].

SFE has been used to extract volatile oils [12], and turmeric curcuminoids have been obtained using pressurized liquid extraction (PLE) with ethanol [6]. This study uses partial-hydrothermal hydrolysis to obtain new products from deflavored and depigmented turmeric (DDT) using pressurized water; DDT is the residue of the SFE and PLE processes. A partial-hydrothermal hydrolysis was performed to generate two main products: the partial-hydrolyzed deflavored and depigmented turmeric (PHDDT), which is a mixed biopolymer, and turmeric hydrolysate (TH), which is the liquid fraction source of low-chain sugars.

Few studies exist regarding the potential use of turmeric

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rhizomes after the deodorization and depigmenting processes. In most of cases, the material is not reused, increasing the amount of environmental waste [13]. Processes are needed that can generate added-value products from food waste, which can be used for feed, cosmetics, energy and pharmaceuticals.

This study qualitatively determines the chemical composition of PHDDT and TH obtained via the partial-hydrothermal hydrolysis of DDT using TLC.

Standards were used to assist in the identification of compounds present in the extracts when known compounds were present in the mixture, including phenolics, antioxidants, volatile oil compounds and sugars. The theoretically known compounds presented in the samples were identified via R_F calculations of the separated zones. The resulting R_F values of the samples were compared to the R_F values of the standards.

2. Materials and Methods

2.1. Material

Deflavored and depigmented turmeric (DDT) was obtained from the crude raw material purchased from the Oficina de Ervas Farmácia de Manipulação Ltda (lot 065DM, Ribeirão Preto, Brazil), from which volatile oil was removed using supercritical CO_2 at 60°C and 250bar, while curcuminoids were removed using pressurized ethanol at 60°C and 100bar [6].

2.2. Experimental Methods

Partial hydrolysis procedures were performed in a home-made PLE apparatus, shown in Figure 1. Three temperature levels (40, 70 and 100°C) and seven pressure levels (10, 20, 30, 40, 50, 60 and 70bar) were used.

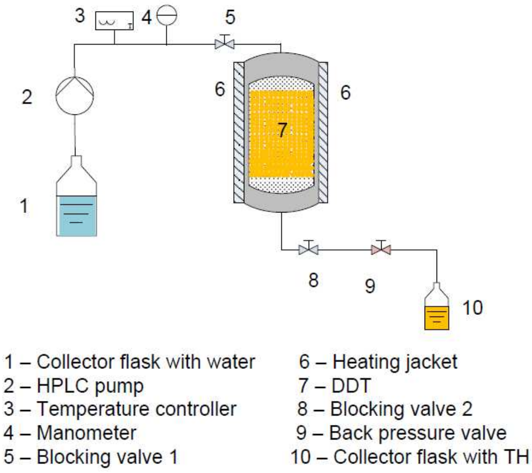

Figure 1. Home-made PLE system

Milli-Q water (EMD Millipore Corporation, Merck, Darmstadt, Germany) was used as a solvent, which was pumped into the extraction cell using an HPLC pump (Thermoseparation Products, Model ConstaMetric 3200 P/F, Fremoni, USA). The extraction cell was placed in an electrical heating jacket at the desired temperature until the required pressure was obtained. Stainless steel tubes were used for all connections in the system.

Approximately 3.3 g of DDT was placed in a 5 ml extraction cell (MV-10 ASFE, Waters, Milford, USA) containing a sintered metal filter at the top and bottom.

The cell containing the sample was heated for 5 min to ensure that the extraction cell would remain at the desired temperature. Then, the first blocking valve was opened to pressurize the cell with solvent until the desired pressure was reached for 20 minutes (static time).

The second blocking valve and the back pressure valve were carefully opened, keeping the pressure at an appropriate level for the desired flow (1 ml/min). The extraction cell was rinsed with fresh extraction solvent for approximately 15 min (dynamic time, i.e., the period of time that the TH samples are collected).

After the experiments, the partial-hydrolyzed deflavored and depigmented turmeric (PHDDT) and turmeric hydrolysates (TH) were maintained in the dark at -18 °C until further analysis.

2.3. Thin Layer Chromatography

Silica gel plates with aluminum backs were used as the stationary phase, including ultraviolet light-sensitive (UV_{254}, Alugram®, Xtra SIL G, Macherey-Nagel, Germany) and non-UV-sensitive plates (Alugram®, Xtra SIL G, Macherey-Nagel, Germany) with 10 cm × 10 cm dimensions. The TLC plates were prepared by establishing a 1 cm distance from the origin, 8 cm solvent travel distance and 1 cm distance from the solvent front.

Approximately 10 µL of the samples were spotted on the TLC plates using capillary glass tubes with an approximately 1 cm distance from each band. The plates were then developed in glass chambers via mobile phase elution.

The bands of compounds generated by the constituents that could not be detected in the visible region were visualized using a UV (Multiband UV – 254-366 nm, UVGL-58, Mineralight® Lamp, Upland, CA, EUA) equipped with a cabinet (UVP-Chromato-VUE, CC-10, Upland, CA, EUA) for short wavelength (254 nm) and long wavelength (366 nm) analyses.

2.3.1. Sample Preparation and Identification

Ethanol was used as solvent to identify phenolics, antioxidants and volatiles because bioactive turmeric compounds are insoluble in water and soluble in organic solvents, such as ethanol, ethyl acetate and acetone. The standards used to identify these PHDDT and TH compounds included curcumin, demethoxycurcumin, bisdemethoxycurcumin and turmeric volatile oil, which were obtained from the SFE process (Table 1). These standards were diluted in ethanol until a concentration of 15 mg/ml was reached. All solvents and chemicals were of analytical grade.

PHDDT samples were diluted in ethanol until the adequate concentration (30 mg/ml) was reached. TH samples were filtrated and concentrated using a freeze-dryer (L101, Liobras, São Carlos, Brazil). The lyophylizated TH samples were diluted in ethanol until a final concentration of 30 mg/ml was reached.

PHDDT dilutions were made to identify sugars using Milli-Q water (EMD Millipore Corporation, Merck, Darmstadt, Germany) at a concentration of 200 mg/ml. Liquid TH was used without any further treatment. The glucose, maltose and lactose standards (Table 1) were diluted in water until a concentration of 10 mg/ml was reached.

Table 1. Standards used in TLC

Phenolics, antioxidants and volatiles	Origin
Bisdemethoxycurcumin	Sigma-Aldrich
Curcumin	(Darmstadt, Germany)
(≥94% curcuminoids; ≥80% curcumin)	
Demethoxycurcumin	
Volatile oil	[6]
Sugars	**Origin**
D (+) lactose	Dinâmica (Diadema, Brazil)
D-(+)-glucose (minimum 99.5%)	Sigma-Aldrich
D-(+)-maltose monohydrate	(Darmstadt, Germany)
(from potato, ≥99%)	

The mobile phase used to develop phenolics, antioxidants and volatiles was composed of chloroform, ethanol and glacial acetic acid at 95:05:01 (v/v) [14]. A mobile phase that consisted of ethyl acetate, acetic acid, methanol and water at 60:15:15:10 (v/v) was used to develop the sugars [15]. Table 2 provides the reagents and their origins.

Table 2. Reagents used to formulate the mobile phases

Phenolics, antioxidants and volatiles	Origin
Chloroform	Merck (Darmstadt, Germany)
Ethanol (99.5%)	Chemco (Hortolandia, Brazil)
Glacial acetic acid	Synth (Diadema, Brazil)
Sugars	**Origin**
Acetic acid (≥99.7%)	Sigma-Aldrich (Darmstadt, Germany)
Ethanol (99.5%)	Chemco (Hortolandia, Brazil)
Ethyl acetate	Dinâmica (Diadema, Brazil),
Methanol	Dinâmica (Diadema, Brazil).

2.3.2. Detection

The phenolics were detected using an NP (2-aminoethylborinate) spray reagent, according to the Wagner and Bladt [14], which was adapted by Albuquerque et al. [16].

Antioxidant compounds were detected by spraying a DPPH solution, in which 0.5 g of DPPH (2, 2-diphenyl-1-picrylhydrazyl) was diluted in 250 ml of methanol [16].

Volatiles were detected by spraying a sulfuric vanillin (SV) reagent, using the formulation suggested by Krishnaswamy [17], in which 0.5 g of vanillin (3-hydroxy-4-methoxybenzaldehyde) was diluted in 20 ml of ethanol and 80 ml of sulfuric acid.

Before and after spraying with NP, DPPH and SV reagents, the plates were inserted into a UV chamber to visualize the compound bands that could not readily be observed.

The sugar detection methodology of Lewis and Smith [18], which was adapted by Fried and Sherma [15], was used. A 0.1 M sodium bisulfite (Dinâmica, Diadema, Brazil) solution was used to impregnate the plates and facilitate the resolution of the samples in the mobile phase. This solution was formulated by diluting 10.4 g of sodium bisulfite in 1 liter of Milli-Q water. The TLC plates were then pre-washed in a glass chamber containing this solution, air dried and activated in an oven (Tecnal, TE-385-1, Piracicaba, São Paulo) at 100°C for 30 minutes prior to spotting.

Carbohydrates are extremely hydrophilic compounds. Therefore, they strongly attach to adsorbents, such as silica gel, alumina and cellulose. Thus, highly polar solvents were necessary in the mobile phase of TLC development [18].

The sugar mobilities on silica gel primarily depend on the molecular weights and the number of hydroxyl groups. The resolution is improved by impregnating silica gel with weak acid salts or via the use of cellulose layers [18].

A sulfuric α-naphthol (SAN) reagent was used to detect sugars. This reagent was prepared by adding 5 g of α-naphthol to 33 ml of ethanol (solution A). Then, 21 ml from solution A were combined with 81 ml of ethanol, 8 ml of water and 13 ml of sulfuric acid. After spraying, the plates were heated for approximately 5 minutes at 100°C. The visualizing reagents (spray solutions) were formulated using the reagents listed in Table 3.

Table 3. Reagents used to formulate the spray solutions

Phenolics, antioxidants and volatiles	Origin
2-aminoethyl-diphenylborinate (99.8%)	Sigma-Aldrich
2,2-diphenyl-1-picrylhydrazyl	(Darmstadt, Germany)
3-hydroxy-4-methoxybenzaldehyde	Synth (Diadema, Brazil)
Sugars	**Origin**
1-naphtol (or α-naphthol)	Dinâmica (Diadema, Brazil)
Ethanol (99.5%)	Chemco (Hortolandia, Brazil)
Sulfuric acid	Exodo Científica
	(Hortolandia, Brazil)

3. Results and Discussion

3.1. Standards Fingerprints

A sufficiently strong TLC solvent causes a sample to shift into the R_F range of 0.2–0.8. In addition, if the correct selectivity is attained, the solvent will evenly distribute the sample components throughout this range. If the sample contains a wide range of sample sizes, then the correct mobile phase will ensure the adequate separation of the major and minor components, rather than an even distribution throughout the R_F range [19]. Table 4 lists the standards used in this study and their R_F values.

Table 4. TLC plate standards with 8 cm elution heights and R_F values

Identity	Standard	Height (cm)	R_F (cm/cm)
BH	DDT (sample before hydrolysis)	5.52 – 7.04	0.69 - 0.88
C	Curcumin	5.52 – 7.04	0.69 - 0.88
DMC	Demethoxycurcumin	4.48 – 5.52	0.56 - 0.69
BDMC	Bisdemethoxycurcumin	3.04 – 4.48	0.38 – 0.56
LAC	Lactose	1.70	0.21
MAL	Maltose	2.30	0.29
GLU	Glucose	3.0	0.38
VO	Turmeric volatile oil	4.48 – 5.52	0.56 - 0.69

The TLC plate stationary phase used silica, which is a polar material. Lower polarity compounds are carried throughout the mobile phase, resulting in high R_F values. Higher polarity compounds are generally retained, resulting in lower R_F values [20].

The curcuminoids and volatile oil standards without a spray reagent appeared as yellowish spots in the visible (Figure 2A) and light-blue zones (Figure 2B) at a long wavelength, as well as in the black zone against a green background at a short wavelength (Figures 2C and 2F).

After spraying the UV-sensitive plates with NP, intense-orange zones were detected in the visible zone (Figure 2D) at 366 nm (Figure 2E).

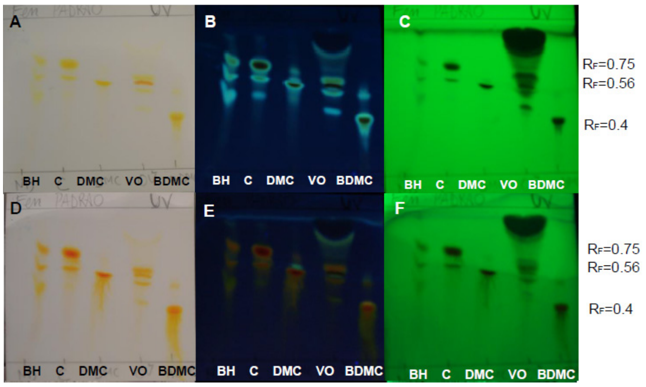

Figure 2. Curcuminoids standards, turmeric volatile oil and DDT solutions on UV-sensitive plates without a spray reagent (A, B and C) and sprayed with NP (D, E and F) at UV 366 nm and UV 254 nm

Curcuminoids and turmeric volatile oil displayed yellow spots in the visible zone after being sprayed with DPPH via UV-sensitive and non-sensitive plates (Figures 3A and 4G). DDT resulted in a very weak yellow spot, indicating that the sample possesses poor or no antioxidant activity (Figures 3A, 3B, 3C, 4G, 4H and 4I).

After spraying with SV, purple bands appeared on the turmeric volatile oil, indicating the presence of terpenes (Figure 3D) at R_F=0.63-0.75. The light-red color attributed to the volatile oil at R_F=0.38 (Figures 3D and 3E) is associated with the presence of thymol, which varies from red to purple. The same red color is visualized on bisdemethoxycurcumin after spraying with SV (Figure 3D). The color completely disappeared on the bisdemethoxycurcumin sample after 30 minutes and partially disappeared on the other standards in the visible zone (Figure 3G). Light-green spots are observed on the standards at R_F values of 0.38 and 0.4 at 366 nm. Light-blue spots are observed on the volatile oil at R_F=0.63 and R_F=0.74 (Figures 3H and 3I).

After treatment with the SV reagent, the monoterpene alcohols, esters, cineole, aldehyde citral and citronellal exhibited blue or blue-violet colors in the visible zone. The phenylpropane derivatives, including safrole, anethole, myristicin, apiol and eugenol, appeared as brown-red/violet spots, while thymol and carvone were red to red-violet. Piperitone displayed a typical orange color [14].

The oils from the *curcuma* species displayed seven to eight blue, red or violet-blue zones with an R_F of 0.3 at the solvent front. A prominent sesquiterpene zone can be see with an R_F of 0.8 at the solvent front [14].

Based on preliminary analyses, the standards used for the detection of volatile oil constituents can be well identified under UV-light using UV-sensitive TLC plates (Figure 3). The standards and samples used for the detection of sugars could not be visualized under UV-light. Therefore, UV-light and UV-sensitive plates were not used to detect sugars.

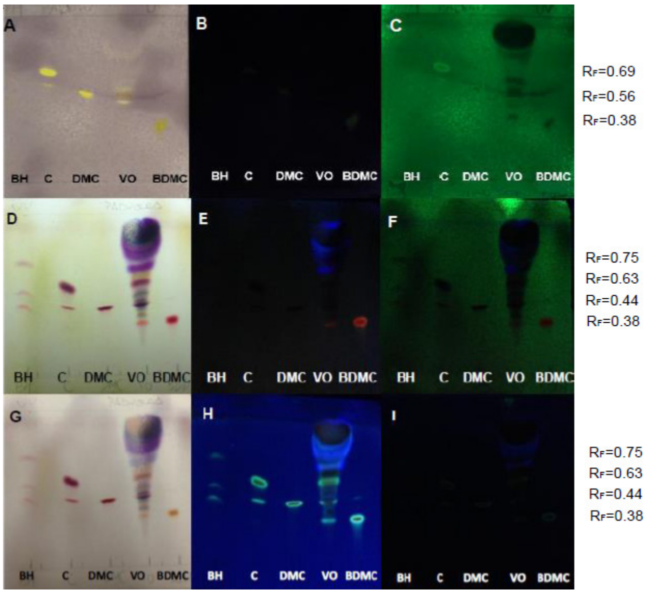

Figure 3. Curcuminoid standards, turmeric volatile oil and DDT solutions on UV-sensitive plates sprayed with DPPH (A, B and C) and SV immediately (D, E and F) and after 30 minutes (G, H and I) at 366 nm and 254 nm

According to Morlock et al. [21], the shortest possible wavelength yielded the best sensitivity when a UV detection analysis was performed. UV values of 200 or even 190 nm were preferred. However, these low UV wavelengths lack the selectivity required by complex food sample matrices.

DTT samples displayed three yellow zones in the visible spectrum (Figure 4A) and light green zones on the non-UV-sensitive plates (Figures 4B and 4C). Intense orange zones appeared after being sprayed with NP (Figures 4D, 4E and 4F).

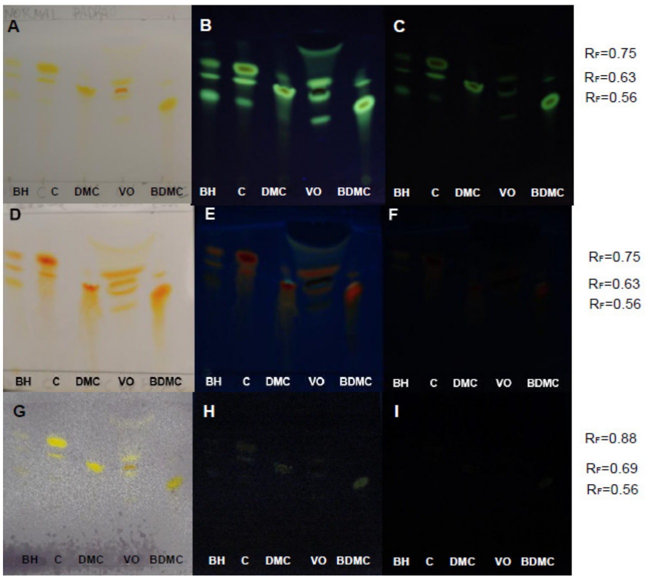

Figure 4. Curcuminoid standards, turmeric volatile oil and DDT solutions on non-UV-sensitive plates without a spray reagent (A, B and C), sprayed with NP (D, E and F) and sprayed with DPPH (G, H and I) at 366 nm and 254 nm

Kulkarni et al. [22] separated curcuminoids by TLC and obtained R_F values of 0.67 for curcumin, 0.6 for demethoxycurcumin and 0.51 for bisdemethoxycurcumin using chloroform: methanol (19:1) as the mobile phase.

Rafi et al. [23] detected R_F values corresponding to 0.05, 0.14 and 0.37 for curcumin, demethoxycurcumin and bisdemethoxycurcumin, respectively, using chloroform: dichloromethane (32.5:67.5) as the mobile phase.

Zhao et al. [24] used petroleum ether: ethyl acetate (90:10) as the mobile phase, which separated low polarity compounds from four *curcuma* species, and sesquiterpenoid standards provided a good resolution. TLC of *Curcuma xanthorriza* Roxb extract diluted in 70% ethanol with n-hexane:ethyl acetate (14:1) was developed using silica gel 60 F_{254} plates, resulting in R_F values that varied from 0.16 to 0.86 [25].

TLC plates with sugars standards are listed in Figure 5. A large and uncommon spot can be visualized after being sprayed with SAN and activated at 100°C for 5 minutes. The R_F calculations for each standard were based on the initial distance from the definitive spot formation. Various sugar standard concentrations were tested, yielding the same type of spot with various intensities.

No published studies were found that used the methodology adopted in this study. The type of stationary phase, salt solution and mobile phase likely influenced the shape of the spot.

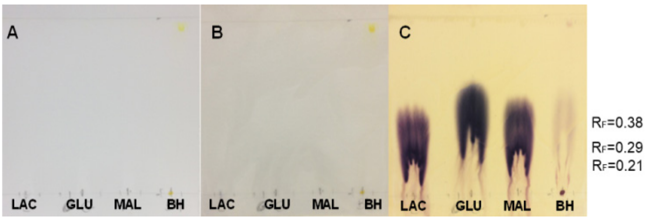

Figure 5. Sugar standard solutions and DDT samples on non-UV-sensitive plates before being sprayed (A), after being sprayed with SAN (B) and after activation at 100°C (C)

Morlock et al. [21] used the same mobile phase constituents employed in this study, excluding water, to analyze *Stevia* formulations, stating that the use of ethyl acetate as the major mobile phase component provided a fast separation of the bands, while the elution strength was adjusted with methanol and the addition of acetic or formic acid focused the zone to a sharp band.

3.2. Sample Fingerprints and Chemical Composition

Partial hydrolysis reactions occurred at three temperature levels (40, 70 and 100°C). The sample identities on the plates are listed as a function of the pressure in Table 5.

Table 5. Sample identities obtained by hydrolysis with PLE

Identity	Pressure (bar)
1	10
2	20
3	30
4	40
5	50
6	60
7	70

Three yellow zones were observed on the TLC plates after elution with chloroform, ethanol and glacial acetic acid (95:05:01) for DDT samples without a spray solution, as observed in Figures 6A, 7A and 8A. The R_F values of the DDT and TH samples ranged from 0.44 to 0.69, which are similar to the R_F values of the curcuminoid standards.

The obtained DDT and TH fingerprints can be used to qualitatively determine the active compound and sugar yields according to the temperature and pressure.

Light-blue fluorescent bands were detected on DDT samples against a dark blue background at 100°C and 366 nm using non-UV-sensitive plates (Figure 8B, non-UV-sensitive plate). Samples obtained at 40 and 70°C displayed light-blue and light-green zones (Figures 6B and 7B, non-UV-sensitive plates).

Green fluorescent zones were detected on the DDT samples obtained at 70°C at 366 nm (Figure 7B, UV-sensitive plate) using UV-sensitive plates. No visible differences were displayed by samples at 254 nm using UV-sensitive plates.

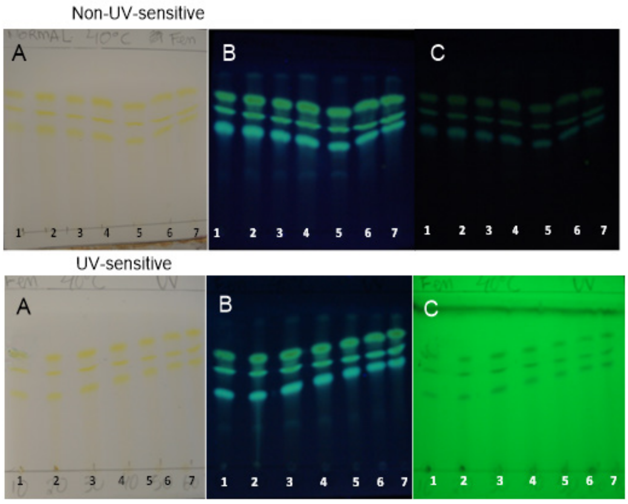

Figure 6. PHDDT samples obtained at 40°C on non-UV-sensitive and UV-sensitive plates without a spray reagent at visible (A), UV 366 nm (B) and UV 254 nm (C) levels

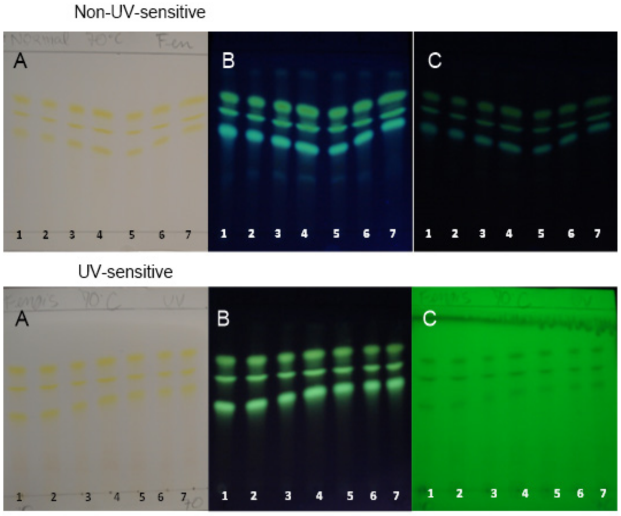

Figure 7. PHDDT samples obtained at 70°C on non-UV-sensitive and UV-sensitive plates without a spray reagent at visible (A), UV 366 nm (B) and UV 254 nm (C) levels

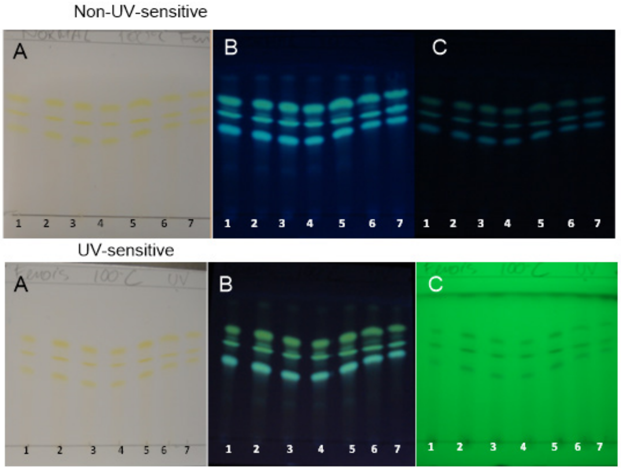

Figure 8. PHDDT samples obtained at 100°C on non-UV-sensitive and UV-sensitive plates without a spray reagent at visible (A), UV 366 nm (B) and UV 254 nm (C) levels

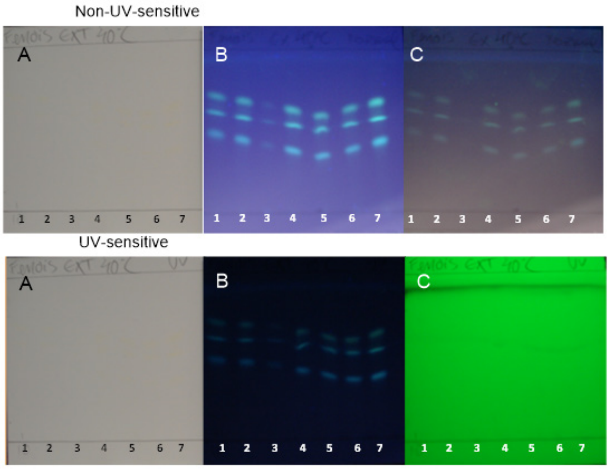

Figure 9. TH samples obtained at 40°C on non-UV-sensitive and UV-sensitive plates without a spray reagent at visible (A), UV 366 nm (B) and UV 254 nm (C) levels

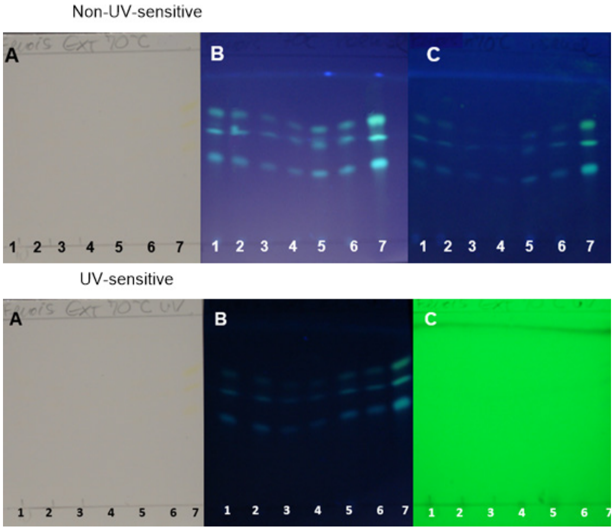

Figure 10. TH samples obtained at 70°C on non-UV-sensitive and UV-sensitive plates without a spray reagent at visible (A), UV 366 nm (B) and UV 254 nm (C) levels

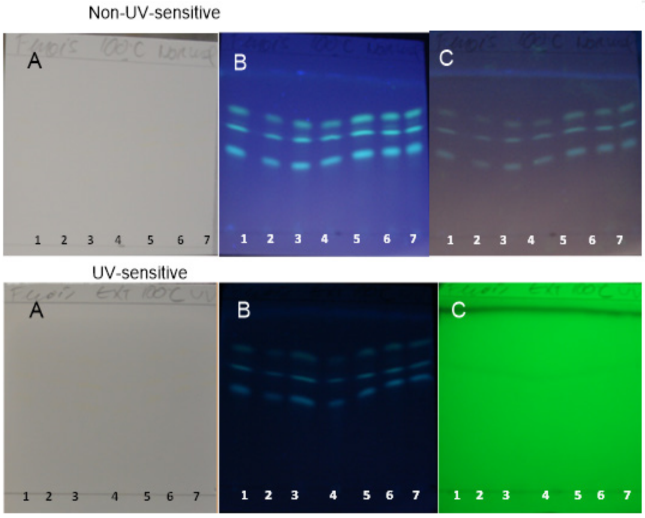

Figure 11. TH samples obtained at 100°C on non-UV-sensitive and UV-sensitive plates without a spray reagent at visible (A), UV 366 nm (B) and UV 254 nm (C) levels

TH samples could not be identified in the visible spectrum regardless of the conditions. However, the TH samples were weakly visualized by UV light on non-UV-sensitive plates. Samples were only identified at 366 nm on UV-sensitive plates (Figures 9, 10 and 11).

3.3. Phenolic Compounds

Curcuminoids and volatile oil are the major bioactive constituents of turmeric. Curcuminoid analyses are essential for determining the quality of the turmeric plant material and processed products [26].

PHDDT and TH sample fingerprints displayed dark yellow and light yellow zones in the visible spectrum after being sprayed with NP (Figures 12-17). Dark-yellow to orange spots were visualized on PHDDT samples at 366 nm, while low intensity pale-yellow spots were visualized on TH samples at 366 nm.

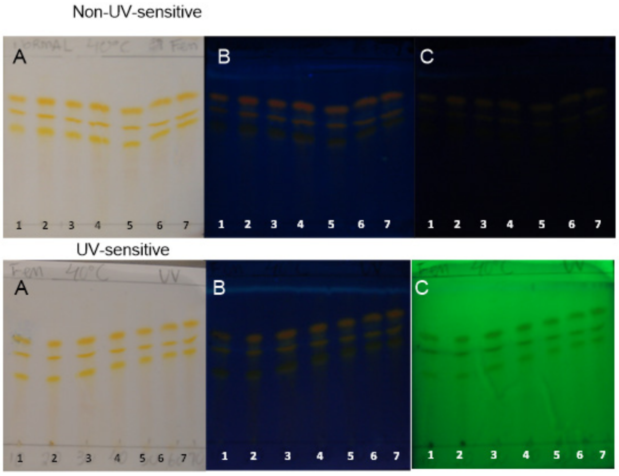

Figure 12. PHDDT samples after hydrolysis at 40°C on non-UV-sensitive and UV-sensitive plates sprayed with NP at visible (A), UV 366 nm (B) and UV 254 nm (C) levels

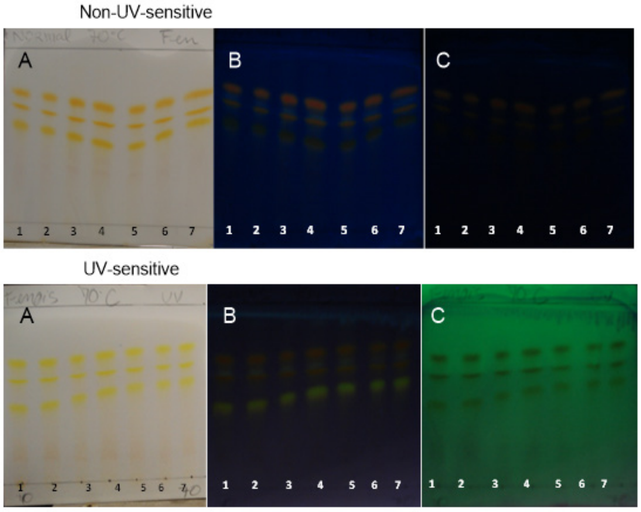

Figure 13. PHDDT samples obtained at 70°C on non-UV-sensitive and UV-sensitive plates sprayed with NP at visible (A), UV 366 nm (B) and UV 254 nm (C) levels

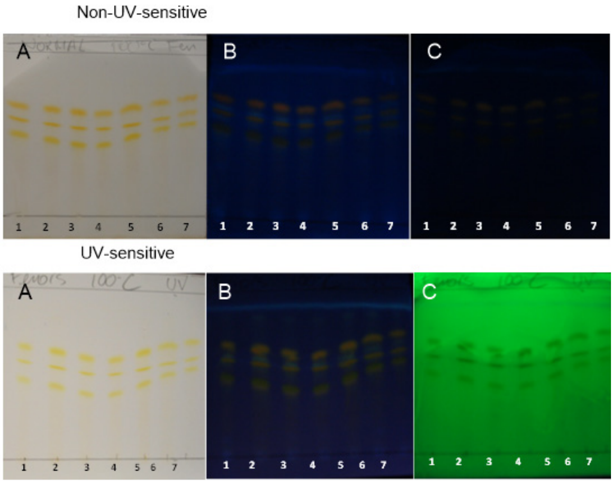

Figure 14. PHDDT obtained at 100°C on non-UV-sensitive and UV-sensitive plates sprayed with NP at visible (A), UV 366 nm (B) and UV 254 nm (C) levels

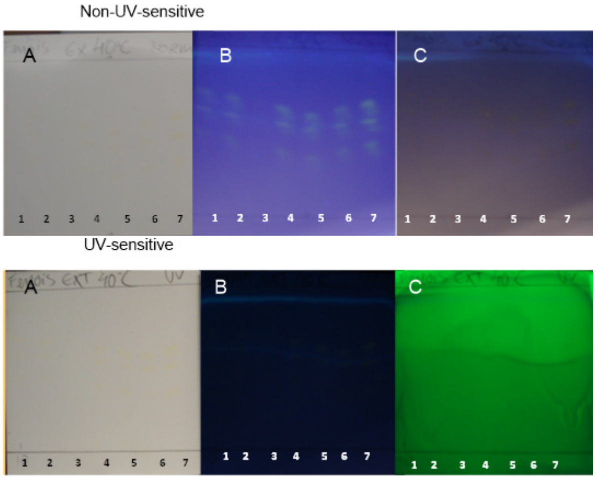

Figure 15. TH obtained at 40°C on non-UV-sensitive and UV-sensitive plates sprayed with NP at visible (A), UV 366 nm (B) and UV 254 nm (C) levels

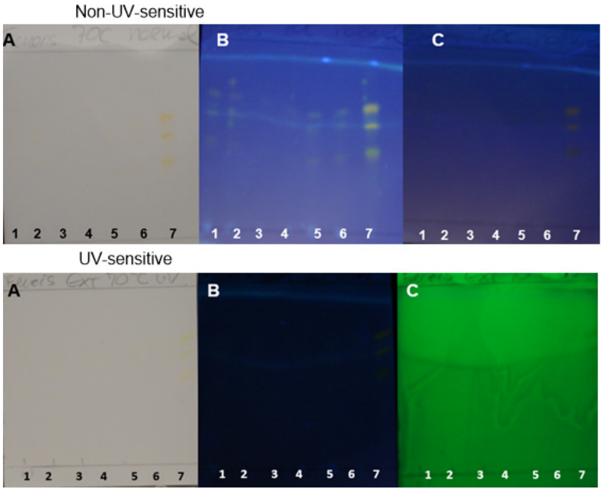

Figure 16. TH obtained at 70°C on non-UV-sensitive and UV-sensitive plates sprayed with NP at visible (A), UV 366 nm (B) and UV 254 nm (C) levels

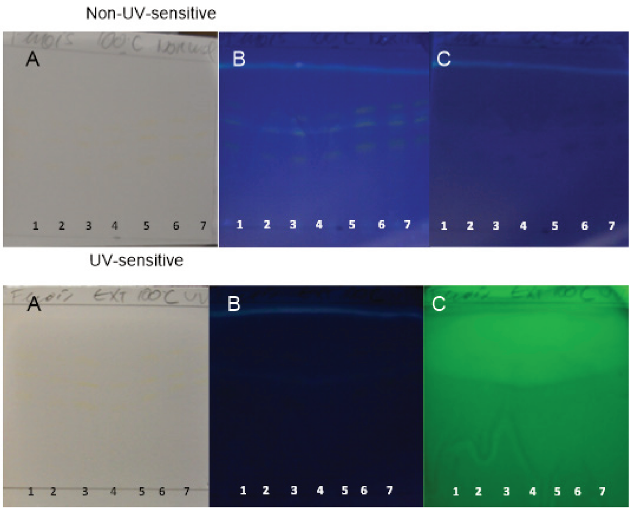

Figure 17. TH samples obtained at 100°C on non-UV-sensitive and UV-sensitive plates sprayed with NP at visible (A), UV 366 nm (B) and UV 254 nm (C) levels

After chromatographic separation and spraying with NP/PEG, pomegranate juice samples were analyzed at 366 nm, displaying dark blue and light blue zones [27]. Annatto oil samples were visualized as orange, brown, black and light blue zones after spraying with NP at 366 nm [16].

It is relatively challenging to identify phenolic compounds using TLC. The most common strategy uses a set of reference compounds on the TLC plate. However, this approach incorporates inherent uncertainties, because two different compounds can have the same R_F value, requiring further characterization to establish compound identities at a higher confidence level. A higher confidence level can be achieved by scraping areas of the TLC plate where the compound of interest has migrated, followed by a solvent extraction of the matrix and detailed chemical analysis, such as gas chromatography or mass spectrometry [28].

The UV-sensitive plates in Figures 15-17 do not exhibit TH sample bands, suggesting that the samples contain few phenolics.

Definitive pressure influences are difficult to qualitatively analyze based on samples obtained under different conditions.

The temperature influenced the quality of the samples, as is evident in the differences among the fluorescences emitted by the samples at 366 nm.

3.4. Antioxidant Compounds

Antioxidant agents can be used for several cosmetic and medicinal applications [29]. Free radical scavenging compounds appeared as yellowish spots against a purple background, indicating a positive antioxidant activity due to the presence of an active antioxidant [30].

The TH samples were not visualized before or after DPPH detection at all temperature or pressure conditions and independent of the type of TLC plate used.

The PHDDT samples were not detected using UV-sensitive plates after being sprayed with DPPH. The antioxidant strength of PHDDT (Figures 18, 19 and 20) on UV-sensitive plates is classified as a weak activity. The antioxidant composition varied as the temperature increased.

The behaviors observed in the DDT and TH samples vary from the behaviors exhibited by other raw materials, such as bamboo leaves [31] and German Propolis [32], whose constituents were intensively detected by a DPPH solution and exhibited strong antioxidant activities.

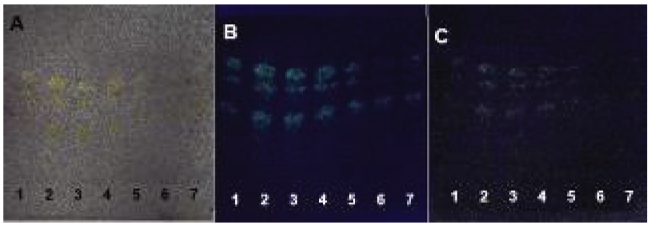

Figure 18. PHDDT samples obtained at 40°C on non-UV-sensitive plates sprayed with DPPH at visible (A), UV 366 nm (B) and UV 254 nm (C) levels

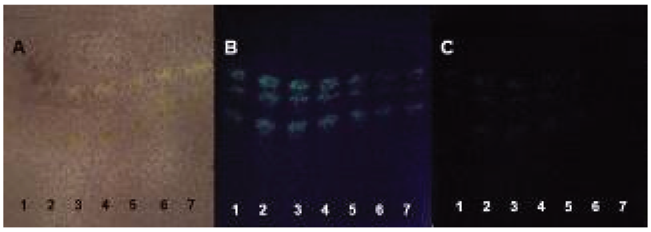

Figure 19. PHDDT samples obtained at 70°C on non-UV-sensitive plates sprayed with DPPH at visible (A), UV 366 nm (B) and UV 254 nm (C) levels

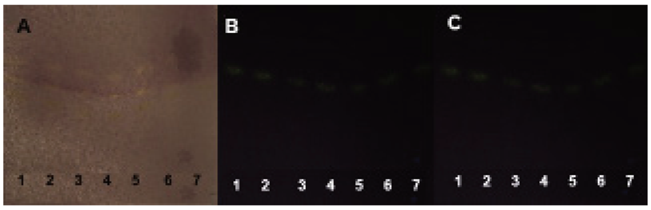

Figure 20. PHDDT samples obtained at 100°C on non-UV-sensitive plates sprayed with DPPH at visible (A), UV 366 nm (B) and UV 254 nm (C) levels

3.5. Volatile Compounds

The SV can be used to detect steroids, volatile oils, terpenes, carotenoids, phenols, catechins, flavonoids, ginsenosides, fatty acids and antibiotics [33]. The SV fingerprints were detected using UV-sensitive plates.

PHDDT sample bands were only visualized at the visible level (Figures 21 and 22). TH samples were not visualized at the visible level or by UV-light after elution and being sprayed with SV.

Phenolic compounds with aromatic structures display intense absorption in the UV region of the spectrum associated with green, yellow, white to pale yellow, purple, pink, red, blue, grey, brown or black spots [34].

Dark red spots immediately appeared on DDT samples after being sprayed with SV (Figure 21) at R_{Fs} of 0.56-0.75, while light-red spots appeared at 0.44-0.5. The intensity of the coloration partially disappeared after 30 minutes

(Figures 22A, 22B and 22C).

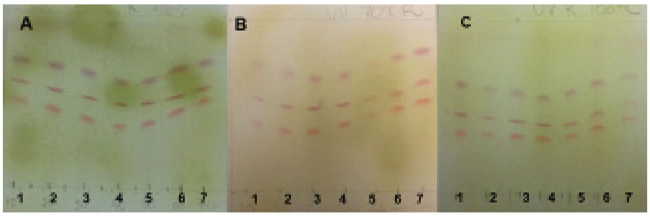

Figure 21. PHDDT samples obtained at 40 (A), 70 (B) and 100°C (C) after being sprayed with SV at the visible level

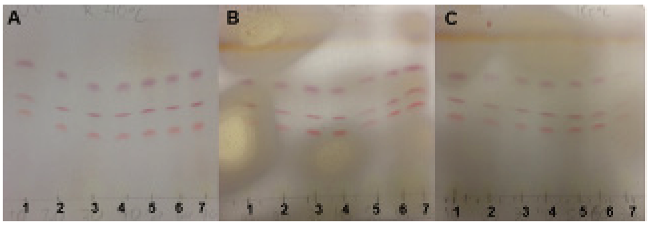

Figure 22. PHDDT samples obtained at 40 (A), 70 (B) and 100°C (C) 30 minutes after being sprayed with SV at the visible level

3.6. Sugars

The sugars detection via TLC uses furfuraldehyde in conjunction with numerous phenolic reagents, which give rise to different colors, e.g., α-naphtol yields a blue-violet coloration. The ketone and aldehyde groups of the reducing sugars preferentially react [35].

Carbohydrates attach to adsorbents. Thus, the mobile phase must be extremely polar. Buffering the silica gel with weak salt acids enhances the monosaccharide separation during TLC [35].

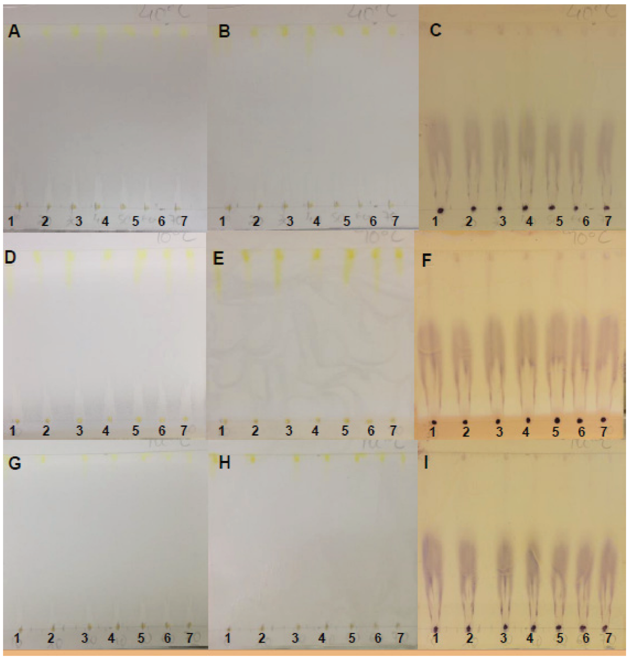

Figure 23. PHDDT samples obtained at 40 (A, B and C), 70 (D, E and F) and 100°C (G, H and I) on non-UV-sensitive plates before spraying (A, D and G), after spraying with a SAN reagent (B, E and H) and after activation at 100°C (C, F and H) at the visible level

Band separation did not occur on PHDDT samples (Figure 23), because the material is a source of high-molecular- weight sugars, such as starch [36].

TLC is commonly used to analyze low-molecular-weight sugars and their derivatives. Aniline diphenylamine - phosphoric acid, aniline phthalate, p-anisidine phosphate, sulfuric anisaldehyde and others are spray reagents that are used to detect sugars on TLC plates [37].

Carbohydrates are difficult compounds to separate from each other. They primarily differ based on the number of carbon atoms they possess, their chiral center configurations and their molecule sizes, i.e., their classification as di-, tri- or oligosaccharides. If two carbohydrates have any one of the three characteristics in common, they can be difficult to separate [38].

Two purple zones are clearly identified on TH samples at 40°C (Figure 24C) and 70°C (Figure 24F) at the visible level with R_F values of 0.24 (dark purple) and 0.36 (light purple), respectively. These R_F values are similar to the sugar standards used in this study. Only a weak purple zone with an R_F of 0.24 can be visualized on TH samples at 100°C (Figure 24I).

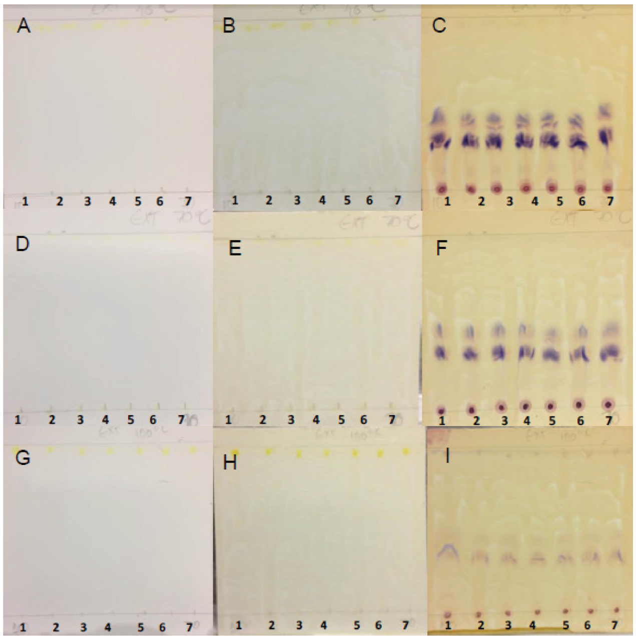

Figure 24. TH obtained at 40 (A, B and C), 70 (D, E and F) and 100°C (G, H and I) on non-UV-sensitive plates before spraying (A, D and G), after spraying with SAN (B, E and H) and after activation at 100°C (C, F and H) at the visible level

Only the process temperature influenced the composition (qualitative sugar analysis) of TH samples. The lowest sugar intensities were observed as the temperature increased, which can be attributed to the degradation of these constituents, resulting in furfural production.

The acid hydrolysis of cellulose and pentosans (xylans, arabinans and polyuronides) in plants and waste materials produces hydroxymethylfurfural and furfural, which are organic substances that serve as inputs for various industrial processes, including furfuryl alcohol and tetrahydrofuran preparation [39].

The sugar constituent bands of edible mushrooms displayed the best resolution using a acetonitrile: water (70:30) and 20% sulphuric acid solution as a spray solvent [40].

The hydrolysis products of glycosides were identified using ethyl acetate:2-propanol:water (65:30:10) and detected with a sulphuric naphtoresorcinol reagent in an enzymatic grape skin hydrolysis study based on endoglycosidase [41].

Okonkwo et al [42] identified sugar constituent bands in pineapple juice samples using butane-1-ol:acetone:water (4:5:1), resulting in R_F values of 0.19 and 0.3, which were associated with the R_F values of glucose (0.34) and fructose (0.17), concluding that the sample contained these two sugars.

An n-butanol:acetone:diethylamine:water (10:10:2:6 v/v) solvent system was used to identify sugars from the outer almond fruit skin, resulting in R_F values of 0.18 for lactose, 0.24 for maltose and 0.41 for glucose [43].

4. Conclusions

Turmeric is an important plant that is used as a medicine, condiment and cosmetic due to its wide range of bioactive substances. However, few studies have evaluated the functionality and processing feasibility of deflavored and depigmented turmeric.

This study explores a method that reuses waste turmeric from extraction processes via partial hydrothermal hydrolysis, generating partial-hydrolyzed deflavored and depigmented turmeric and turmeric hydrolysates products. The chemical profiles of these products were evaluated using thin layer chromatography, which analyzed phenolics, antioxidant, volatiles and sugars.

According to the TLC fingerprints, PHDDT and TH samples are predominant in phenolic compounds, presenting light-blue and light-green fluorescences at 366 nm and 254 nm without a spray reagent.

Establishing a comparison between these two products, PHDDT samples provide the most bioactive compounds, including curcuminoids, antioxidants and volatiles. However, TH is a considerable source of low-chain sugars when submitted to partial hydrolysis at 40°C.

Finally, this studied showed that waste turmeric can be reused for subsequent processes that generate new products with promising applicabilities.

ACKNOWLEDGEMENTS

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- CAPÍTULO 4 –

Partial-hydrothermal hydrolysis is an effective way to recover bioactives from turmeric wastes

A aplicação dos ensaios de hidrólise hidrotérmica parcial aos rejeitos de cúrcuma foi analisada como uma alternativa economicamente viável para o aproveitamento desses produtos. A aplicação deste processo a partir de uma matéria-prima de baixo custo resultou em dois produtos: uma fração líquida e uma fração sólida, ambas fontes promissoras de polifenóis e carboidratos.

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Partial-hydrothermal hydrolysis is an effective way to recover bioactives from turmeric wastes

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Abstract

Partial-hydrothermal hydrolysis using pressurized hot water was applied in waste turmeric, derived from extraction processes that employed supercritical and pressurized fluids, as a sustainable alternative for the recovery of bioactive constituents from this material. The reaction products consisted of a liquid extract of fermentable sugars and a solid fraction, which is a mixed biopolymer with relevant composition in terms of starch and antioxidant constituents. The effects of reaction conditions on resulting products were investigated. Economic evaluation was also performed showing that application of partial-hydrothermal hydrolysis from a residual feedstock is feasible in terms of low spend of energy and materials.

Practical Application

The extraction of volatiles and coloring agents from turmeric generates a residue that contains carbohydrates and phenolic compounds with relevance for industry purposes. A possible alternative to reuse turmeric wastes from extraction processes is analyzed in this work by application of hydrolysis reaction under mild conditions in order to provide two products with potential application for formulation of foods, medicine and cosmetics. For practical purposes, this work shows an effective way to reduce the amount of food wastes, turning it a product of commercial value from an economically feasible process.

Keywords Biowastes, Carbohydrates, Partial Hydrolysis, Phenolic compounds.

1 INTRODUCTION

In a commercial perspective, turmeric rhizomes are traded as dye, spice, and non-conventional source of industrial starch (Ching et al., 2014; Santana & Meireles, 2014). Hydrothermal hydrolysis, also known as hydrothermal treatment, hydrothermolysis, liquid hot water and compressed hot water hydrolysis, is an environmentally benign method that has been the object of extensive research since the process only requires water and heat (Orozco et al., 2012).

Although glucose can be formed from starch by hydrolysis in the presence of acid or enzyme, neutralization of the hydrolysate is required after acid hydrolysis, and enzymatic hydrolysis is costly (Nagamori & Funazukuri, 2004). In addition to produce low-chain sugars, hydrothermal hydrolysis acts a physical method used to modify the characteristics of the plant biowastes (Alcázar-Alay et al., 2015; Alcázar-Alay & Meireles, 2015).

Working recently with turmeric our research group has been studying the deodorization of crude rhizomes using supercritical fluid extraction with CO_2 (Carvalho et al., 2015), depigmentation of deflavored turmeric rhizomes using pressurized liquid ethanol (Osorio-Tobón et al., 2014) and starch recovery from deflavored and depigmented turmeric, DDT (Santana et al., 2017) which is the raw material used in this work.

Partial hydrothermal hydrolysis was applied on DDT in order to investigate the reaction performance, composition and marketing potential of two new products obtained from reaction assays, i.e., turmeric hydrolysates (TH), which is the liquid fraction, and partial-hydrolyzed deflavored and depigmented turmeric (PHDDT), the solid fraction.

2MATERIAL AND METHODS

2.1 Material

Deflavored and depigmented turmeric (DDT) was obtained from the crude raw material purchased from Oficina de Ervas Farmácia de Manipulação Ltda (lot 065DM, Ribeirão Preto, Brazil), from which volatile oil was removed using supercritical CO_2 at 60 °C and 25 MPa (Carvalho et al., 2015), while curcuminoids were extracted using pressurized ethanol at 60 °C and 10 MPa (Osorio-Tobón et al., 2014).

2.2 Experimental

A home-made pressurized liquid extraction (PLE) apparatus was used for the reaction assays. Three levels of temperature (40, 70 and 100 °C) and seven levels of pressure (1, 2, 3, 4, 5, 6 and 7 MPa) were used. Milli-Q water (EMD Millipore Corporation, Merck, Darmstadt, Germany) was used as solvent, which was pumped with the aid of a high-performance liquid chromatography (HPLC) pump (Thermoseparation Products, Model ConstaMetric 3200 P/F, Fremoni, USA) into the reaction vessel which was placed in an electrical heating jacket at the desired temperature, until the required pressure was obtained. All connections within the system were made using stainless steel tubes. Approximately 3.3 g of DDT was placed in a 5 mL reaction vessel (MV-10 ASFE, Waters, Milford, USA) containing a sintered metal filter at the bottom and upper parts.

The cell containing the sample was heated for 5 min to ensure that the reaction vessel would be at the desired temperature. Afterwards the first blocking valve was opened to pressurize the cell with solvent, until the desired pressure for 20 minutes (static time). Established the static time, the second blocking valve and the back pressure valve were carefully opened.

Preliminary tests established 20 minutes as static time (period of inserting water inside the reaction vessel at the desired temperature and pressure) and 15 minutes as dynamic time (period of hydrolysate collecting) at 1 $mLmin^{-1}$ (Santana & Meireles, 2016). After experiments, partial-hydrolyzed deflavored and depigmented turmeric

(PHDDT) and turmeric hydrolysates (TH) were maintained at -18 °C, in the dark, until further analysis.

2.2.1 Calculations

Global yield (%, in dry basis) was calculated according to Equation 1 as the ratio of the total mass of hydrolysates (m_H, in g) and the mass of feed (F_0, in g).

$$X_0 = \left(\frac{m_H}{F_0} \right) \times 100 \qquad (1)$$

Degree of hydrolysis (D_H, %), or material conversion, is defined by Equation 2:

$$D_H = \left(\frac{F_1 - F_0}{F_0} \right) \times 100 \qquad (2)$$

Where F_1 is the mass of PHDDT quantified in the reaction vessel, after reaction.

Reducing sugars reaction yield (X_{RS}, %) is defined by Equation 3.

$$X_{RS} = \left(\frac{RS_E + RS_W}{F_0} \right) \times 100 \qquad (3)$$

Where RS_E is the mass of reducing sugar in the product stream (in the collected hydrolysate), R_{SW} is the mass of reducing sugar in the unreacted solid material, i.e., PHDDT.

Total sugars reaction yield (X_{TS}, %) is defined by Equation 4:

$$X_{TS} = \left(\frac{TS_E + TS_W}{F_0} \right) \times 100 \qquad (4)$$

Where TS_E is the mass of total sugar in the product stream, TS_W is the mass of total sugar quantified in the unreacted material.

2.3 Solid fraction composition

For the calculations of X_{RS} and X_{TS} parameters, the content of sugars from

TH and DDT, i.e., reducing (g glucose/100 g) and total sugars (g sucrose/100 g) were determined according to Somogyi (1937) method adapted by Nelson (1944).

The raw material, i.e. DDT, was characterized in terms of: starch, using an enzymatic kit purchased from Megazyme® (Bray Business Park, Bray, Co. Wicklow, Ireland), method number 996.11 (AACC, 1976). The following analysis were carried out using standard methods (AOAC, 1995): protein was determined using the micro-Kjedahl method (976.05), ash (ignition at 550 °C in an electric furnace, number 923.03), total fiber (method number 991.43, using a Megazyme® enzymatic kit), lipids (Soxhlet apparatus, method 920.39), moisture content (over-drying at 60 °C until constant weight, method 925.40).

Total phenols (g gallic acid/100 g), were analyzed using the Folin-Ciocalteau reagent (Singleton et al., 1999). Curcuminoids were quantified by High Performance Liquid Chromatography (HPLC), according to Osorio-Tobón et al. (2014) using a Waters Alliance Separation Module (269SD, Milford, USA), diode array detector (2998), flow rate of 1.25 $\mathrm{mLmin^{-1}}$ and a C18 column (150×4.6 nm, id., 2.6. µm, Phenomenex, Torrance, USA) that was maintained at 50 °C. The mobile phases were solvent A, which consisted of 0.1% glacial acetic acid (Ecibra, Brazil) in Milli-Q water (Millipore®), and solvent B, which consisted of 0.1% glacial acetic acid in acetonitrile (JT Baker, USA). Curcuminoids were separated by increasing the content of solvent B from 45% to 65% at a constant flow rate.

Antioxidant activity (AA) expressed as % protection against oxidation, was obtained according to the methodology of Hammerschmidt &Pratt (1978) adapted by Leal et al. (2003).

The moisture of PHDDT was identified using an infrared digital moisture balance (A&D, AD4714A, San Jose, USA), in which 5 g of sample (a single sample that represents all the analyzed conditions) was injected in the apparatus for 15 minutes, which temperature increased gradually until 125 °C. Because of low sample availability PHDDT samples from each reaction condition could be characterized only according to starch, total phenols, curcuminoids, and antioxidant activity. All analysis were performed in triplicate, except for fibers and curcuminoids that were made by duplicate, and antioxidant activity that were carried out once.

2.3.1 Scanning Electron Microscopy (SEM)

The structure of turmeric products was examined using a scanning electron microscope (Leo 440i, Cambridge, England), accelerating potential of 15 kV, current of 50 pA and resolution of 1500 ×. The samples were applied on circular aluminum stubs with double carbon sticky tape and coated with 200 Å of gold on the Sputter Coater (EMITECH, K450, Kent, United Kingdom).

2.3.2 Differential Scanning Calorimetry (DSC)

Thermal properties were measured using a differential scanning calorimeter DSC 1 STARe System (Mettler Toledo, DSC1, Zurich, Switzerland). The used sample to water ratio was 1:3 (w/w), in with 5 mg of sample and 15 mg of distilled water were weight in a microanalytic balance (Mettler Toledo, MX5, Zurich, Switzerland). The sample pans with a thin hole in the covers were heated at a rate of 10 °C/min from 20 °C to 120 °C. The heat flow curves, on set temperature (T_{OS}), peak temperature (T_{PEAK}), endset temperature (T_{ES}) and enthalpy of gelatinization (ΔH_{GEL}) were obtained.

2.3.3 Pasting Properties

The Rapid Visco Analyser, RVA (4500, Perten Instruments, Hägersten, Sweden), was used to measure the pasting properties and viscosity curves according to AACC method number 76.21-01 (AACC, 2000).

2.4 Liquid fraction composition

The reaction products were characterized with respect to the quantities of total phenols, curcuminoids and antioxidant activity.

2.5 Statistical analysis

Analysis of variance (Tukey test) using Minitab v.16 software was performed to determine the overall performance of partial-hydrothermal hydrolysis on the composition of TH and PHDDT samples.

2.6 Process simulation

SuperPro Designer 8.5® (Intelligen Inc., Scotch Plains, NJ, USA) software was used to simulate partial-hydrothermal hydrolysis in a PLE apparatus. The process consisted of a solvent storage tank, a pump to pressurize the system, a heating bath and two extractors allowing for semi-continuous operation (while one reaction vessel was in operation, the other one was cleaned and prepared for the next reaction cycle). Initially, DDT is loaded in the reaction vessel Afterwards, water is pressurized (1 MPa) using a pump and heated (40 °C) using heating bath. Once reached the temperature and pressure conditions into the vessel, 20 min of static time are counted. The reaction begins, TH is collected and PHDDT is recovered.

2.7 Economic evaluation

2.7.1 Economic evaluation parameters

To scale the equipment cost to the required capacity is possible using Equation 5, where C_1 is the equipment cost with capacity Q_1, C_2 is the known base cost for equipment with capacity Q_2 and n is a constant related to the type of equipment. Values of n were collected from literature (Green & Perry, 2007; Silla, 2003; Smith, 1995; Turton et al., 2009).

$$C_1 = C_2\left(\frac{Q_2}{Q_1}\right)^n \qquad (5)$$

Cost of manufacturing (COM) was estimated according to the methodology proposed by Turton et al. (2009), which components for each process section were estimated in terms of five major costs: fixed capital of investment (FCI), cost of operational labor (COL), cost of utilities (CUT), waste treatment cost (CWT) and cost of raw material (CRM). The FCI involves expenses related to the implementation of the production line, COL is related to the operators of the units and the CUT considers the energy used in the solvent cycle for steam generation, water refrigeration and electricity requirements. The CRM consists of raw material and solvent costs. In this work, the cost of the raw material is zero because it is the waste from deodorization and depigmenting processes. Finally, CWT was considered to be zero because the waste generated by the process is harmless and clean. The base costs, and the input economic parameters used for simulation are available in the supplementary material.

2.7.2 Scale-up process

For the scale-up, it was assumed that the yield and composition of the reaction products obtained at laboratory scale would also be obtained in industrial scale (Santos et al., 2012). The process was designed to operate for 7920 h per year, which corresponds to 3 daily shifts for 330 days per year considering reaction vessels in volumes of 2×5 L, 2×50 L and 2×500 L. The number of required operators were 1, 2 and 3 for the units of 2×5 L, 2×50 L and 2×500 L, respectively (Veggi et al., 2014). The amount DDT to be processed in each stage was calculated based on the extractor size and apparent density of raw material (838 kg/m^{-3}).

3 RESULTS AND DISCUSSION

3.1 Hydrothermal hydrolysis experiments

Partial hydrolysis was successful resulted on less than 50% of starch content in solid turmeric were converted into glucose (Figure 1). Degree of hydrolysis close to 80% was found on acid hydrolysis of turmeric and ginger wastes using supercritical CO_2 and subcritical water at 130-150 ^oC (Moreschi et al., 2006). Nor temperature, neither pressure influenced the reaction parameters according to Tukey test.

Reaction conditions had no effect on the content sugar yields and converted material (Figure 3), which were comparable to that reported to hydrothermal hydrolysis of sweet potato starch (Nagamori & Funazukuri, 2004), and lower than those reported to acid hydrolysis applied to avocado seeds (Woldu & Tsigie, 2015), and defatted annatto, Brazilian ginseng and pressed palm fiber (Alcázar-Alay et al., 2015).

In terms of a qualitative approach, the increasing of temperature decreases the quality of sugars from turmeric hydrolysates, analyzed using thin-layer chromatography (Santana & Meireles, 2016).

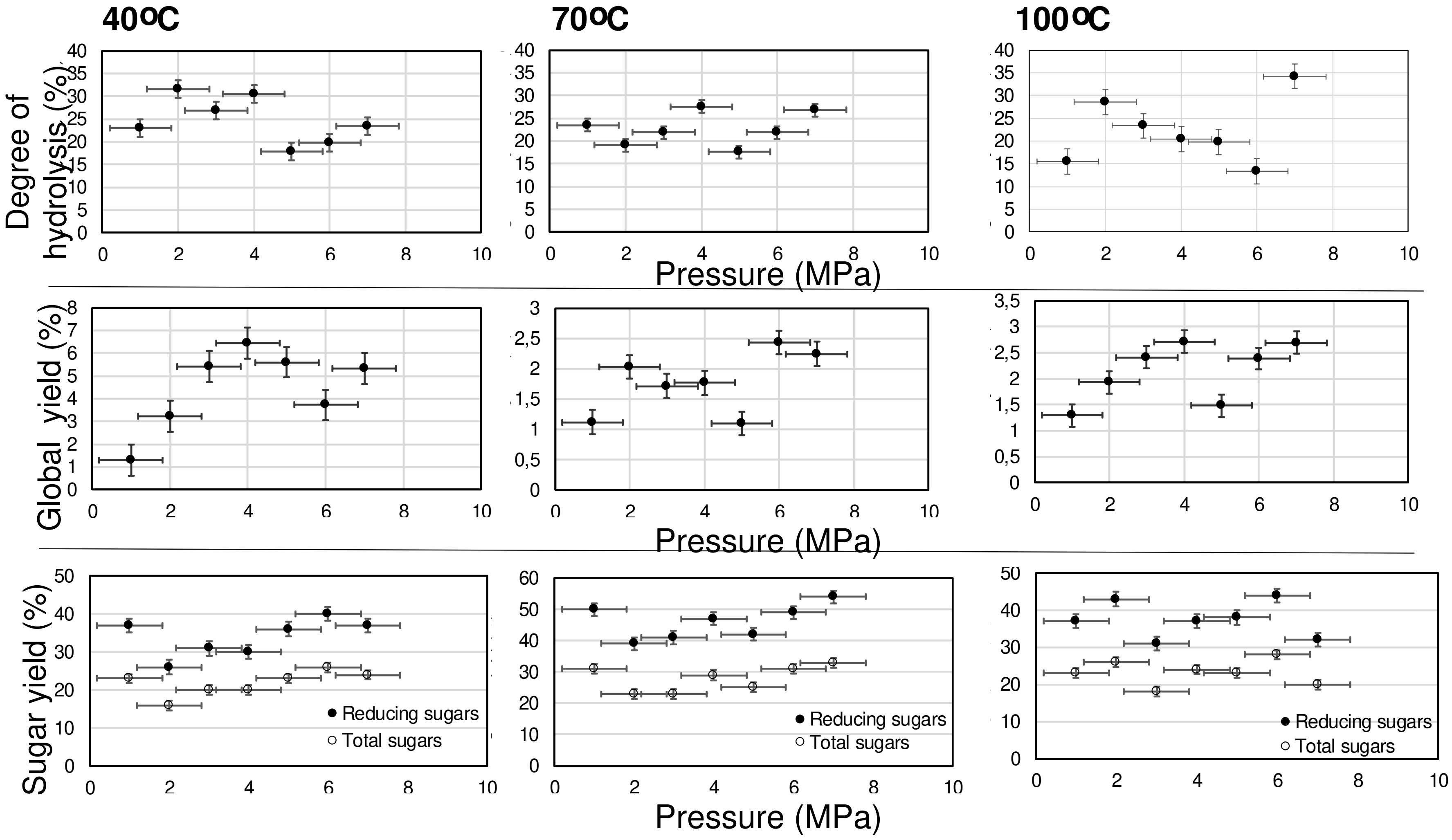

Figure 1 Hydrolysis parameters variation.

3.2 Solid fraction composition

The composition of DDT resulted on moisture value of 5.0±0.2 g/100 g, protein content of 3.1±0.2 g/100 g, ashes of 4.4±0.2 g/100 g and lipids of 0.5±0.3 g/100 g. From the total carbohydrates content of 86.9±0.3 g/100g, were analyzed fibers (28.4±0.9 g/100 g), starch (36±3 g/100 g), reducing sugars (0.10±0 g/100 g) and total sugars (0.31±0.1 g/100 g). Total phenols were 0.66±1 g/100 g. Antioxidant activity was 36.8% after 1 hour of reaction. According to the infrared moisture balance, PHDDT presented 59.8 g/100g of moisture. The effects of reaction conditions on the composition of the resulted solid fraction is reported on Table 1.

Table 1 Composition of PHDDT samples.

Temperature (ºC)	Pressure (MPa)	Starch (g/100g)	AA (%)	Total phenols (g/100g)	Total curcuminoids (g/100g)	BDMC (%)	C (%)	DMC (%)
40	1	25±2^{a}	11.72^{a}	27±3^{a}	3.56±0.009^{a}	50.10±0.001	33.26±0.007	16.65±0.001
	2	25±1^{a}	13.90^{a}	52±2^{a}	4.94±0.027^{a}	48.05±0.011	29.30±0.000	23.56±0.016
	3	24±2^{a}	12.72^{a}	47±3^{a}	3.50±0.002^{a}	50.59±0.002	31.99±0.001	17.49±0
	4	26±1^{a}	27.75^{a}	32±3^{a}	3.34±0.001^{a}	49.29±0	33.36±0	17.40±0.001
	5	23±0^{a}	28.25^{a}	58±1^{a}	4.23±0^{a}	49.64±0	32.95±0	17.39±0
	6	25±1^{a}	28.53^{a}	54±1^{a}	3.72±0^{a}	51.88±0.001	31.09±0.001	17.03±0
	7	29±1^{a}	29.37^{a}	39±2^{a}	3.76±0.001^{a}	48.84±0.001	33.50±0	17.63±0
70	1	25±2^{a}	22.59^{b}	25±0^{b}	1.79±0.001^{a}	51.32±0.001	31.92±0	16.84±0
	2	25±1^{a}	29.82^{b}	45±0^{b}	2.33±0.001^{a}	50.31±0.001	32.67±0	17.07±0
	3	25±2^{a}	38.40^{b}	59±1^{b}	4.02±0.008^{a}	50.76±0.004	31.80±0.003	17.67±0
	4	25±1^{a}	27.80^{b}	52±0^{b}	3.73±0.001^{a}	51.98±0.002	30.62±0.001	17.43±0.001
	5	32±2^{a}	30.33^{b}	51±0^{b}	1.49±0.002^{a}	48.42±0.001	34.83±0	16.92±0.001
	6	32±2^{a}	35.54^{b}	39±5^{b}	3.64±0.001^{a}	51.62±0.001	31.14±0	17.27±0.001
	7	28±0^{a}	33.74^{b}	46±2^{b}	4.83±0.006^{a}	49.89±0	33.16±0.005	17.11±0.001
100	1	28±3^{a}	33.02^{b}	55±0^{b}	2.74±0.010^{b}	55.76±0.010	28.73±0	15.93±0
	2	30±1^{a}	24.44^{b}	29±1^{b}	1.29±0.002^{b}	49.29±0.001	34.39±0.001	16.51±0
	3	29±1^{a}	16.03^{b}	54±7^{b}	2.49±0.001^{b}	51.76±0.001	31.30±0	16.90±0
	4	29±1^{a}	32.85^{b}	78±7^{b}	3.17±0.003^{b}	51.85±0.001	31.37±0.002	16.89±0
	5	28±4^{a}	30.83^{b}	71±3^{b}	2.24±0^{b}	51.48±0	31.67±0	16.85±0
	6	27±2^{a}	17.21^{b}	61±1^{b}	2.49±0^{b}	51.54±0	31.57±0.001	16.88±0
	7	24±0^{a}	36.49^{b}	64±1^{b}	1.36±0.012^{b}	60.32±0.013	26.55±0	14.02±0

Mean ± standard deviation of determinations. Different letters in the same column inidicate significant difference related to the effects of temperature ($p<0.05$).

BDMC – bisdemethoxycurcumin, C – curcumin, DMC – demethoxycurcumin.

The reaction temperature influenced the resulting composition of PHDDT samples in terms of starch, antioxidant activity and total phenols, on the contrary of pressure, as showed in Table 1 (Tukey test). The content of starch from PHDDT was comparable to those from semi-defatted annatto seeds (Alcázar-Alay et al., 2016).

Considering total curcuminoids, bisdemethoxycurcumin occupied approximately 50% of composition (Table 1), differently from those reported elsewhere for crude turmeric and its recovered starch (Santana et al., 2017), from which most of the curcuminoids composition was attributed to curcumin.

Antioxidant activity values were lower (Table 1) when compared to those reported in literature for turmeric extracts microparticles (Santana & Meireles, 2017) and turmeric extracts obtained by supercritical fluid extraction (Braga et al., 2003). Total phenols were higher than that registered for semi defatted annatto seeds (Torres et al., 2015) and lower than in breads prepared by the substitution of wheat flour with turmeric powder (Lim et al., 2011).

3.2.1 Differential Scanning Calorimetry

The DSC transition temperatures and enthalpy of gelatinization of solid turmeric were next (Table 2). These variables are comparable (Santana et al., 2017) and different (Leonel et al., 2003) from those reported for turmeric starches, because of differences attributed to the cultivation conditions applied to the raw material.

The gelatinization temperature (T_{OS}) and enthalpy (ΔH_{GEL}) of starches depend on the microstructure, the degree of crystallinity within the granule and on the amylose to amylopectin ratio. Normally, a smaller granule will result in a greater gelatinization temperature (Hansdah et al., 2015).

Thermal behavior of starch is complex because of the physicochemical changes that occur during heating that may involve gelatinization, melting, glass transition and crystallization, change of crystal structure, volume expansion, molecular degradation and motion of water. All these thermal behaviors depend upon the moisture content and the water contained in starch is not stable during heating (Yu & Christie, 2001).

Table 2 DSC gelatinization parameters of DDT and PHDDT samples.

Temperature (°C)	Pressure (MPa)	ΔH_{GEL} (J/g)	T_{OS} (°C)	T_{PEAK} (°C)	T_{ES} (°C)
Before hydrolysis		29.93	97.4	101.88	142.74
40	1	28.75	98.07	105.36	141.56
	7	27.94	97.81	105.26	147.24
70	1	29.07	97.37	104.89	140.14
	7	29.98	97.04	102.77	137.81
100	1	29.51	97.31	102.42	142.85
	7	28.97	97.53	106.94	144.53

3.2.2 Scanning Electron Microscopy

Solid turmeric presented cellulosic structures and oval-elliptical starch granules with fissures (Figure 2). The exposure, dispersing and fissures of starch granules on DDT are attributed to the previous extraction stages that acted as pretreatments of turmeric for the subsequent reaction assays (Figure 2A). The presence of ruptured cellulosic structures together with starch granules (Figure 2) occurred because cellulose is more difficult to be hydrolyzed than the starch (Nagamori & Funazukuri, 2004). According to the SEM photos, there is no visible morphological changes in the products obtained for most of reaction conditions (Figures 2B-2F). This indicate that reaction conditions, mainly the pressure, may enhance the diffusion of water into the granules, without affect the granule structure (Liu et al., 2009). Nevertheless, it is noted that the conditions of 100 °C and 7 MPa contributed to the leaching of soluble portion of starch into solvent, transforming the granules into formless sacs (Figure 2G).

The impact of partial hydrothermal hydrolysis on these products has taken the form of heat-moisture-treatments, which is a type of hydrothermal treatment considered natural and safe when compared to chemical modification (Khunae et al., 2010). The reaction assays modified the starch structure promoting the pre-gelatinization the granules (Walter, 1998).

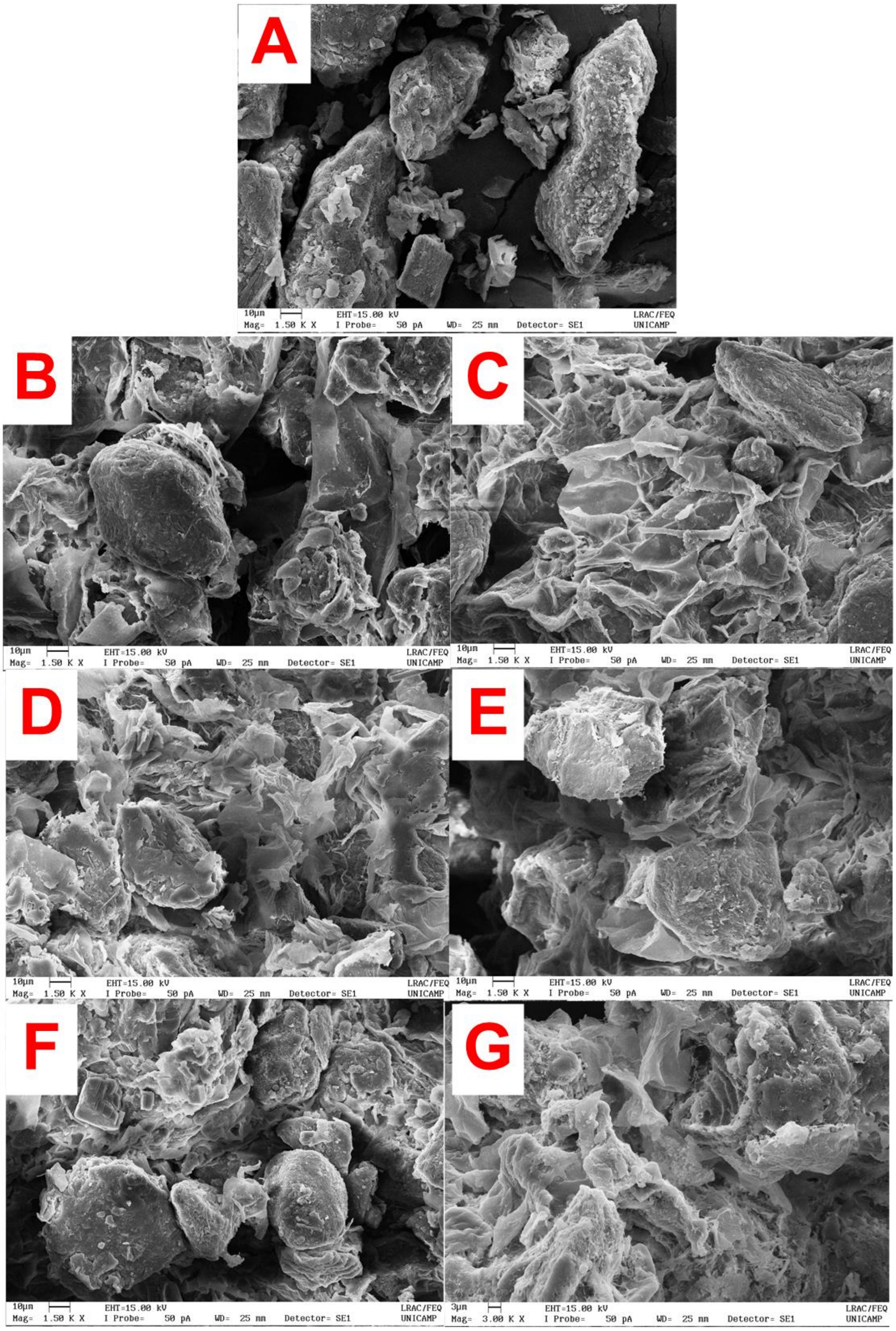

Figure 2 Micrographies of DDT (A) and PHDDT samples at 40 ºC/1 MPa (B), 40 ºC/7 MPa (C), 70 ºC/1 MPa (D), 70 ºC/7 MPa (E), 100 ºC/1 MPa (F) and 100 ºC/7 MPa (G).

3.2.3 Pasting properties

Rapid Visco Analyser (RVA) is used to evaluate all phases of extruded product during production, including crude raw material, dough, intermediates, dried half-products and final products (Elliott et al., 2015).

The RVA curves of solid hydrolyzed products (Figures 3B-3D) are characterized by a peak rise time followed by constant increasing, similar as isolated starches from white turmeric (Leonel et al., 2003). The behavior of these curves differs from DDT in terms of a stationary phase after the peak rise followed by constant increasing (Figure 3A). There is no decrease in viscosity, therefore the breakdown viscosity does not exist.

Partial hydrolysis provided the increased substantially moisture content in solid turmeric. This factor, associated to the reaction conditions contributed to the partial gelatinization of starch granules. Partial gelatinization contributed to the increasing of viscosity values (Figures 3B-3D), which are comparable to the starches of turmeric (Braga et al., 2006), corn and potato (Santana et al., 2017). High viscosity is desirable for industrial uses which objective is the thickening power. The curves denote a high setback behavior (Figure 3), which indicate strong tendency to retrograde.

For the materials hydrolyzed at 40 °C it is noted an almost linear influence of pressure on pasting properties, and high pasting behavior at lower pressures, differently from the materials hydrolyzed at higher pressures, except for 6 MPa, which curve was overlapped by the product hydrolyzed at 4 MPa.

Nevertheless, considering the solid materials hydrolyzed at 70 °C and 100 °C, the effects of pressure resulted in a complex behavior described by absence of linearity, when compared to the curves obtained from the materials hydrolyzed at 40 °C.

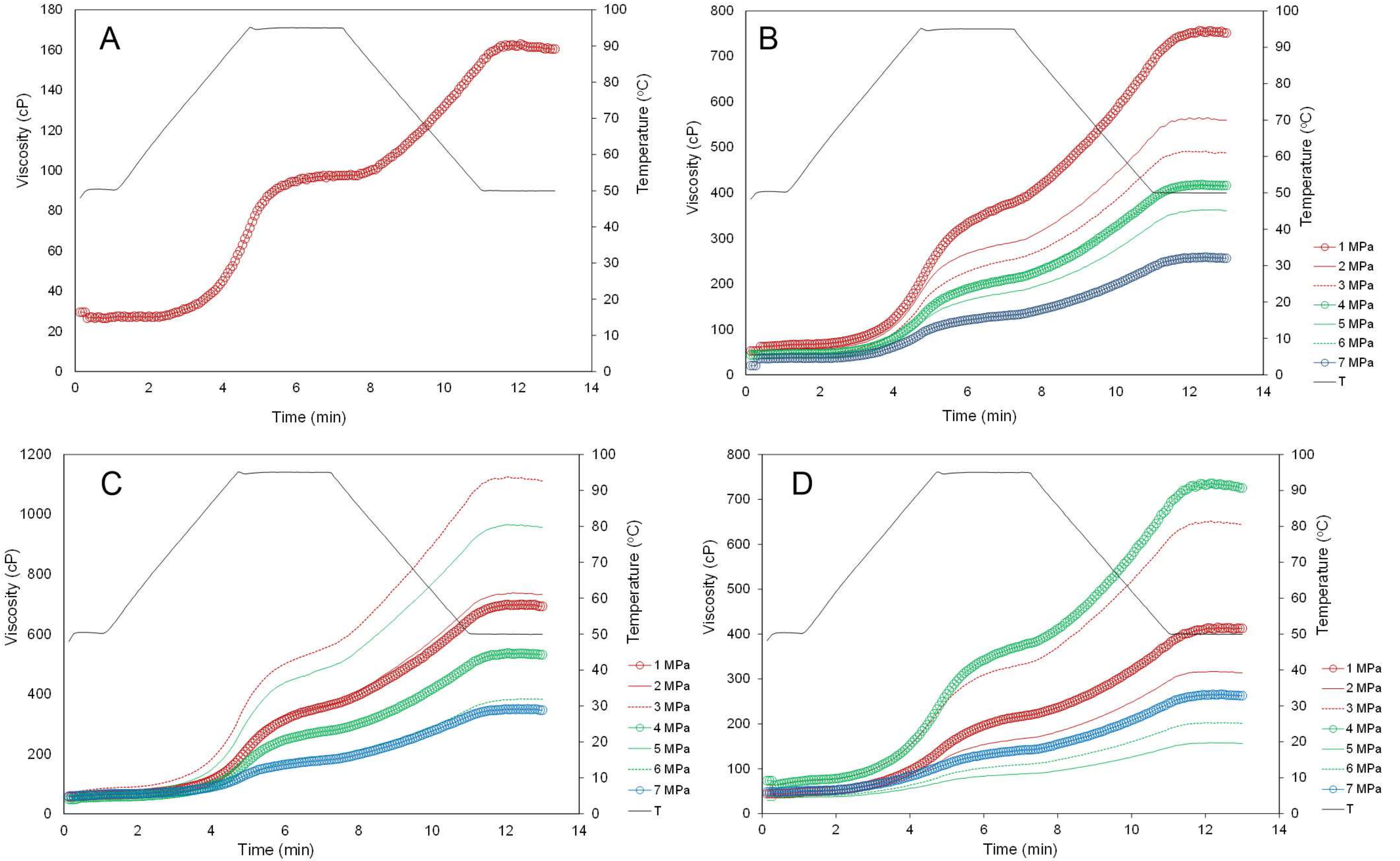

Figure 3 Pasting Properties of DDT (A) and PHDDT at 40 ºC (B), 70 ºC (C) and 100 ºC (D).

3.3 Liquid fraction composition

Reaction temperature variations influenced the content of antioxidant activity and total phenols (Table 3), which increased slightly as a function of temperature, on the contrary of most phenolic compounds that are unstable and highly susceptible to thermal degradation. The quality of curcuminoids detected in TH differs from the PHDDT with respect to the quantity and to the highest proportion of curcumin (Table 3). The content of curcuminoids was lower when compared to that reported to ethanolic extracts obtained from deodorized turmeric rhizomes (Osorio-Tobón et al., 2014).

Antioxidant activity values of TH were lower than those higher than 50% reported for turmeric volatile oil and curcuminoids extracts (Santana & Meireles, 2017), and Brazilian ginseng extracts (Debien et al., 2015).

Considering the fact that the raw material used in this work is a waste from extraction processes, it was already expected the bioactives constituents quantified would be lower than those from crude or minimally extracted plant materials. Nevertheless, the quality of the products obtained is relevant in terms of carbohydrates and curcuminoids, which contribute to the antioxidant effectiveness. Therefore, partial hydrolysis is an interesting alternative to prevent DDT from being discarded.

Table 3 Composition of TH samples.

Temperature (^{o}C)	Pressure (MPa)	AA (%)	Total phenols (g/100g)	Total curcuminoids (g/100g)*	BDMC (%)	C (%)	DMC (%)
40	1	1.68^{a}	16±4^{a}	0.44^{a}	27.27	39.20	33.52
	2	0^{a}	16±2^{a}	0.36^{a}	26.56	39.61	33.84
	3	12.44^{a}	7±3^{a}	0.46^{a}	25.96	39.97	34.08
	4	0.50^{a}	12±5^{a}	0.30^{a}	25.13	40.87	34.00
	5	7.06^{a}	11±4^{a}	0.32^{a}	22.22	36.61	30.89
	6	1.18^{a}	16±2^{a}	0.41^{a}	25.63	40.37	34.00
	7	0^{a}	16±5^{a}	0.29^{a}	32.83	49.54	42.44
70	1	19.73^{b}	48±1^{b}	0.39^{a}	28.10	41.79	35.67
	2	13.68^{b}	31±3^{b}	0.35^{a}	30.05	45.90	39.23
	3	22.48^{b}	25±0^{b}	0.47^{a}	32.10	51.40	43.95
	4	14.63^{b}	19±1^{b}	0.41^{a}	23.68	37.65	32.80
	5	9.64^{b}	49±1^{b}	0.42^{a}	24.84	39.55	34.48
	6	12.78^{b}	23±2^{b}	0.44^{a}	30.15	47.06	41.37
	7	20.96^{b}	25±0^{b}	0.41^{a}	35.83	53.45	46.04
100	1	13.85^{b}	27±1^{b}	0.28^{a}	36.63	53.50	44.87
	2	16.03^{b}	20±2^{b}	0.56^{a}	28.10	44.32	37.34
	3	7.23^{b}	25±3^{b}	0.32^{a}	30.23	55.05	47.09
	4	13.12^{b}	32±4^{b}	0.57^{a}	33.96	50.01	43.34
	5	13.85^{b}	34±1^{b}	0.43^{a}	39.41	54.78	48.07
	6	15.92^{b}	32±0^{b}	0.25^{a}	34.96	48.86	41.72
	7	12.11^{b}	38±4^{b}	0.43^{a}	35.41	48.36	41.70

Mean ± standard deviation of determinations. Different letters in the same column inidicate significant difference related to the effects of temperature ($p<0.05$)

BDMC – bisdemethoxycurcumin, C – curcumin, DMC – demethoxycurcumin/*Deviations lower than 0.001.

3.4 Economic evaluation of the process

The COM of PHDDT was US$ 0.90 kg^{-1} for a process capacity of 2×5 L, US$ 0.31 kg^{-1} for 2×50 L plant and US$ 0.14 kg^{-1} for a 2×500 L (Figure 4A). The COMs of TH were estimated to be US$ 2.56 kg^{-1}, US$ 0.96 kg^{-1} and US$ 0.43 kg^{-1} for processes with capacity of 2×5 L, 2×50 L and 2×500 L, respectively (Figure 4B). The process employed in this work is advantageous due to the relatively short duration of reaction assays and the use of water, a cheap and safe solvent.

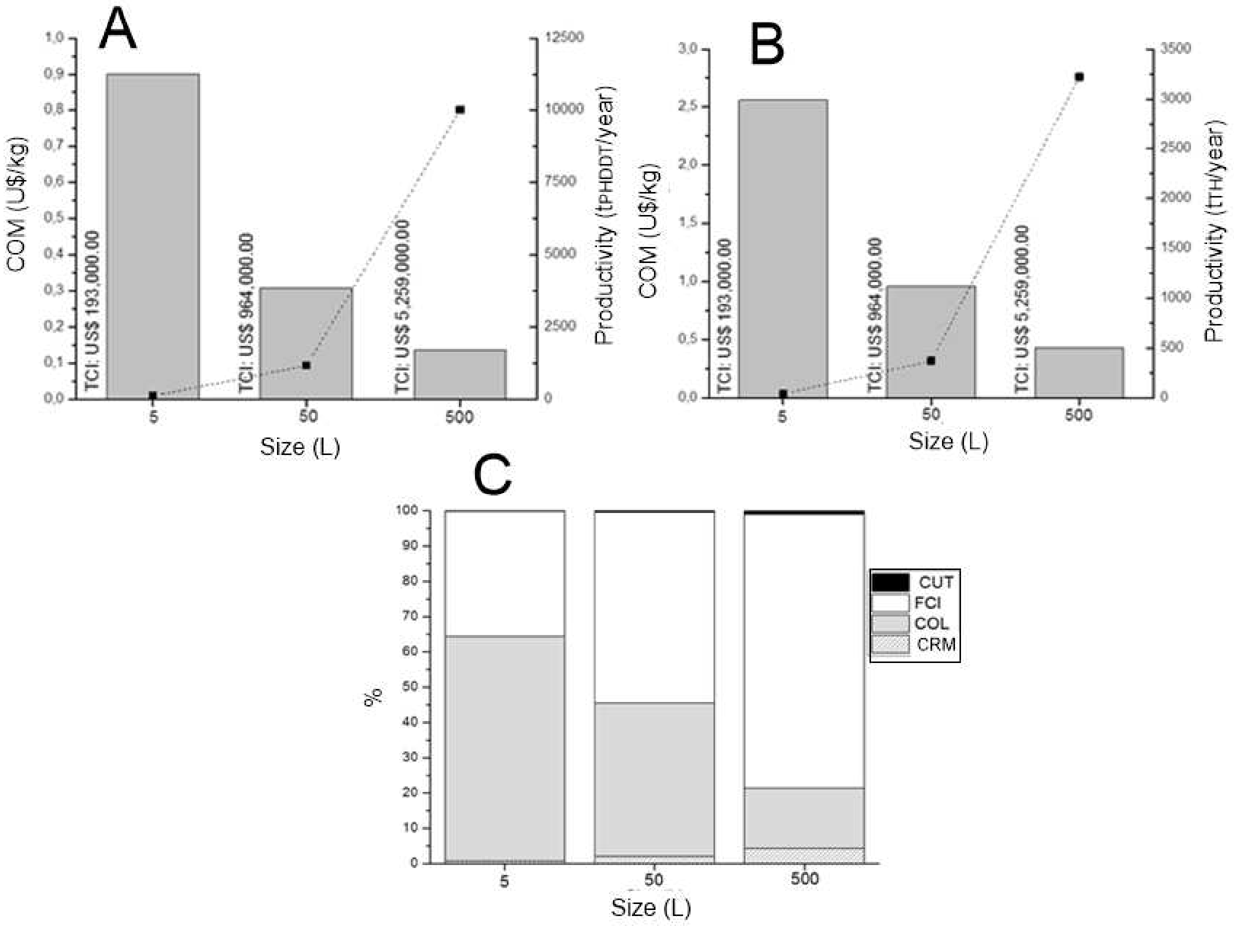

Figure 4 Cost of manufacture (COM) of PHDDT (A) and TH (B) using reactors with different capacities and contribution of different shares to COM of partial hydrolysis (C): cost of utilities (CUT), investment cost (FCI), cost of operational labor (COL) and cost of raw material (CRM).

Considering a process using a two 50 L vessel system, the calculated COMs for TH and PHDDT were approximately 5.6 and 17.38 times lower than the COMs obtained by Osorio-Tobón et al. (2014) in the extraction of curcuminoids from deflavored turmeric via PLE using ethanol as solvent and considering the cost of the raw material equal to zero.

As have been established by other researchers, the CRM plays a very important role in COM. However, in this work, as the cost of raw material is zero and the extract solvent is water, it was possible to obtain a very low COM. Therefore, partial hydrothermal hydrolysis appears to be an attractive and economically feasible technique for obtaining new products from plant wastes. The raw material used is a waste with no monetary value, thus the participation of DDT in the COM is zero. However, the solvent contributes with a slight increase in the participation of the CRM in the COM when the process is scaled-up, i.e., participation of the CRM in the COM increased from 0.71% to 4.41% when the process is scale-up from 5 L to 500 L (Figure 4 C).

As the process scale increased, the COL decreased its impact on the COM, whereas as the process scale increased, the FCI increased its impact on the COM. For example, the COL decreased from 63.64% to 17.05%, whereas the FCI increased from 35.48% to 77.5% when the process is scale-up from 5 L to 500 L (Figure 4 C). Although with the scale-up process is necessary more quantity of workers, the impact related with the implementation of the production line at higher scales, contributed with a decrease in the participation of COL in the COM, instead of an increased in the participation in COM due to the increased in the number of workers. The CUT almost had not participation in COM (Figure 4 C). A slight increase in the participation of the CUT in the COM was observed. Factors such as quantities of solvent, energetic expenditures and energy requirements, product of the longer processing time, contributed with the increase in the participation of the CUT in the COM due to the scale-up procedure.

This section provided an economic evaluation of partial hydrolysis using pressurized hot water for the recovery of bioactive constituents from waste turmeric to the scientific community and companies. In this context, the presented behavior gives relevant information for further systematic and more accurate studies or projects. Besides, further studies on economic evaluation of application of partial hydrolysis should evaluate carefully the characteristics of the raw material, demand, the market that is focused, the country, the quality requirements and local fees, among other issues, to provide more deterministic results.

4 CONCLUSIONS

Partial hydrolysis using pressurized hot water contributed to the polymer modification of deflavored and depigmented turmeric waste, which can attribute to this material application in industry as complementary starch source to the conventional ones, like corn and rice, besides adding color and improving antioxidant effectiveness on products. Furthermore, the process provided a liquid fraction source of simple sugars and curcuminoids.

The effects of temperature and pressure on the composition of liquid fraction were statistically irrelevant, except in terms of total phenolics, which increase in temperature contributed to increase the availability of these constituents. Nevertheless, reaction conditions provided pregelatinized granules on the solid fraction with viscosity values comparable to those reported on literature.

Economic evaluation showed that the process applied in this work appears to be an attractive and economically feasible technique to reuse deflavored and depigmented turmeric due to the short duration and the use of water, a cheap and considered safe solvent.

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- CAPÍTULO 5 –

Starch recovery from turmeric wastes using supercritical technology

O efeito das extrações com CO_2 supercrítico e etanol pressurizado na estrutura dos rizomas de cúrcuma e em seus amidos isolados foi verificado. Afim de propor uma alternativa eficiente, limpa e viável para obtenção de novos produtos de valor agregado a partir de resíduos, foi realizada neste trabalho a integração de processos e análise econômica da hidrólise parcial combinada com o posterior isolamento do amido.

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Starch recovery from turmeric wastes using supercritical technology

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ABSTRACT

Extraction processes that employ supercritical fluid technology has been extensively applied for the obtaining of high-quality extracts from turmeric rhizomes. Nevertheless, these processes generate high quantities of wastes, which are potential sources of antioxidant constituents and carbohydrates. In this work, mixed biopolymers composed of starch and curcuminoids were recovered from supercritical fluid and pressurized liquid extraction processes. The quality of these materials was investigated in terms of experimental and economic approaches. The application of supercritical fluid and pressurized liquid extraction resulted on products with relevant quality in terms of curcuminoids and modified polymer matrix, which can attribute inclusion in industry as a colorant agent, and in human diet as a resistant starch source. Economic evaluation reports that recovery of biopolymers from turmeric wastes is a feasible alternative considering 80% yield and capacities of 50 L and 500 L.

1. Introduction

The composition of turmeric rhizomes in terms of starch and curcuminoids are responsible for the wide application of this crop as dietary food ingredient (Lim and Han, 2016; Mancini et al., 2015; Park et al., 2012) and therapeutic agent for treatment of diseases (Irving et al., 2011; Nguyen et al., 2017; Sahne et al., 2016).

The isolation of starch from crude turmeric has been performed with the application of several washings with water, followed by a final washing with alcohol with further drying (Kuttigounder et al., 2011; Leonel et al., 2003). Nevertheless, extraction of curcuminoids has been performed in several different ways with the application of nonpolar solvents hexane, chloroform, ethyl acetate, ethanol and acetone (Osorio-Tobón et al., 2014; Revathy et al., 2011).

Global starch consumption is projected to reach 133.5 million metric tons by 2018, driven primarily by the diversity and sheer number of end-use applications in both food and non-food industries (GIA, 2016). Although there is a large consume of conventional sources of starch, such as corn and potato, the application of non-conventional raw materials as complementary sources may provide cost reduction of raw material in industries, besides offering new products with differentiated characteristics (Santana and Meireles, 2014).

Nowadays methods that employs supercritical fluids and pressurized liquids were successfully applied in the field of starch chemistry for the production of fermentable sugars from the starchy wastes from annatto (Alcázar-Alay et al., 2016) with the employment of partial hydrolysis with pressurized water, and total hydrolysis from ginger wastes using subcritical water and carbon dioxide (Moreschi et al., 2006). In addition, critical water and ethanol were applied for lipid extraction of corn starch (Peterson et al., 2008), while supercritical carbon dioxide induced gelatinization of potato starch (Muljana et al., 2009), and was used for the obtaining of corn starch aerogels (De Marco and Reverchon, 2017).

Supercritical fluid extraction (SFE) with carbon dioxide has been used to extract volatile oils from crude turmeric (Carvalho et al., 2015) and pressurized liquid ethanol has been applied on deflavored turmeric waste for the obtaining of extracts composed of curcuminoids (Osorio-Tobón et al., 2014). As consequence of these processes, solid wastes with high quality in terms of curcuminoids and fermentable sugars are generated (Santana et al., 2017; Santana and Meireles, 2016).

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In this context, we investigate the effects of extraction technologies that employs supercritical carbon dioxide and pressurized liquid ethanol on the recovery of starch and curcuminoids from turmeric wastes. In order to evaluate the feasibility of inclusion of these materials in industries as a complementary starch source, economic evaluation was performed.

2. Materials and methods

2.1. Material

2.1.1. Raw material

Crude turmeric (CT) was purchased from the Oficina de Ervas Farmácia de Manipulação Ltda (lot 065DM, Ribeirão Preto, Brazil).

2.1.2. Reagents

Carbon dioxide (99.9%) was obtained from White Martins (Campinas, Brazil). Ethanol (99.5%, pure) was purchased from Dinâmica (São Paulo, Brazil). Glacial acetic acid (Ecibra, Brazil), Milli-Q water (Millipore®), and acetonitrile (JT Baker, USA) were used in high-performance liquid chromatography (HPLC) analysis. Chloroform (Merck, Darmstadt, Germany), glacial acetic acid (Synth, Diadema, Brazil) and ethanol (Sinergia, Campinas, Brazil) were used in thin-layer chromatography (TLC) analysis. Curcuminoids standards of curcumin ($\geq$94% curcuminoids; $\geq$80% curcumin), demethoxycurcumin, bisdemethoxycurcumin and the volatile standard of ar-turmerone were purchased from Sigma-Aldrich (Darmstadt, Germany).

2.2. Supercritical fluid extraction

Supercritical fluid extraction (SFE) was carried out using a homemade equipment, described by Johner and Meireles (2016). Approximately 70 g (dry basis) of CT was placed inside the extraction cell occupying its total volume, i.e., 100 mL. The solvent was carbon dioxide, which was cooled with the aid of a cooling bath (Thermo Haake, C10, Eindhoven, Nederlands) and was fed into the pneumatic pump (Maximator, M-111L, Nordhausen, Germany) entrance in a liquid form.

The extraction vessel was heated using a heating jacket using circulating water from a heating bath (Thermo Haake, DC30/DL30, Eindhoven, Nederlands) at 333 K. When the extraction vessel achieved the desired temperature, the extraction vessel was pressurized with carbon dioxide at 24 MPa for 20 min (static time). Afterward, the blocking valves were opened, and the micrometering valve was carefully adjusted to maintain the constant carbon dioxide flow of 4.5×10^{-4} kg/s and a solvent-to-feed ratio (S/F, dimensionless) of 12.1. The time of extraction was 31 min (dynamic time).

The applied conditions of 333 K and 25 MPa were selected, according to the highest yield of volatile oil, obtained elsewhere (Osorio-Tobón et al., 2014).

2.3. Pressurized liquid extraction

After the SFE process was completed, deflavored turmeric (DT) was depigmented using ethanol. The curcuminoids extraction was performed in a pressurized liquid extraction (PLE) apparatus described elsewhere (Farias-Campomanes and Meireles, 2013). Approximately 47 g of DT was placed inside the extraction vessel. During the PLE process, the solvent was first pumped into the extractor using a HPLC pump (Thermo Separation Products, ConstaMetric, 3200 P/F, Fremont, USA).

The extraction vessel was heated as previously described. After reaching the desired pressure, the extraction cell was maintained at the desired temperature for a static period carefully adjusted to maintain the system pressure and a constant solvent flow of 1.24×10^{-4} kg/s. The dynamic extraction time was 60 min, and the S/F was 9.5. The resulted waste was identified as deflavored and depigmented turmeric (DDT). The applied conditions of 333 K and 10 MPa were attributed to the higher curcuminoids removing from DT (Osorio-Tobón et al., 2014).

2.4. Recovery of starches

Starches from solid turmeric were recovered using a methodology applied for several starchy crops (Bello-Pérez et al., 1998, 2005; Leonel et al., 2003). The flowchart of this process is showed on Fig. 1.

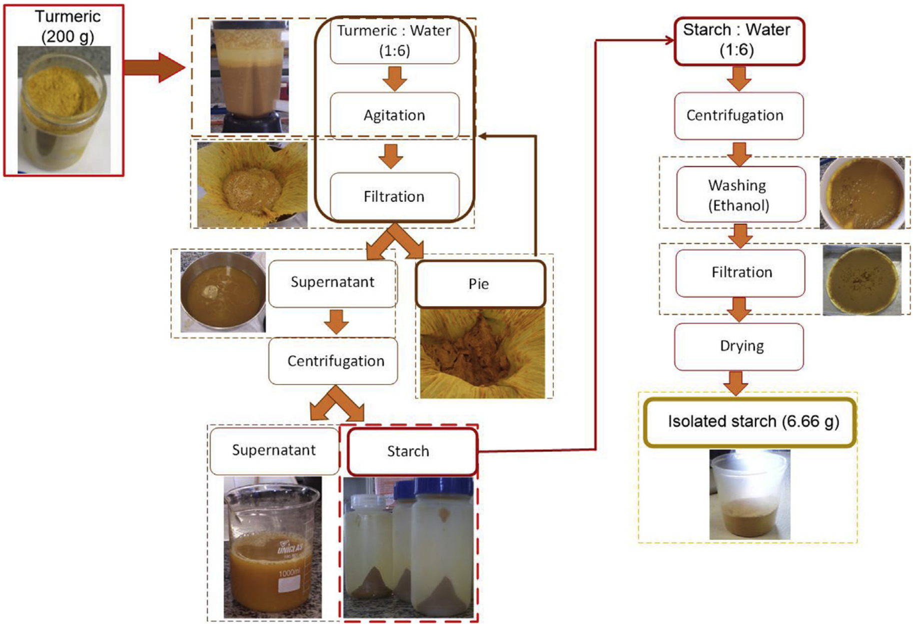

Fig. 1. Flowchart for the turmeric starch recovery experimental procedure.

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Solid turmeric was suspended in water at a ratio of 1:6. The suspension was stirred in a domestic blender (Walyta, São Paulo, Brazil) for 10 min, followed by filtration using a nylon mesh (88 micron) cloth. The filtration pie was resuspended in water and inserted into centrifugue (FANEM, FR22, São Paulo, Brazil) at 1700–1800 g for 10 min.

The isolated starch was washed with ethanol and the resulted suspension was filtered for 10 min with the aid of a vacuum pump (Tecnal, TE-058, Piracicaba, Brazil). Afterward, the isolated starch was dried at 313 K in an oven (Tecnal, TE-385-1, Piracicaba, Brazil) for 240 min.

2.5. Composition

2.5.1. Starch and curcuminoids

Total starch content was determined using an enzymatic kit purchased from Megazyme® (Bray Business Park, Bray, Co. Wicklow, Ireland), method number 996.11 (AACC, 1976).

Curcuminoids (bisdemethoxycurcumin, curcumin and demethoxycurcumin) were determined using two approaches, one quantitative and another qualitative. The quantitative approach consists on the application of HPLC based on the method described previously (Osorio-Tobón et al., 2014) using a flow rate of 1.25 mL/min, a Waters Alliance separation module (269SD, Milford, USA), a diode array detector (2998), and a C18 column (150 × 4.6 nm, id., 2.6 μm, Phenomenex, Torrance, USA) that was maintained at 323 K. The mobile phases were solvent A, which consisted of 0.1% glacial acetic acid in Milli-Q water (Millipore®), and solvent B, which consisted of 0.1% glacial acetic acid in acetonitrile. The curcuminoids were separated by increasing the content of solvent B from 45% to 65% at a constant flow rate.

The qualitative approach consists on the application of TLC. The stationary phase was composed of silica gel plates with aluminum backs (Alugram®, Xtra SIL G, Macherey-Nagel, Germany) and the mobile phase was composed of chloroform, ethanol and glacial acetic acid at a proportion of 95/05/01 (v/v/v). The detection of polyphenols (curcuminoids) and compounds related to the volatile oil fraction (ar-turmerone) was performed using the vanillin-sulfuric acid spray reagent (Krishnaswamy, 2003).

2.5.2. Scanning electron microscopy (SEM)

The structure of starch granules was examined using scanning electron microscopy (SEM). The samples were applied to circular aluminum stubs with double carbon sticky tape and coated with 200 Å of gold using a sputter coater (EMITECH, K450, Kent, United Kingdom). The micrographs with magnification of 300× were obtained using scanning electron microscope (Leo 440i, Cambridge, England) at an accelerating potential of 15 kV and current of 50 pA.

2.5.3. Differential scanning calorimetry (DSC)

Thermal properties were measured using a differential scanning calorimeter DSC 1 STARe System (Mettler Toledo, DSC1, Zurich, Switzerland). The used turmeric to water ratio was 1:3 (w/w) with 5 mg of the sample and 15 mg of distilled water, weighed using a microanalytic balance (Mettler Toledo, MX5, Zurich, Switzerland). The lids of the pans were pierced. The initial temperature of the pans was 293 K, programmed to increase to 423 K by 283 K/min. The onset, or gelatinization temperature (T_{OS}), peak temperature (T_{PEAK}), end set temperature (T_{ES}) and the enthalpy of gelatinization (ΔH_{GEL}) were obtained.

2.5.4. Pasting properties

The viscosity curves and pasting properties of the materials were measured using a Rapid Visco Analyser, RVA (4500, Perten Instruments, Hägersten, Sweden), method 76.21–01 (AACC, 2000). Native potato (Emsland Stärke, Emlichheim, Germany), and corn (Labcer, Unicamp, Brazil) starches were used for comparative purposes because these products are conventional starch sources with standardized viscosity behavior.

Instruments like RVA describe the viscosity (expressed in terms of cP, or mPa.s) parameter as function of temperature and time into three periods. The procedure starts with a controlled heating period, which consists in increasing the temperature of the suspension, formulated with the raw material and water, until 368 K. Afterward, the maximum temperature for analysis is maintained (isothermal period), and lastly, occurs the decreasing the temperature to approximately 323 K (cooling period).

2.6. Process simulation and economic evaluation

Simulations of starch recovery plant were performed using the SuperPro Designer 8.5® software (Intelligen Inc., Scotch Plains, NJ, USA). The starch recovery simulation in large scale was performed with 1 kg of raw material, based on the experimental methodology used in this work. The base costs for the starch recovery unit are showed on Table 1.

At first, turmeric was homogenized with water in the mixing vessel (P-1/A-101) for 10 min. The resulted mixture was filtrated in P-2/F-101 equipment (Fig. 2), followed by centrifugation of the aqueous phase (suspended starch) in P-3/C-101 for 10 min. The predrying of starch was performed by inserting the material into P-4/W-101 to be washed with ethanol, with following filtration at P-5/F-102 for 10 min. The recovered starch was finally dried on P-6/D-101 at 313 K for about 240 min. Fig. 2 provides the schematic diagram of process simulation.

2.6.1. Scale-up process

In the first stage of a project, the obtaining of equipment costs based in past vendor quotations and literature is essential. Although current vendor quotations are the most accurate to obtain the values of the equipment, generally these costs are related to equipments with different capacities than what is required (Silla, 2003).

In this context, Equation (1) was used to scale the equipment cost to the required capacity, where C_1 is the equipment cost with capacity Q_1, C_2 is the known base cost for equipment with capacity Q_2 and η is a constant depending on equipment type. Values of η were collected from literature (Green and Perry, 2007; Silla, 2003; Smith, 1995; Turton et al., 2009).

$$C_1 = C_2\left(\frac{Q_2}{Q_1}\right)^{\eta} \tag{1}$$

For the scale-up, the assumed procedure is that the industrial-scale unit has the same performance as the laboratory-scale unit. Industrial scale vessel volumes of 2 × 5 L, 2 × 50 L and 2 × 500 L were considered (Table 2). The process was designed to operate for 7920 h per year, which corresponds to 3 daily shifts for 330 days per

Table 1
Base cost for the equipment composing the plant.

Equipment	η[a]	Unit base cost (US$) 1 L
Mixing vessel/agitator	0.57	1600
Filter	0.57	100
Centrifuge	0.67	836
Ethanolic washing vessel	0.57	800
Fluid bed dryer	0.10	7000
Total process		**US$ 10, 336.00**

[a] η constant depending on equipment type based on references (Green and Perry, 2007; Silla, 2003; Smith, 1995; Turton et al., 2009).

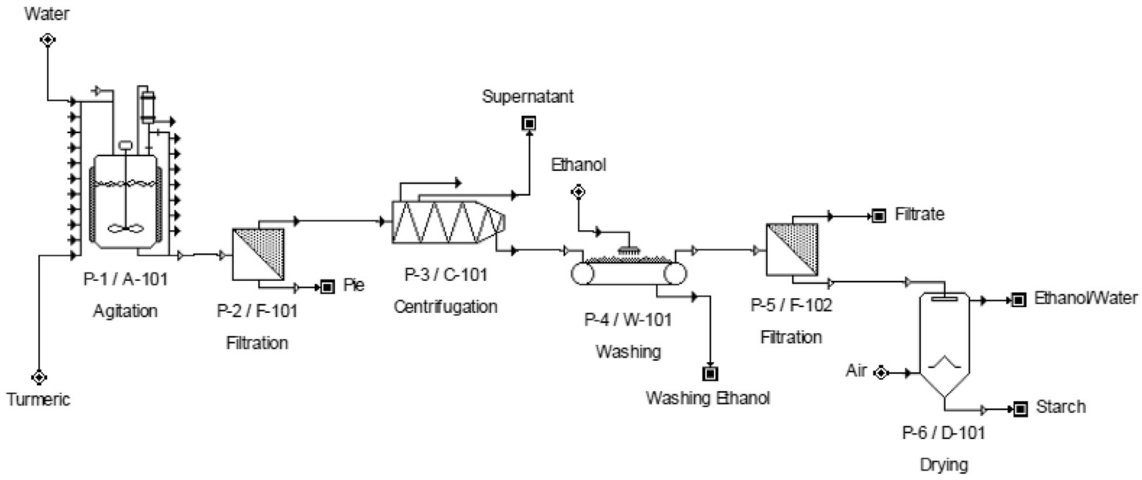

Fig. 2. Schematic diagram of starch recovery procedure built in SuperPro Designer®.

Table 2
Input economic parameters used in the SuperPro Designer 8.5® software.

	Scale		
	5 L	50 L	500 L
Fixed capital investment (FCI)			
Starch isolation plant[a]	US$ 16,937.00	US$ 45,092.00	US$ 153,066.00
Depreciation rate[b]	10%/year	10%/year	10%/year
Annual maintenance rate[b]	6%/year	6%/year	6%/year
Operational labor (COL)	1	2	3
Operator[c]	US$ 5.95/h	US$ 5.95/h	US$ 5.95/h
Cost of raw material	US$ 7.27/kg	US$ 7.27/kg	US$ 7.27/kg
Ethyl alcohol	US$ 1.35/L	US$ 1.35/L	US$ 1.35/L
Water[d]	US$ 0.05/t	US$ 0.05/t	US$ 0.05/t
Utilities (CUT)			
Electricity[e]	US$ 0.092/kWh	US$ 0.092/kWh	US$ 0.092/kWh
Water steam[f]	US$ 4.2/t	US$ 4.2/t	US$ 4.2/t

[a] Estimated cost using the Eq. (1).
[b] Based on Peters et al. (2003).
[c] Bureau of Labor Statistics, http://www.bls.gov/fls/country/brazil.htm, USA, last accessed on 27/08/2016; Turton et al. (2009).
[d] http://www.sanasa.com.br, BRAZIL, last accessed on 27/08/2016.
[e] http://www.eia.gov, USA, last accessed on 27/08/2015.
[f] SuperPro designer 8.5® database.

year. The number of operators required to operate the industrial units of 2 × 5 L, 2 × 50 L and 2 × 500 L was 1, 2 and 3, respectively, according to the procedure of Veggi et al. (2014).

The amount of turmeric to be processed in each stage was calculated based on the vessel size and apparent density of raw material, i.e., 838 kg/m^3 (Osorio-Tobón et al., 2014).

2.6.2. Economic evaluation parameters

The cost of manufacturing (COM) evaluate the feasibility of an industrial project and is determined by the sum of three main components: direct costs, fixed costs and general expenses, according to the methodology proposed by Turton et al. (2009). Input parameters for process simulation are available on Table 2.

The economic evaluation consists in determining the parameters that influences COM, i.e., fixed capital investment (FCI), cost of operational labor (COL), cost of raw material (CRM), cost of waste treatment (CWT) and cost of utilities (CUT).

The FCI involves expenses related to the implementation of the production line (extraction units and other equipments), while COL is related to the operators of the processing units and CUT considers the energy used in the solvent cycle for steam generation, water refrigeration and electricity requirements.

The cost of raw material (CRM) for starch recovery from crude turmeric was assumed to be U$ 7.01/kg (Oficina de Ervas, Ribeirão Preto, Brazil). Considering the extraction processes, the CRM was considered zero because the raw material was a waste.

Finally, CWT was considered to be zero because the remaining solid and liquid material generated from isolation processes can be considered harmless and clean and may be reused for further application as fertilizer and colorant aqueous extract.

2.6.3. Sensitivity analysis

Taking into account that turmeric wastes and the subsequently recovered starches are not commercialized yet, i.e., there is no a selling price for this type of product, some commercial products with similar characteristics to those produced in this article were used as a reference. The average market selling price practiced worldwide for 1 kg of starch from conventional sources typically ranges from US$ 0.80/kg to US$ 1.80/kg (ISI, 2016).

The sensitivity study was done with the selling price of US$ 1.00/kg using two scenarios regarding the recovered starch yield reported in this work and the recovered starch yield of 80%, according to the literature (Braga et al., 2006; Leonel et al., 2003). The main general profitability factors were evaluated, as return on investment (ROI), payback time, gross margin (GM) and internal rate of return (IRR) after taxes.

3. Results and discussion

3.1. Recovery of starches

According to Sajitha and Sasikumar (2015) the characteristics of turmeric rhizomes and their subsequently recovered starches is known to vary with location, maturity and accession. In this work, the starch recovery in dry basis yielded approximately 3.33%, which is comparable to the yield obtained for Indian arrowroot, 7.07–8.50%, (Paikra et al., 2014), and mango ginger, 7% (Policegoudra and Aradhya, 2008).

Nevertheless, it was very low than that reported elsewhere for turmeric (70–80%) from which rhizomes were cultivated in specific conditions for the production of crops with high quantity of starch, i.e., temperate climate with wet winter and clay textured latosoil (Leonel et al., 2003). The supplier did not specify the cultivation conditions applied in the raw material studied in this work.

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3.2. Composition

3.2.1. Starch and curcuminoids

The recovered starches consisted of mixed biopolymers composed of starch and curcuminoids. Despite the successive washings performed according to the recovery methodology, yellow coloration remained because of low solubility of curcuminoids in water (Fig. 4). Presence of curcuminoids is a factor that can attribute antioxidant effects and commercial value to these products.

It was observed that in the residues submitted to subsequent extraction procedures occurred an increase in the starch content in detriment of the recovered starches (Table 3). Starch content on turmeric wastes was lower than those 70% or 80% found for the recovered starches from turmeric (Braga et al., 2006; Kuttigounder et al., 2011).

Considering another *curcuma* species, the starch content for the studied materials (Table 3) was comparable to those found for mango ginger (48.48 g/100 g), wild turmeric (45.90 g/100 g), black turmeric (45.24 g/100 g), and java ginger (46.11 g/100 g) (Sajitha and Sasikumar, 2015).

Supercritical carbon dioxide applied to deodorize CT provided a volatile oil yield of 2.34 ± 0.80%, from which the total curcuminoids detected of 3.02 ± 0.10 g/100 g (Table 3), which value was higher

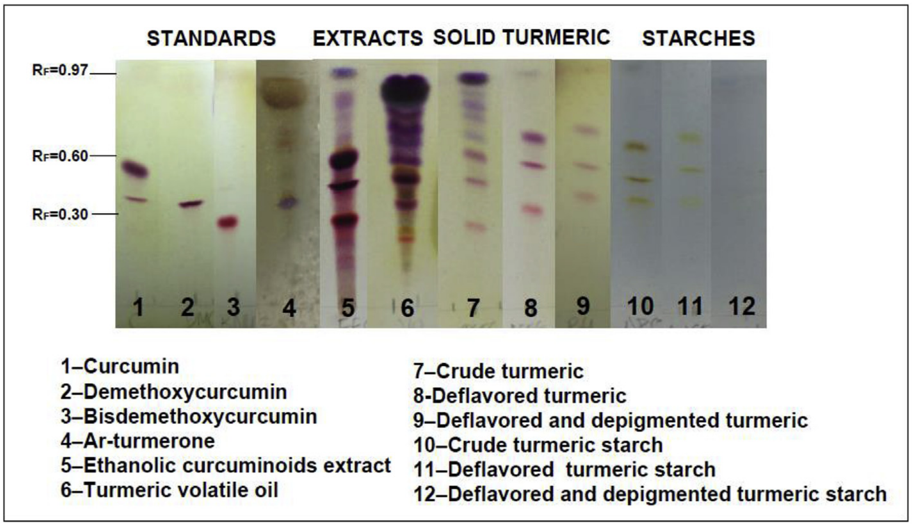

Fig. 3. Thin-layer chromatography profile.

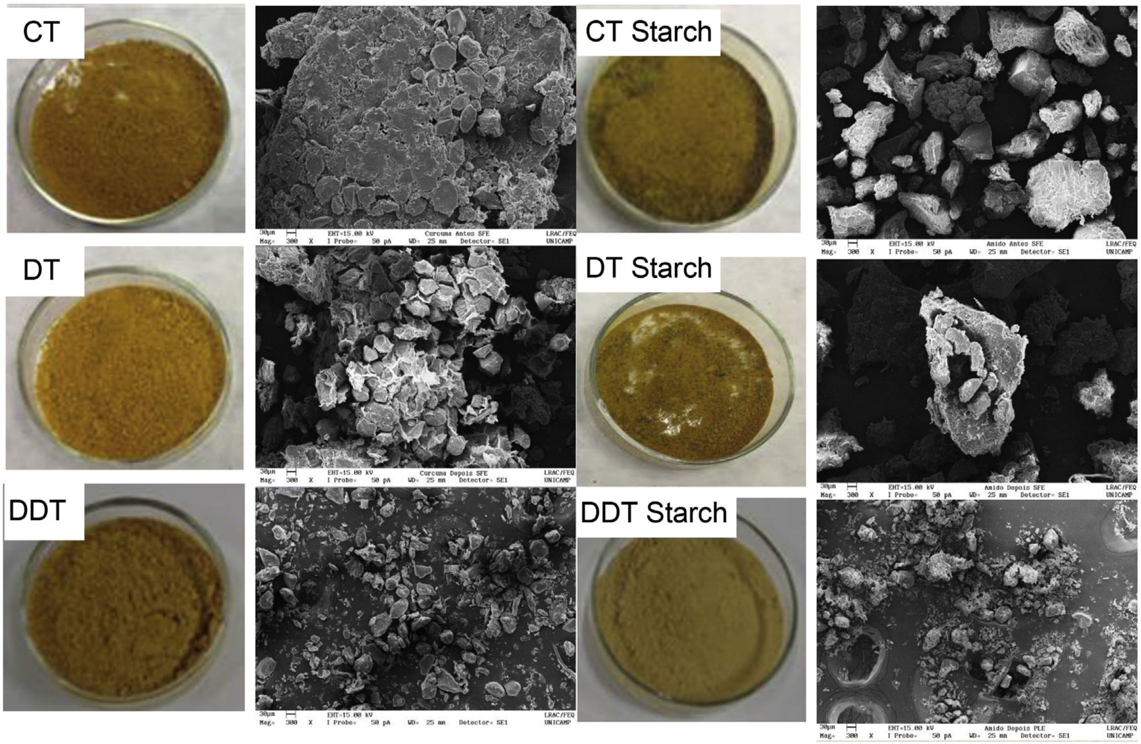

Fig. 4. Scanning electron microscopy.

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Table 3
Content of starch and curcuminoids.

	Starch (g/100 g)	Curcuminoids			
		TOTAL (g/100 g)	BDMC (%)	C (%)	DMC (%)
CT	26 ± 2	13.13 ± 3.02	39.08 ± 2.27	43.11 ± 1.26	17.81 ± 1.01
CT starch	46 ± 4	6.72 ± 1.41	23.17 ± 7.69	53.92 ± 5.24	22.94 ± 2.44
Turmeric volatile oil	–	3.02 ± 0.10	0.73 ± 0.20	87.12 ± 0.26	12.15 ± 0.06
DT	35 ± 3	12.5 ± 0.10	35.12 ± 0.33	46.06 ± 0.29	18.81 ± 0.03
DT starch	32 ± 2	9.96 ± 2.77	44.75 ± 8.66	36.63 ± 5.24	18.66 ± 1.93
Curcuminoids ethanolic extract	–	12.08 ± 1.05	37.50 ± 0.69	42.77 ± 0.61	19.71 ± 0.08
DDT	36 ± 3	4.12 ± 0.32	43.50 ± 3.97	31.09 ± 1.66	25.41 ± 5.64
DDT starch	27 ± 2	0.29 ± 0.03	36.86 ± 0.88	48.47 ± 0.10	14.66 ± 0.49

BDMC=Bisdemethoxycurcumin, C=Curcumin, DMC = Demethoxycurcumin.

than those reported for fractionated turmeric volatile oils (Santana et al., 2017). Pressurized liquid ethanol applied on the DT waste provided a curcuminoids extract that yielded 13% (Osorio-Tobón et al., 2014), from which total curcuminoids content was 12.08 ± 1.05 g/100 g.

Curcuminoids content in DT waste and in the ethanolic extract are comparable with commercial turmeric, curry powders (Tayyem et al., 2006), and ethanolic extract obtained with soxhlet distillation (Himesh et al., 2011).

The successive washings performed in the starch recovery procedure contributed to the removal of 48.82% of curcuminoids from CT, 20.32% from DT and 92.68% from DDT (Table 3).

The qualitative approach for detection of curcuminoids performed in this work corroborates to the quantitative approach, in which was noted a progressive declining on the intensity provided on the bands of compounds, which was attributed to the procedures of extraction. A prominent zone in ar-turmerone standard at R_F of 0.97 is detected on turmeric volatile oil (Fig. 3), similarly as reported for crude turmeric extracts TLC profile detected with p-anisaldehyde-sufuric acid spray reagent (Santana and Meireles, 2017).

Crude turmeric is characterized by 8 absorbed zones range of R_F ranging from 0.26 to 0.94, with spots coloration varying from red to purple (Fig. 3). The vanillin-sulfuric acid spray reagent can detect both volatile (terpenes) and non-volatile (polyphenols, i.e., curcuminoids) constituents. The sulfuric acid from the spray reagent is used as oxidant, which reaction of vanillin with terpenes resulted on the formation of purple spots, and reaction with curcuminoids resulted on the formation of dark red spots, similarly as reported to partial-hydrolyzed turmeric wastes (Santana and Meireles, 2016).

3.2.2. Scanning electron microscopy (SEM)

The micrographs showed cellulosic walls and rigid starch granules with fissures and ovular and irregular elliptical forms (Fig. 4), similar with those obtained for white turmeric (Kuttigounder et al., 2011), Indian palo (Das et al., 2015) and mango ginger (Policegoudra and Aradhya, 2008).

Supercritical carbon dioxide applied on CT caused physical modification, characterized of stiffening of the granules with disruption of cellulosic walls, which contributed to the increasing of availability, or exposition, of starch granules. Pressurized liquid ethanol contributed for the dispersing of the granules previously exposed (Fig. 4).

Literature reports that heat treatment and hot solvent extractions remove surface lipids causing changes in the packing arrangement of the polymer chains and partial crystal melting or retrogradation, resulting on the production of starch granules that are more rigid and less deformable under shear and heat (Moorthy, 2002; Peterson et al., 2008).

In addition, the micrographs of the recovered starches from the SFE and PLE biowastes suggest that part of the granules was left behind, because of the increased availability of granules, associated to the washings performed in the recovery procedure. This result is confirmed by the starch content detected in the recovered starches from the SFE and PLE biowastes (Table 3).

Table 4
Thermal properties of turmeric products.

	ΔH_{GEL} (J/g)	T_{OS} (K)	T_{PEAK} (K)	T_{ES} (K)
CT	16.47	371.19	375.33	389.67
CT starch	24.78	370.24	376.49	404.76
DT	22.19	371.10	376.68	418.94
DT starch	23.15	371.05	379.93	408.29
DDT	29.93	371.19	375.33	389.67
DDT starch	27.90	370.20	374.97	392.97

CT – Crude turmeric; DT – Deflavored turmeric; DDT – Deflavored and depigmented turmeric.

3.2.3. Differential scanning calorimetry (DSC)

Extraction with pressurized liquid ethanol increased thermal properties of the materials (Table 4). The enthalpy of gelatinization (ΔH_{GEL}) values were comparable to those obtained elsewhere (Braga et al., 2006). Nevertheless, T_{OS} values were higher than those reported in literature because of the possibility of curcuminoids forming complexes with starch molecules, associated to the heat treatment (Moorthy, 2002) provided by SFE and PLE processes. The high values of T_{PEAK} and T_{ES} values indicate high ranges of gelatinization found in turmeric, similarly as T_{OS} (Table 4).

The gelatinization process is represented by T_{OS} and ΔH_{GEL} in the material. These parameters are particular from each specie source of starch (Hansdah et al., 2015). High T_{OS} values correspond to a high degree of crystallinity, high stability and resistance of the granule structure to gelatinization (Tester et al., 2004).

The gelatinization process is affected by solvent type and starch/solvent proportions (Jiménez et al., 2012) and is required for particular processes, e.g., textile and hydrolyzed starch industries (Alcázar-Alay and Meireles, 2015).

3.2.4. Pasting properties

Pasting properties describe the changes that occur in starch after gelatinization in excess water. During the analysis with RVA, shear stresses are applied to the raw material suspended in water. Suspensions from standardized raw materials, like wheat, corn and potato, typically exhibit a peak in viscosity that starts after gelatinization and increases as the granules swell, followed by a decrease in viscosity due to granule disintegration and polymer realignment (Alcázar-Alay and Meireles, 2015).

The pasting profiles showed by turmeric differs from typical pasting curves described by the starches of corn and potato (Fig. 5), because of characteristic viscosity behavior of turmeric starch.

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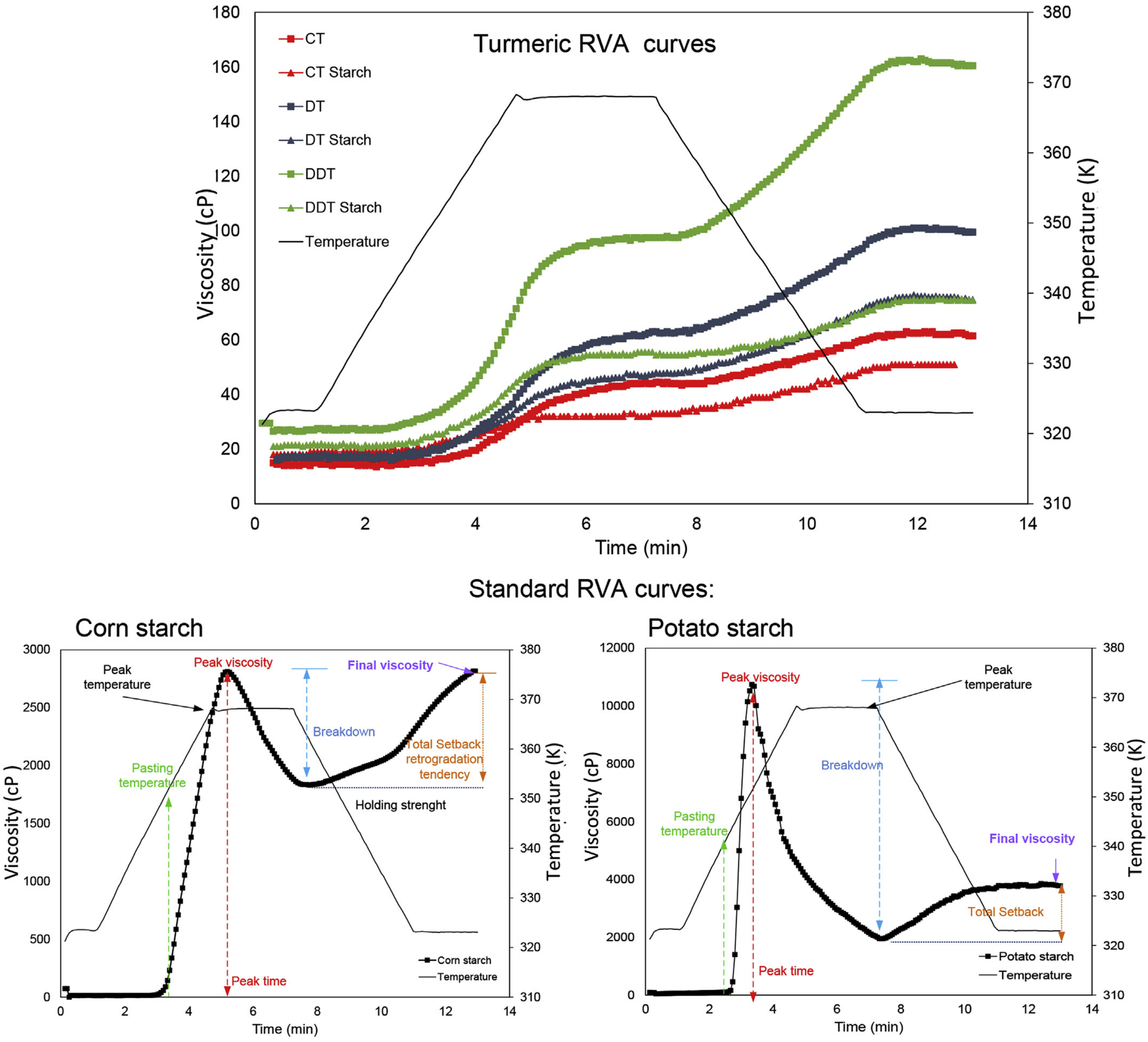

Fig. 5. RVA curves of turmeric products and conventional starch sources.

The pasting temperature ranged between 341.60 K and 357.5 K (Table 5), which is comparable to those obtained for turmeric starches (Braga et al., 2006; Leonel et al., 2003). According to Fig. 5, high viscosity behavior is observed on the wastes when compared to the crude raw material, because of the increase of availability and physical modification of the starch granule provided by the SFE and PLE processes. Literature associate this behavior to the removal of curcumin (Moorthy, 2002). The increase in viscosity of turmeric studied in this work differs from that obtained after SFE with carbon dioxide and cosolvents ethanol and isopropyl alcohol at 30 MPa and 303 K (Braga et al., 2006).

Nevertheless, this behavior is similar to those reported to defatted corn starch treated with critical water and ethanol at 383 K and 10 MPa (Peterson et al., 2008), and defatted annatto wastes treated with hot pressurized water and supercritical carbon dioxide at 353 K and 15 MPa (Alcázar-Alay et al., 2016).

The differences of pasting properties in turmeric wastes and starches are attributed to differences in structure and composition. Extraction with pressurized liquid ethanol contributed to the increase of peak viscosity and retrogradation tendency, characterized by the highest setback behavior, similarly as corn starch, and different from potato starch (Fig. 5). Setback viscosity is the interval ranging from the breakdown ($\mu_{BREAKDOWN}$) and final (μ_{FINAL}) viscosities (AACC, 2000), considering corn and potato starches (Fig. 5).

Breakdown viscosity ($\mu_{BREAKDOWN}$), which behavior is characterized by fallen in viscosity values after the peak, is absent in turmeric (Fig. 5).

In this context, the starchy matrix from turmeric studied in this work is considered a type of resistant starch from which starch is physically inaccessible and the breakdown of the granular structure does not occur (Hasjim and Jane, 2009). Resistant starch associated with small chains of fructooligosaccharides act synergistically in the digestive system to cause a prebiotic effect that benefits human health (Fuentes-Zaragoza et al., 2011).

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Table 5
Pasting properties of turmeric products and conventional starch sources.

	T_{PASTE} (K)	μ_{TROUGH} (cP)	μ_{PEAK} (cP)	$\mu_{SETBACK}$ (cP)	t_{PEAK} (min)	μ_{FINAL} (cP)	$\mu_{BREAKDOWN}$ (cP)
CT	352 ± 6	40 ± 1	40 ± 1	63 ± 1	6 ± 0	63 ± 1	–
CT starch	345 ± 1	31 ± 1	31 ± 1	51 ± 1	5 ± 0	51 ± 1	–
DT	346 ± 5	55 ± 1	55 ± 4	100 ± 2	6 ± 0	100 ± 2	–
DT starch	345 ± 3	44 ± 1	44 ± 6	76 ± 6	6 ± 0	76 ± 5	–
DDT	349 ± 2	87 ± 1	87 ± 4	161 ± 3	6 ± 0	161 ± 3	–
DDT starch	342 ± 5	52 ± 2	51.90 ± 5	75 ± 4	3 ± 0	75 ± 4	–
Corn starch	356 ± 4	959 ± 1	2835 ± 1	992 ± 0	5 ± 0	2867 ± 0	1876 ± 1
Potato starch	345 ± 0	8736 ± 0	10682 ± 4	1836 ± 1	7 ± 0	3782 ± 2	1946 ± 8

CT – Crude turmeric; DT – Deflavored turmeric; DDT – Deflavored and depigmented turmeric.

Through viscosity (μ_{TROUGH}) is defined as the interval between the peak and breakdown viscosities. Considering the fact that turmeric does not contains breakdown viscosity, the value of μ_{TROUGH} is the same as μ_{PEAK} and $\mu_{SETBACK}$ is the same as μ_{FINAL} (Table 5).

3.3. Economic evaluation

Initially, for the obtaining of CT starch, CT purchasing cost of US$ 7.27/kg and three different production scales (2 × 5 L, 2 × 50 L and 2 × 500 L) were considered as shown in Fig. 6a. For the obtaining of DT and DDT starches, no purchasing cost was considered and the resulted COMs were equivalent (Fig. 6b).

Establishing comparisons between both scenarios, it is notable that adopting a raw material with 3.33% of recovered starch in an industrial scale is not feasible. For example, with this CT purchasing cost, the COMs of CT starch were estimated to be US$ 966.55/kg, US$ 872.94/kg and US$ 858.52/kg for the first scenario and US$ 39.86/kg, US$ 35.86/kg and US$ 35.41/kg for the second scenario with capacities of 2 × 5 L, 2 × 50 L and 2 × 500 L respectively.

Even for the DT and DDT starches production when the scale-up was simulated a decrease in the COM was observed. COMs of US$ 85.85/kg, US$ 14.89/kg and US$ 5.09/kg were obtained in the first scenario, while the COMs of US$ 3.52/kg, US$ 0.62/kg and US$ 0.22/kg were calculated for the second scenario for the capacities of 2 × 5 L, 2 × 50 L and 2 × 500 L, with DT and DDT purchasing cost considered as zero. Considering wastes as the main raw materials for starch obtaining, it is possible to increase the productivity and obtain lower COM (Fig. 6b).

As shown in Fig. 7a the participation of CRM affects completely the COM for the obtaining of CT starch. For the obtaining of DT and DDT starches CRM have lower contribution to the COM because of the zero cost of raw material (Fig. 7b).

Although for the scale-up process is necessary more quantity of workers, the impact related with the implementation of the production line at higher scales contributed with a decrease in the participation of COL in the COM (Fig. 7b).

The CUT almost had not participation in COM. Factors such as higher quantities of solvent, higher energetic expenditures and

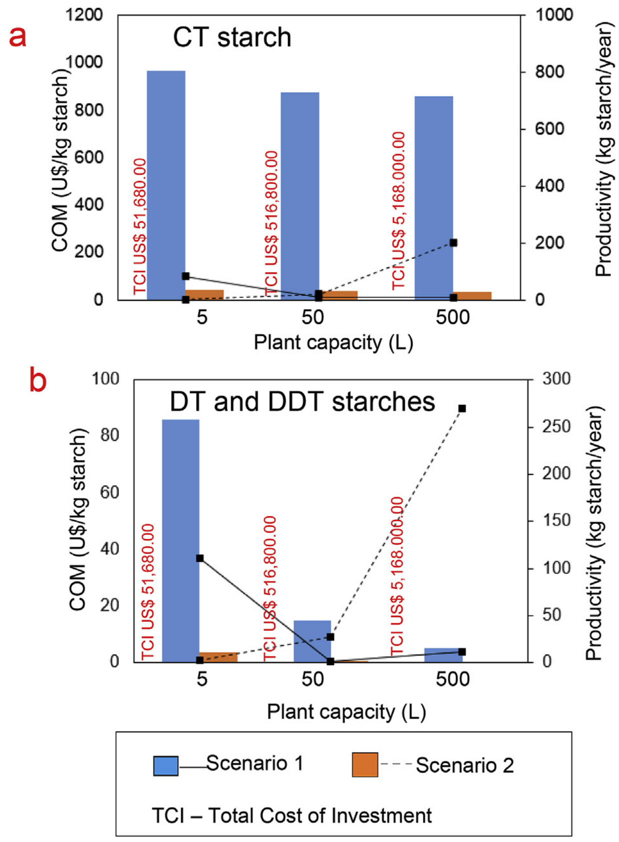

Fig. 6. Values of COM for starch recovery in different capacities.

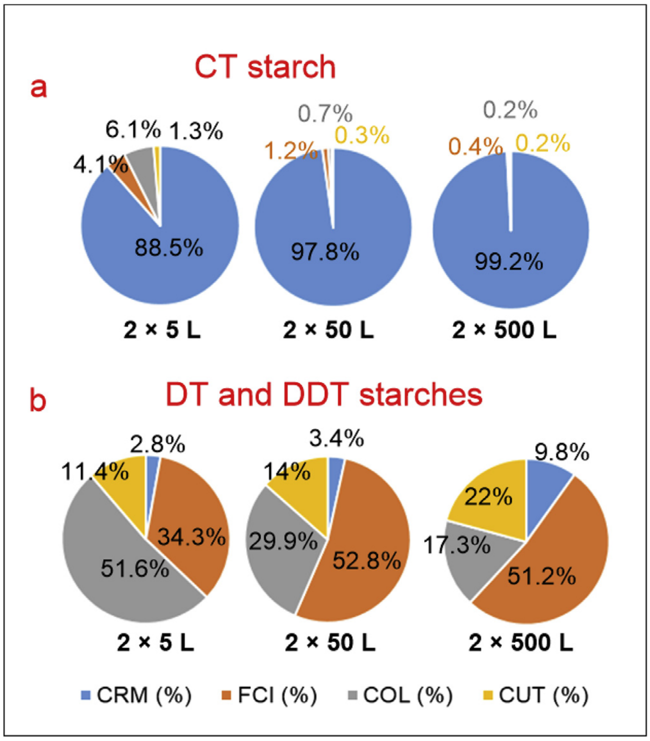

Fig. 7. Contribution of each component (CRM, CUT, COL and FCI) on the COM for starch recovery.

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Table 6
Project indices for starch recovery from solid turmeric.

Capacity	Starch	Scenario	Gross margin (%)	Payback time (years)	ROI (%)	IRR (%)	NPV (US$)
5 L	CT	Yield: 3.33%	NA	NA	NA	NA	NA
		Yield: 80%	NA	NA	NA	NA	NA
	DT	Yield: 3.33%	NA	NA	NA	NA	NA
		Yield: 80%	NA	NA	NA	NA	NA
	DDT	Yield: 3.33%	NA	NA	NA	NA	NA
		Yield: 80%	NA	NA	NA	NA	NA
50 L	CT	Yield: 3.33%	NA	NA	NA	NA	NA
		Yield: 80%	NA	NA	NA	NA	NA
	DT	Yield: 3.33%	NA	NA	NA	NA	NA
		Yield: 80%	47.59	4.00	25.32	38.98	80,000.00
	DDT	Yield: 3.33%	NA	NA	NA	NA	NA
		Yield: 80%	45.88	4.1	23.98	35.55	74,000.00
500 L	CT	Yield: 3.33%	NA	NA	NA	NA	NA
		Yield: 80%	NA	NA	NA	NA	NA
	DT	Yield: 3.33%	NA	NA	NA	NA	NA
		Yield: 80%	81.55	0.90	106.92	>999.99	1,638,000.00
	DDT	Yield: 3.33%	NA	NA	NA	NA	NA
		Yield: 80%	80.88	1.00	102.37	>999.99	1,562,000.00

CT – Crude turmeric; DT – Deflavored turmeric; DDT – Deflavored and depigmented turmeric; NA – Not applicable; ROI – Return on investment; IRR – Internal rate of return; NPV – Net present value.

energy requirements, product of the longer processing time, contributed with the increase in the participation of the CUT in the COM due to the scale-up process.

3.3.1. *Sensitivity study*

The sensitivity analysis is presented in terms of the project indices calculated after performing the simulation (Table 6). The revenue is calculated considering the sale of starch in a year. Some scenarios of this process are not applicable (NA) because the COM was closer or higher than the selling price of US$ 1.00/kg. The process is NA when an infinite payback time and/or negative return taxes are obtained.

The ROI is a performance measure used to evaluate the efficiency on investment, which is defined as the percentage of money recovered annually from the plant's profit (Mexandre, 2003). Therefore, the higher the ROI the more desirable is the project.

The values of ROI were obtained only for the second scenario, which highest values were obtained for the recovery of DT and DDT starches with the capacity of 2 × 500 L. The values of ROI over 15% seem to be suitable for recommending a project to operate with profitability (El-Halwagi, 2012). In such context, the capacities of 50 L and 500 L presented larger values of ROI. This finding enables us to consider the feasibility of the recovery of starch from turmeric wastes with a scenario of 80% yield and capacities of 2 × 50 and 2 × 500 L, similar to those obtained for curcuminoids powdered particles (Osorio-Tobón et al., 2016).

Gross margin (GM) represent a company's total sales revenue minus the cost of goods sold, divided by the total sales revenue, expressed as percentage (Towler and Sinnott, 2013). In example, when DT is used at a 2 × 500 L capacity, the GM is 81.55% (Table 6), which means that the company would retain US$ 0.81 from each dollar generating by selling DT starch. When the CT is used the gross margin is NA for both scenarios.

The net present value (NPV) represents the difference between the present value of cash inflows and the present value of cash outflow, i.e., it is the remaining surplus for the investor to have regain the initial investment. If the NPV of a project is positive after assuming a discount interest of 7%, as shown in Table 6, the project should be considered as feasible. (Terry et al., 1992). For the second scenario, the NPV increased with the scale. The highest NPV of US$ 1,638,000.00 was obtained for the wastes with a 2 × 500 L plant.

In addition, the internal rate of return (IRR) attempts to measure the profitability of a project or asset. The IRR represent the average intrinsic profitability of a project and is defined as the rate that makes the NPV of all cash flows from a particular project equal to zero. In other words, to undertake a project, the IRR should be higher as possible because it indicates the rate that makes the NPV null for all cash flows (Vučurović et al., 2012). For the second scenario, IRR increased with the scale (Table 6). Once again, the obtaining of starches from the wastes in the 2 × 50 L and 2 × 500 L plants considering the second scenario have shown to be most feasible.

It is important to emphasize that the economic analysis performed in this work is a preliminary study. The generally accepted classification of capital cost estimates that are most applied in process industries are based on that published by the Association for the Advancement of Cost Engineering (AACE), with adaptations of Turton et al. (2009), which consists in five classes: 1) detailed estimate; 2) definitive estimate; 3) preliminary estimate; 4) study estimate; and 5) order-of-magnitude estimate.

This work is performed according to the Class 4, which is as a type of estimate that uses a list of the major equipment found in the process. Each piece of equipment is roughly sized and the approximate cost is determined. The total equipment cost is then factored to give the estimated capital cost, i.e., the results from the performed economic analysis provide information to decide if the project can be continued or not.

The purpose of this section was to provide an economic evaluation of the recovery of starch from turmeric wastes derived from SFE and PLE processes based on two different scenarios to the scientific community and companies. Therefore, the presented behavior gives relevant information for further systematic and more accurate studies or projects. Besides, further studies on economic evaluation of using turmeric wastes for further starch recovery should evaluate carefully the characteristics of the raw material, demand, the market that is focused, the country, the quality requirements and local fees, among other issues, to provide more deterministic results.

4. Conclusions

In this work, mixed biopolymers composed of starch and curcuminoids derived from turmeric wastes were recovered from extraction processes that applied supercritical carbon dioxide and

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pressurized liquid ethanol.

Curcuminoids detected varied from 0.29 to 13.13 g/100 g, while the starch quantified varied from 26 to 46 g/100 g. These attributes provide practical applications of turmeric wastes in foods, cosmetics and medicaments. The particularities of the crude raw material resulted on products with low starch recovery, besides some similarities with another *curcuma* species. In addition, extraction processes contributed to the physical modification of turmeric wastes, which consisted on starches granules with high rigidity and less deformability.

The increase in viscosity values were attributed to the extraction processes that provided physical modification, associated to the increased availability of starch granule.

Economic evaluation analysis showed that starch isolation process from turmeric wastes at high scales is a feasible alternative to avoid material discarding when applying a scenario of 80% of starch recovery and plants with capacities of 50 L and 500 L.

Conflict of interest

The authors declare that they have no conflict of interests.

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Symbols

T_{PASTE}	Pasting temperature (K)
μ_{TROUGH}	Hot viscosity pasting (cP)
μ_{PEAK}	Viscosity peak (cP)
$\mu_{SETBACK}$	Setback viscosity (cP)
t_{PEAK}	Time peak (min)
μ_{FINAL}	Final viscosity (cP)
$\mu_{BREAKDOWN}$	Breakdown viscosity (cP)

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jfoodeng.2017.07.010

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- CAPÍTULO 6 –

High-pressure phase equilibrium methodologies applied for food systems

Trata-se de uma investigação modesta dos métodos experimentais usados para se obter informação relacionada ao comportamento de fases a altas pressões de substâncias que possuem relevância para a indústria alimentícia. Além disso há a apresentação da unidade de equilíbrio de fases usada nesta tese, que emprega o método sintético-visual, construída e adaptada para a realidade do grupo de pesquisas do Lasefi.

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High-Pressure Phase Equilibrium Methodologies Applied to Food Systems

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Abstract In addition to new methods to produce safe, healthy and shelf-stable products, food industries aim to recover valuable products or to separate undesirable compounds from natural food matrices. One possible alternative to achieve this goal is to apply high-pressure technologies such as supercritical fluid extraction (SFE), pressurized liquid extraction etc. Phase equilibrium and thermodynamic properties of food systems as well as transport properties, such as viscosity, thermal conductivity, or diffusivity, are important parameters for the food industry. In the design and operation of such high-pressure technological processes, a large amount of reliable data on the equilibrium properties of materials is necessary, for instance, in the case of SFE the separation step in entirely depended on the phase equilibria of the extract and the supercritical fluid. Experimental techniques for high-pressure phase equilibrium measurements of substances relevant to the food industry are summarized in this review in terms of the advantages, disadvantages and common applications of the methods.

Keywords Food systems, High pressure, Supercritical fluids, Phase equilibria apparatus, Phase equilibrium

1. Introduction

Foods, a mixture of volatile and nonvolatile components, are considered multiphase systems composed of liquid, solid, and gaseous phases. A practical example is the partition between phases of flavor compounds that can change the perceived flavor of food during consumption due to the affinity of each compound for different phases [1].

The use of high pressure as a technology for pasteurization of different types of foods, such as juices, ham, sauces and seafood, has been a growing trend in the food industry sector since the 1990s [2].

Cheeses manufactured from pressurized milk achieve higher production yields compared with cheeses prepared using thermally treated milk [3].

High-pressure processing helps to retain the antioxidant activity of individual fruit juices and the intensity of green characteristics due to cell disruption and the subsequent leakage of pigments [4].

In 2014, more than 252 pieces of high-pressure equipment produced over 500000 metric tons of high-pressure-treated foods, which were placed on the market worldwide [2].

The knowledge of the phase equilibrium behavior of the volatile and nonvolatile fractions of foods is of crucial importance for many applications in the food industry, such as the design of distillation processes in alcoholic beverage production [5], the extraction of limonene from citrus peel [6], the extraction of phenolic compounds from cashew shell [7] and the separation of triacylglycerols from sardines [8].

The growing interest in the high-pressure carbon dioxide treatment used for the pasteurization and sterilization of liquid foods emphasizes the importance of a better understanding of the physical behavior of systems composed of water-based liquid food and carbon dioxide [9].

High-pressure processing claims to retain the sensory and nutritious value of food, maintaining the original freshness, color, flavor and taste. However, the high pressure may cause changes in the crystal structure of the lipids, thus changing the characteristics of the raw material [10].

The products of a process using supercritical fluids are frequently formed at high temperatures and pressures. For the recovery of heat and of the hydrocarbon products, a recovery process must be designed using phase equilibria as the basis [11].

The importance of reliable and precise experimental phase equilibrium data is unanimously recognized by the scientific community, although the accuracy of published experimental data does not always correspond to the accuracy claimed by the authors for the apparatus used [12].

The choice of an adequate experimental method for the determination of reliable and precise experimental phase equilibrium data should match the best compromise from the viewpoint of speed, simplicity and precision of measurements [13].

The fluid phase behavior of mixtures is inherently complicated at high pressures. Deviations from ideal behavior are stronger at high pressures than under ambient or

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low-pressure conditions, and the phase behavior is often more complex and difficult to predict with thermodynamic models. In the majority of cases, attaining these data is difficult and involves elevated costs [14].

A variety of experimental equipment and techniques designed to perform phase equilibrium measurements are available. However, such equipment typically requires a large volume of chemical species to obtain measurements. Therefore, new techniques and equipment must be developed to measure phase equilibrium data for small volumes over reasonable temperature and pressure ranges [15].

An understanding of the different methods and of the respective error sources is crucial. Experience and practical knowledge are essential because experimental problems and mistakes are seldom published [16].

A large number of recent scientific investigations concerning phase equilibrium for food systems has been published. Table 1 shows the literature search results from the "Scopus" database using the keywords "phase equilibria", "experiments" and "food".

Table 1. Number and type of documents published in the Scopus database between 2010 and 2014

Year	**Publications**
2014	350
2013	435
2012	364
2011	347
2010	278
Document Type	
Article	1261
Review	337
Book chapter	72
Conference paper	35

Table 2 provides a summary of the available literature review on the high-pressure phase behavior experimental methods.

Table 2. Reviews of experimental methods for phase equilibrium measurements

Publication	**Period**	**Reference**
Chemical Thermodynamics	1970 – 1980	[17]
DECHEMA Chemical Data Series	1970 – 1980	[18]
Fluid Phase Equilibria	1978 – 1987	[19]
Fluid Phase Equilibria	1988 – 1993	[20]
Fluid Phase Equilibria	1994 – 1999	[21]
Fluid Phase Equilibria	2000 – 2004	[22]
Fluid Phase Equilibria	2005 – 2008	[23]

Other interesting reviews that describe the specificity of certain methodologies have been published [14, 24-29].

This review summarizes various techniques available for measuring phase equilibrium data of substances that are relevant to the food industry in terms of main characteristics, advantages, disadvantages and common applications of each method. Initially, the food systems are shown, followed by descriptions of the methods to measure phase equilibrium data for these substances.

2. Food Systems

Most foods are multiphase dispersions structured either by nature, e.g., plant or animal tissues, or by man. The man-made structured foods use assembly or texturing processes, such as emulsification processes (e.g., margarine, ice cream, sauces, mayonnaise) or foaming (e.g., whipped cream, extrusion, dough kneading, baking) [30].

Fewer information sources that contemplate complex matrices or real foods can be found due to the variety and complexity of the chemical functional groups that compose these systems, such as proteins, carbohydrates, lipids, volatile oils and oleoresins. The determination of the phase equilibrium of these systems would not be trivial.

For the separation of components, it is necessary to know the phase equilibrium of the extract in the solvent of interest and of the pure components from the extract in the solvent of interest, as well as the mass transfer aspects of the process [31].

Vapor-liquid equilibria (VLE) are important in oxygen absorption during aerobic fermentation, in de-aeration of liquid foods, and in absorption or stripping of carbon dioxide. Liquid-liquid equilibria (LLE) of two partially miscible phases can be represented in triangular diagrams (equilateral or right-angled). Each of the corners of the triangle represents a pure component, and the two-phase region is enveloped by an equilibrium line [32].

The knowledge of solid–liquid boundaries and of the behavior of simple fatty systems can be helpful to understand the physical properties of complex lipids and their mixtures [33].

For process design, phase equilibrium data for real systems are more appropriate. The sorption of oxygen on solid foods is related to the oxidation of lipids and other labile components. Vapor-solid equilibria (VSE) are important for the study of the behavior of these compounds. The equilibrium data can be fitted to semi-empirical relationships, such as the Freundlich, the Langmuir, and the Brunauer-Emmett-Teller (BET) equations [32].

2.1. Nonvolatile Fraction

2.1.1. Water

Water is an important and common solvent in chemistry and is the main component in most foods. Water in food systems acts as a solvent and as a plasticizer in low-water food solids and in freeze-concentrated solids in the unfrozen phase.

Equilibrium properties of water such as water activity are considered reference properties in food processing in freezing, dehydration, evaporation, and high-pressure processing [34]. However, the presence of water in certain systems can have undesired effects on their properties. Examples of susceptible systems include powdered foods, agricultural chemicals, explosives, nutraceuticals, and pharmaceuticals [35].

2.1.2. Carbohydrate Solutions

Carbohydrate solutions have many applications in the food and pharmaceutical industries. Solubility data for these solutions are needed for many process designs, such as separation and purification processes [36].

Carbohydrates can also lead to retention of flavor compounds in the matrix. This reduction in volatility is due to interactions that can occur between carbohydrates such as starches and flavor compounds [37].

Interactions between proteins and polysaccharides in aqueous systems influence the phase behavior of such ternary blended systems, impacting their structural and textural properties, hence affecting their stability [38].

Almost all empirical correlations developed to design, analyze, optimize or control industrial sugar processes are based on a ternary system characterization: sugar, sucrose, non-sugar and water. Despite extrapolation problems related to these correlations, the characterization using a ternary system cannot take into account phenomena such as degradation reactions or specific effects of some impurities on sucrose solubility [39].

2.1.3. Ethanol

Ethanol in foods can be present as a product of agri-food waste fermentation, a residue after baking, an additive in packed products and an ingredient in candies, confectionery products, sweets, etc. Liquid-vapor partition of ethanol in aqueous systems depends not only on environmental factors such as temperature and water activity but also on its concentration and on the nature and concentration of other compounds that can be present in the food matrix [40].

Several drinks with low ethanol content or without ethanol have been introduced to the market in recent years. Reduction of ethanol content in alcoholic drinks can be accomplished by restricting fermentation or by removing ethanol after the complete fermentation process [41].

The thermodynamic modeling of the CO_2-SFE de-alcoholization of drinks can be carried out representing the beverage as the ethanol + water binary mixture because other components in alcoholic beverages usually represent less than 1% [42].

In the assessment of volatiles in grape and wine, the matrix consists predominantly of the nonvolatile components including sugars, ethanol (in wine) and water (Figure 1). Organic acids, amino acids, phenolic compounds and inorganic ions in water are part of the volatile fraction [43].

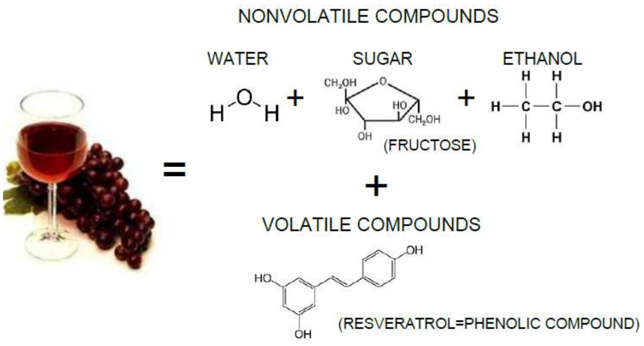

Figure 1. Multicomponent system existing in wine

2.1.4. Lipids

Fatty acids are the major components of oils and fats, and they have critical implications in the understanding of the biological behavior of various lipid systems. Fatty acids have recently been used in the production of coverings, plastics, and cleaning products, phase change materials for energy storage and biodiesel [10].

Vegetable oils consist mainly of triglycerides, with a low fraction of diglycerides, free fatty acids and a number of minor components (sterols, tocopherols, phospholipids, etc.) that have added value as pharmaceuticals and food additives [44].

Lipids are the food ingredients that have been shown to have the most effect on the partitioning of flavor compounds between product and vapor phase [37].

The raw material for the production of omega-3 oils is typically represented by fish oils. Most of the fatty acid chains in fish oil triglycerides have a number of carbon atoms ranging from 14 to 22. Fractionation processes are usually performed on fish oil ethyl esters (FOEEs) to obtain a considerable enrichment in a specific fatty acid, where using supercritical CO_2 is a potential alternative [45].

2.1.5. Proteins

The increasing commercial interest in the contents of protein have led to extensive studies to extract, and/or isolate the proteins [46].

Food proteins have little flavor of their own but are known to bind and trap aroma compounds. Depending on the nature and the strength of the binding, the release of aroma compounds in the vapor phase will be more or less decreased, and this decrease will have a significant impact on the overall aroma perception due to changes in the aromatic balance [47].

Purification of recombinant proteins makes high demands on downstream processes as the target proteins have to be separated from very similar protein variants to very high purities. Among different separation modes such as size exclusion, hydrophobic interaction or affinity chromatography, ion exchange chromatography (IEC) is commonly used; therefore, it is a major unit operation in the purification processes of therapeutic proteins [48].

2.2. Volatile Fraction

2.2.1. Pigments

At low and moderate temperatures high-pressure technologies have a limited effect on pigments (e.g., chlorophyll, carotenoids, anthocyanins, etc.) responsible for the color of fruits and vegetables. The high-pressure process increases the extraction yields of carotenes from the plant matrix and in many cases, increases the intensity of chlorophyll in green vegetables [49].

The volatile products of the degradation of carotenoids can be desirable, as in black tea and wine where they become part of the characteristic aroma. In some processed foods, however, degradation/cleavage of carotenoids is undesirable because it is responsible for the appearance of an off flavor, as in dehydrated carrots and in certain types of wine [50].

Processed mango pulp retained a maximum of 85, 92 and 90% of its original ascorbic acid, total phenolics and in-vitro antioxidant capacity, respectively using high pressure processing at 100 – 600MPa, 303K during 1-20 minutes [51].

2.2.2. Vitamins

Vitamins are usually present at low levels and are accompanied by other compounds. Extraction from foods requires specific conditions, depending on the stability of each vitamin with pH, temperature, light, and oxygen, and its bond to the food matrix [52].

In the chemical and pharmaceutical industries, vegetable oils and their distillates from oil refining are principal sources of valuable components such as squalene, vitamins, sterols and fatty acids [53].

Vitamin C is one of the most important vitamins; thus, reliable information about its content in foodstuffs is a concern to both consumers and quality control agencies [54].

Alpha-Tocopherol is a member of the vitamin E family representing the high biological activities. Most tocopherols are obtained by energetically intensive vacuum distillation of deodorizing step residues generated in the refining of vegetable oils, including several steps such as solvent recovery and purification associated with abundant amounts of organic solvents [55].

2.2.3. Volatile Oils

The volatile oils (or essential oils) are a multicomponent mixture of terpenoids (mono-, sesqui-, and diterpenes, various alcohols, ketones, and aldehydes of terpenoids). Considering the similarities and differences between both types of fluids (mineral oils and volatile oils), it is not surprising that the thermodynamic description and/or prediction of the phase behavior and other related thermodynamic properties of systems with volatile oils is much more problematic [56].

Citrus oils are mixtures of over a hundred compounds, including terpenes, oxygenated compounds, and nonvolatile compounds [57].

Orange volatile oil is widely used in the food industry as an additive, conferring taste to diverse products such as ice cream, candies, carbonated beverages and cakes [58].

The removal of monoterpenes from citrus oils, which is the so-called de-terpenation process, is a common industrial practice that obtains a product more stable and more soluble in water, while maintaining its characteristic flavor and fragrance [59] as shown briefly in Figure 2.

Figure 2. Terpene (limonene) obtained from citrus peel volatile oils

Understanding the physicochemical interactions that occur between aroma compounds and other food constituents is also of great importance when considering each step of the production process. For example, encapsulation may be required to control flavor losses that occur during heating and storage. Eating could also be considered to be a unit operation during which volatile compounds are released in the mouth [60].

The implementation of high-pressure technologies in food industry requires the knowledge of many properties in order to design efficient process that will permit to achieve the expected quality and the stability of the processed products.

3. Thermophysical Properties of Foods

Thermophysical properties can be defined as material properties that vary with temperature without altering the chemical identity of the material, such as density, enthalpy, entropy, viscosity, Joule-Thomson coefficient, thermal conductivity, thermal diffusivity, refractive index, and others.

Since many stages in the processing and preservation of foods involve heat transfer, it is important to understand the thermophysical properties of foods. An energy balance for heating or cooling process cannot be made and the temperature profile within the material cannot be determined without knowing the thermophysical properties of these materials [61].

An appropriate modeling implies a precise knowledge of the thermophysical properties of the involved materials. In the case of conductive heat transfer, thermophysical properties include density, thermal conductivity and specific heat. When the process to model involve a change of phase, the ice fraction, the enthalpy and the initial freezing point are important [62].

The variation of enthalpy can be used to estimate the energy that must be added or removed to effect a temperature change. Above the freezing point, enthalpy consists of sensible energy; below the freezing point, enthalpy consists of both sensible and latent energy. Enthalpy (expressed in

Joule, or J) may be obtained from the definition of constant-pressure specific heat:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{1}$$

Where C_P (kJ/kg°C) is constant pressure specific heat, H is enthalpy, and T is temperature (°C). Mathematical models for enthalpy may be obtained by integrating expressions of specific heat with respect to temperature.

For a phase change process involving either melting or freezing, energy conservation can be expressed in terms of total volumetric enthalpy and temperature for constant thermophysical properties [63].

For cases where there are no experimental values of C_P, it is possible to estimate its value using group contribution methods, such as Joback [64] and Constantinou and Gani [65].

Thermal conductivity relates the conduction heat transfer rate to the temperature gradient and it is dependent of composition, structure, and temperature [62].

$$k = k_C \frac{1 - \left\{\left[1 - a\left(\frac{k_D}{k_C}\right)\right] b\right\}}{1 + \left[(a-1)b\right]} \tag{2}$$

Where k (W/m°C) is the thermal conductivity of the mixture, k_C (W/m°C) is the thermal conductivity of continuous phase, k_D (W/m°C) is the thermal conductivity of the dispersed phase,

$$a = \frac{3k_C}{(2k_C + k_D)} \tag{3}$$

$$b = \frac{V_D}{(V_C + V_D)} \tag{4}$$

V_D (ml) is the volume of the dispersed phase and V_C (ml) is the volume of the continuous phase. For transient heat transfer, the important thermophysical property is thermal diffusivity, α, which appears in the Fourier equation:

$$\frac{\partial T}{\partial t} = \alpha \left[\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}\right] \tag{5}$$

Where x, y and z are Cartesian coordinates, T is the temperature and t is the time (s).

Thermal diffusivity (α), expressed as m^2/s, is used in the determination of heat transfer rates in solid food objects of any shape. Physically it relates the ability of a material to conduct heat to its ability to store heat [66].

This term is defined in the Equation 6:

$$\alpha = \frac{k}{\rho C_P} \tag{6}$$

Where is the density (kg/m^3).

Phase stability during freezing melting would help towards setting heat storage and high density is desirable to allow a smaller size of storage container. Small volume changes on phase transformation and small vapor pressure at operating temperatures to reduce the containment problem [63].

In literature are available a multitude of food items. In Table 3 are summarized thermophysical properties correlations of the main food components.

4. Classification of Phase Equilibrium Methodologies

The methodologies used to obtain phase equilibrium data for food systems are based on the classification systems proposed by Dohrn et al. [22] depending on how the composition of the two coexisting phases is determined, the methods are divided into analytical and synthetic.

At high pressures, the classification of experimental methods is not always simple. In addition, the expression “elevated pressure’’ is relative [23].

Any method for determining reactive phase equilibrium will be analytical in that it has to rely on some analysis of the phase composition, most often accomplished via gas chromatography (GC). Moreover, because conversion is unavoidable, one is concerned with multicomponent mixtures [69].

In the synthetic approach, known amounts of pure substances are charged in a temperature- and pressure-controllable view cell. The overall composition of the mixture is known as well as the volume occupied by the compounds, and the temperature or the pressure is adjusted until a homogeneous phase is obtained [70].

Publications [13, 71-73] have classified these methods, according to the regime of the process, into static (subdivided into analytical and synthetic methods) and dynamic (subdivided into continuous flow and circulation methods) depending on the technique used for equilibration of the phases.

Static methods may be further divided into two categories (analytical and synthetic) according to the type of adopted vessel. In the dynamic methods, one phase is in contact with the other phase, and the adopted operative conditions are chosen so that the outlet streams can be assumed to be at equilibrium [13].

However, static and dynamic methods were considered a subdivision of analytical methods by Fornari et al. [19] who investigated the methods and systems in the period 1978-1987.

To inform the reader through a historical approach, Figure 3 shows a diagram for classification of experimental methods for phase equilibrium measurement divided by the periods of 1990 and 2010.

Table 3. Thermophysical properties for food components ($-40 \le T \le 150$°C)

Food Component	Thermophysical property Model	Reference
Ash	$\rho = 2423.8\text{-}0.28063T$	[67]
	$C_P = 1.0926+1.8896\times10^{-3}T\text{-}3.6817\times10^{-6}T^2$	[67]
	$k = 3.2962\times10^{-1}+1.4011\times10^{-3}T\text{-}2.9069\times10^{-6}T^2$	[67]
	$\alpha = 1.2461\times10^{-7}+3.7321\times10^{-10}T\text{-}1.2244\times10^{-12}T^2$	[68]
Carbohydrate	$\rho = 625.59\text{-}0.41757T$	[67]
	$C_P = 1.5488+1.9625\times10^{-3}T\text{-}5.9399\times10^{-6}T^2$	[67]
	$k = 1.8071\times10^{-1}\text{-}2.7604\times10^{-4}T\text{-}1.7749\times10^{-7}T^2$	[67]
	$\alpha = 8.0842\times10^{-8}+5.3052\times10^{-10}T\text{-}2.3218\times10^{-12}T^2$	[68]
Fiber	$\rho = 1311.5\text{-}0.36589T$	[67]
	$C_P = 1.8459+1.8306\times10^{-3}T\text{-}4.6509\times10^{-6}T^2$	[67]
	$k = 1.8331\times10^{-1}+1.2497\times10^{-3}T\text{-}3.1683\times10^{-6}T^2$	[67]
	$\alpha = 7.3976\times10^{-8}+5.1902\times10^{-10}T\text{-}2.2202\times10^{-12}T^2$	[68]
Lipid	$\rho = 1599.1\text{-}0.31046T$	[67]
	$C_P = 1.9842+1.4733\times10^{-5}T\text{-}4.8008\times10^{-6}T^2$	[67]
	$k = 2.0141\times10^{-1}+1.3874\times10^{-3}T\text{-}2.7178\times10^{-6}T^2$	[67]
	$\alpha = 9.8777\times10^{-8}-1.2569\times10^{-10}T\text{-}3.8286\times10^{-14}T^2$	[68]
Protein	$\rho = 1329.9\text{-}0.5184T$	[67]
	$C_P = 2.0082+1.2089\times10^{-3}T\text{-}1.3129\times10^{-6}T^2$	[67]
	$k = 1.788\times10^{-1}+1{,}1958\times10^{-3}T\text{-}2.7178\times10^{-6}T^2$	[67]
	$\alpha = 6.8714\times10^{-8}+4.7578\times10^{-10}T\text{-}1.4646\times10^{-12}T^2$	[68]
Water	$\rho = 997.18+3.1439\times10^{-3}T\text{-}3.7574\times10^{-3}T^2$	[67]
	$C_P = 4.1762\text{-}9.0864\times10^{-5}T\text{-}5.473\times10^{-6}T^2$	[67]
	$k = 5.7109\times10^{-1}+1.7625\times10^{-3}T\text{-}6.7036\times10^{-6}T^2$	[67]
	$\alpha = 1.3168\times10^{-7}+6.2477\times10^{-10}T\text{-}2.4022\times10^{-12}T^2$	[68]

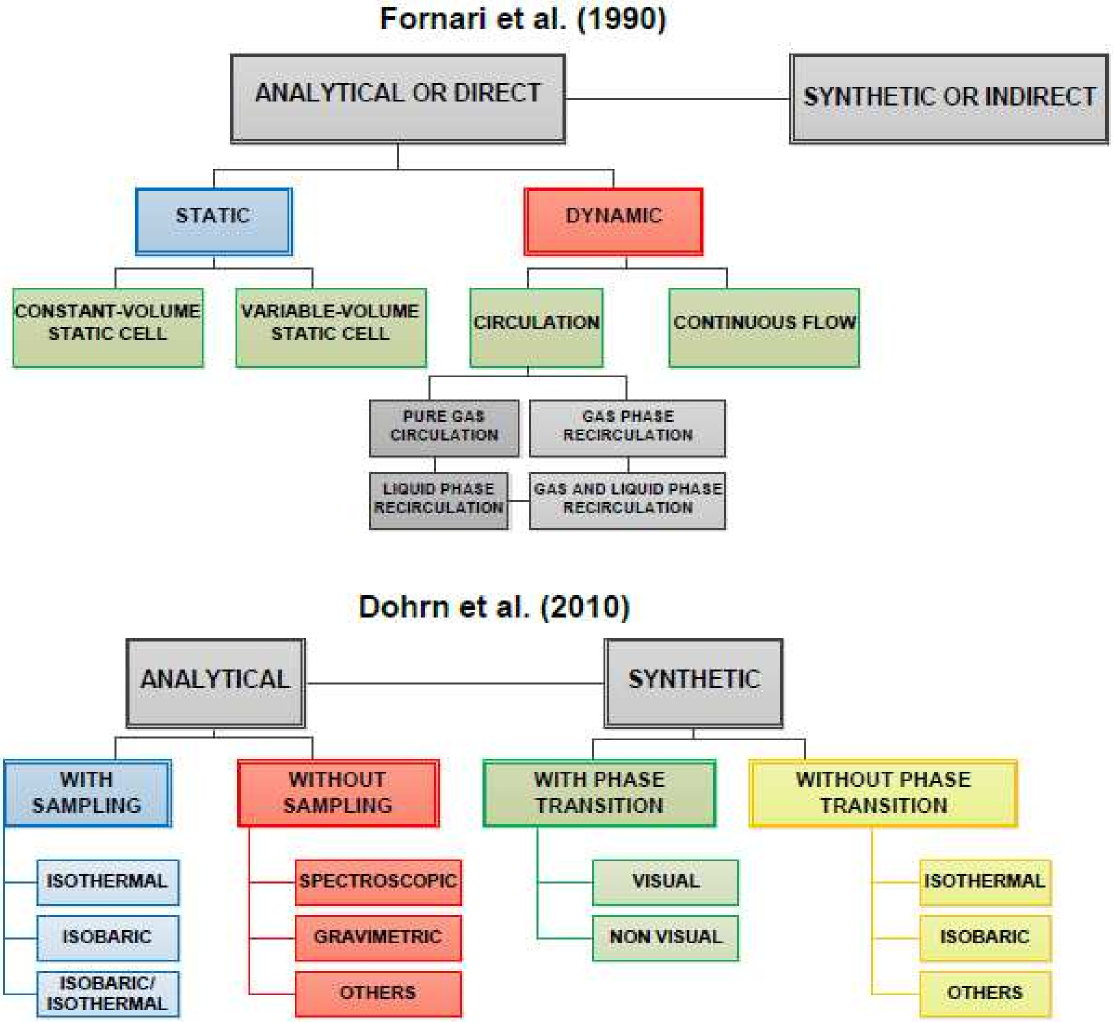

Figure 3. Classification of high-pressure phase equilibrium experimental methods

The variety of experimental methods is even more confusing to the reader because different authors use different names for the same method, and the expressions ‘static’ and ‘dynamic’ are used in connection with many different methods [22].

In addition to the confusion in nomenclature, mixing the terms in some papers further complicates the understanding. For example, “isothermal” vapor–liquid equilibrium (according to the phase transition) data using an apparatus based on the “static-analytic” (a method according to the process regime) equipped with a movable ROLSI^{TM} capillary [74].

A “dynamic-analytical” technique was used to measure the solubility of β-carotene in carbon dioxide (CO_2), triolein-modified CO_2 and in ethanol-modified CO_2 using a stirred equilibrium cell with sapphire windows for visual observations, syringe pump to reach the desired system pressure and after reaching equilibrium, the samples were analyzed by high performance liquid chromatography, HPLC [75]. The description of such a method suggests the classification as an analytical isobaric-isothermal method, which are often called dynamic methods.

5. Analytical Methods

The determination of the composition from the coexisting phase by sampling each of them is involved in analytical methods. The samples are analyzed inside (spectroscopy) or outside (refractometry, chromatography or pressure drop) the equilibrium cell.

The drawback of this method is that the withdrawal of the samples of equilibrium phases from the cell can easily modify the equilibrium of the system, and their transport to analytical devices might change their homogeneity [70].

Sampling at high pressures is a hard task, and it can cause disturbances in the equilibrium. The sample may not be representative of the desired phase [76].

According to the withdrawal of the samples from the equilibrium cell, analytical methods are subdivided into isothermal, isobaric and isobaric-isothermal. Analytical methods are dependent on the procedure used to achieve the equilibrium [22].

5.1. Analytical Methods with Sampling

5.1.1. Isothermal

The temperature of the system is maintained constant during the equilibrium. The other equilibrium properties like the pressure and the composition of the phases reach equilibrium values, depending on other variables like mole numbers and volume.

Before taking samples from the coexisting phases, the mixture is given sufficient time without stirring, rocking or recirculation for the separation of the phases. Otherwise the sample might not be homogeneous but contain material from another phase, e.g. droplets, bubbles or solid particles [22].

A two-phase mixture is enclosed in a pressure vessel with no phase recirculation. Equilibrium is attained via rapid agitation, usually through efficient stirring, and the vapor and liquid phases are carefully sampled and analyzed at equilibrium [77].

At the beginning of an experiment, an equilibrium cell is charged with the substances of interest. The pressure is adjusted above or below the desired equilibrium value, depending on whether the pressure will rise or fall during equilibration [21].

VLEs of β-caryophyllene+CO_2 were obtained by the recirculation method, with an apparatus consisting of two isothermal chambers (one loaded with solute and another empty) where CO_2 is fed to both chambers up to the desired pressure. Then, the gas phase is continuously recirculated (for approximately 6 h) between the two chambers to reach equilibrium in the cell. After the recirculation period, the two chambers are separated by closing valves to allow the whole content of the gas chamber to be sampled [78].

Isothermal recirculation methods appear aim at solving the problem of pressure drop inherent to the withdrawals of samples and are based on the circulation of one phase, for example, volatile substance as vapor are entered into the liquid, and the exit vapor is analysed [79].

5.1.2. Isobaric

Both the vapor and the liquid phase circulate continuously to provide intimate contact of the phases [80]. Tipically, isobaric experiments are performed in an ebulliometer [23]. A mixture of known composition is brought to a boil at a controlled pressure.

Isobaric vapor–liquid equilibrium data for the binary system of cinnamaldehyde and benzaldehyde (natural flavors from cinnamon oil) were measured in a circulation VLE-type still (a modified Othmer still), in which pressure was maintained constant by using a vacuum pump. Later, a given liquid solution was charged into the equilibrium still and heated, when condensed vapor was delivered to the mixing chamber through the vapor-phase sampling port and continuously circulated to provide intimate contact of the phases to reach equilibrium. Finally, samples of the equilibrium phases were taken out from a vapor and liquid sampling port, respectively [81].

Isobaric vapor–liquid equilibrium (VLE) data for the reactive quaternary system ethanol+water+ethyl lactate +lactic acid have been determined experimentally in an all-glass still of the Gillespie type with circulation of both the liquid and vapor phases [82].

Sampling through capillaries can lead to differential vaporization and scattering results, especially for mixtures containing light and heavy components when no precautions have been taken to prevent a pressure drop all along the capillary [23].

5.1.3. Isobaric-Isothermal

In isobaric-isothermal methods, sometimes called “dynamic methods”, one or more fluid streams are continuously pumped into a thermostatted equilibrium cell. The pressure is kept constant during the whole experiment by controlling an effluent stream, most commonly the vapor phase, using a back-pressure regulator [23].

This method is used to determine the solubility of a low-boiling (liquid or solid) substance in a supercritical fluid. A difficulty is to guarantee the complete saturation of the phase vapor in the output of the saturator. This method does not permit the phase transition visualization, and it is restricted to two-phase equilibrium mixtures [21].

Semi-flow, continuous flow and chromatographic methods are classified as isobaric-isothermal methods.

A semi-flow type phase equilibrium apparatus was used to investigate the solubility of ergosterol, a natural phytosterol exhibiting cholesterol-lowering properties. Ergosterol is of particular interest to the food and nutraceutical industries in supercritical carbon dioxide, where it is pumped at the head by an air-driven booster pump, to the extraction cell with a pressure rating of 70MPa housed in an oven with a temperature controller. To establish dynamic flow, an on-off valve at the cell outlet is opened to allow flow through a pressure-reducing micrometering valve [83].

Caffeine solubility in CO_2 and the co-solvents ethanol and isopropanol were measured in a semi-continuous flow apparatus [84].

When a semi-flow method is used for the measurement of vapor–liquid equilibria, the composition of the liquid phase needs to be determined. Therefore, a sample from the liquid phase is withdrawn through tubing, depressurized, and analysed [22].

The continuous-flow method was adopted using a static mixer followed by a cyclone separator that separates vapor and liquid phases of the systems CO_2+limonene+citral, and CO_2+limonene +linalool [85].

Chromatographic methods measure solute retention in a chromatographic column and connect it with the Gibbs energy of solute transfer between the stationary and the mobile phases [23].

A gas–liquid chromatography method was used to experimentally determine the vapor pressure to obtain solubilities of phenolic compounds in supercritical CO_2

using a method based on the residual chemical potential in terms of the virial coefficients and fluctuation theory [86].

5.2. Analytical Methods without Sampling

5.2.1. Spectroscopic

Non-invasive spectroscopic methods, such as in situ NIR (near infrared) or Raman spectroscopy, have been used. In the NIR region, the optical density of water is sufficiently low to measure the absorption of other compounds next to water.

However, NIR absorption requires two optical windows oriented in the line of sight (exceptions such as attenuated total reflection absorption spectroscopy are given above), while a Raman sensor operating in the back scattering configuration requires only one window. Furthermore, the Raman effect can be excited with visible laser radiation while the radiation used in the NIR absorption method is invisible [87].

Measurement of LLE for δ-tocopherol+CO_2 compositions were performed by chemical analysis of samples withdrawn from the top and bottom phases in the cell, which are taken by expansion through chromatographic valves into a small volume [88].

The solubility of caffeine, theophylline and theobromine in supercritical carbon dioxide was measured by direct coupling of an equilibrium cell to a supercritical fluid chromatographic (SFC) system [89].

The solubility of caffeine in supercritical CO_2, supercritical CO_2+water, supercritical CO_2+ethanol, and supercritical CO_2+water+ethanol were measured with a circulation-type apparatus combined with an on-line Fourier transform infrared (FTIR) spectrometer at 313.2K and 15MPa [87].

5.2.2. Gravimetric

The analytical or static gravimetric technique involves keeping the solute in a small vial where it is subjected to a pressure vessel that contains supercritical fluid. The supercritical fluid dissolves the solute in the vial and brings the dissolved material out from the vial. Eventually, an equilibrium state is achieved. Then, the vessel is depressurized, and the remaining solute is weighed gravimetrically [90].

These methods are based on the monitoring of the mass of a nonvolatile condensed phase, such as a polymer or an ionic liquid in phase equilibrium with a fluid phase. Using additional information like the phase densities, the phase composition can be determined [23].

The solubility of CO_2 and N_2O in olive oil has been measured with a gravimetric microbalance that consists of an electrobalance with sample and counterweight components inside a stainless steel pressure-vessel [91].

5.2.3. Others

Experimental methods for the investigation of phase equilibria that do not fall into the classification as described by Dohrn et al. [22] are designated as other methods. Solubility of β-carotene in the binary system was measured using a quartz crystal microbalance technique at temperatures of 313 and 323K and at pressures ranging from 12 to 20MPa [92].

6. Synthetic Methods

In this technique, no sampling is necessary to determine equilibrium compositions [93].The overall composition of the mixture is known and its behavior is observed as a function of pressure or temperature that is adjusted until a homogeneous phase is obtained.

Synthetic methods can be used when the coexisting phases have similar density [94] such as in the critical region [21].

These methods are applied when the analytical path fails, i.e., when the phase separation is difficult due to the similar densities of the two phases or in barotropic systems where, under certain conditions, the densities of the two coexisting phases have the same value

The problems associated with analyzing the composition of an equilibrium mixture are replaced by the problem of synthesizing the equilibrium mixture and effectively observing its behavior. The classification is based on the means of observation for the appearance of a new phase. Synthetic methods are based on the presence or absence of a phase transition [22].

For multicomponent systems, experiments with synthetic methods yield less information than those with analytical methods because the tie lines cannot be determined without additional experiments. Therefore, synthetic methods are used mainly for binary or pseudo-binary systems [23].

6.1. Synthetic Methods with Phase Transition

6.1.1. Visual

The appearance of a new phase is detected by visual observation from a cell provided with a transparent window resulting in a turbidity or the appearance of a meniscus in a view cell [93]. One advantage of this method is that unusual behaviors, like foaming, can be visualized.

Also called the “static synthetic” method, the main advantage is to dismiss the withdrawal of samples of the phases and, consequently, to preserve the equilibrium state. Another advantage is the least use of chemical species, reducing the cost with the experiment [95]. For iso-optic systems where the coexisting phases have approximately the same refractive index, visual observation is impossible [23]. Solubility measurements of sunflower, castor and rapeseed oils in CO_2 were performed in a variable volume high pressure cell that consists of a horizontal hollow stainless steel cylinder, closed at one end by a movable piston and at the other end by a sapphire window that allows a visual observation of the interior of the pressure cell [96].

The high-pressure phase behavior of the systems carbon dioxide + limonene + linalool [57] and ethane + orange peel oil [97] were determined using a Caillettet apparatus. At any desired temperature, the pressure is varied for a sample of constant overall composition until a phase change is observed visually.

LLE Aqueous two-phase poly (ethylene glycol)–sodium polyacrylate system, using the using the turbidimetric titration method, which poly (ethylene glycol)–stock solution (1.0g) was added to a glass tube and titrated with small aliquots of the sodium polyacrylate stock solution, approximately (0.01–0.05)g, until the solution became turbid, indicating the formation of a two-phase system [98].

The “vanishing point” method was used to measure the solubility of lycopene in mixtures of CO_2 and ethyl acetate, performed in a variable volume high pressure equilibrium cell, equipped with a stirrer to improve mixing of the phases, four sapphire windows and a heating jacket which allows adjusting a constant temperature [99].

Recently experimental data for food and pharmaceutical compound were acquired [100-102] using the synthetic visual method in a high-pressure variable-volume view cell. Briefly, the apparatus consists of a variable-volume view cell, with a maximum internal volume of 27 cm^3, with two sapphire windows for visual observations, an absolute pressure transducer, a portable programmer for the pressure data acquisition and a syringe pump. The equilibrium cell contains a movable piston, which permits the pressure control inside the cell. Phase transitions were recorded visually through manipulation of the pressure using the syringe pump and the solvent (carbon dioxide) as a pneumatic fluid.

Figure 6 shows the experimental apparatus adapted to the reality of our research group from Lasefi (FEA/Unicamp): a HPLC pump (Thermoseparation Products, ConstaMetric, 3200 P/F Fremoni, USA) takes place the syringe pump (ISCO, 260 D, USA).

6.1.2. Non-visual

Other physical properties can be monitored to detect phase transitions, i.e., if the total volume of a variable volume cell can be measured accurately, the appearance of a new phase can be obtained from the abrupt change in the slope on the pressure-volume plot more accurately than it can be done on the basis of visual observations [93].

6.2. Synthetic Methods without Phase Transition

In synthetic methods without a phase transition, equilibrium properties like pressure, temperature, phase volumes and densities are measured and phase compositions are calculated using the material balance. They can be divided into isothermal, isobaric and other synthetic methods [104].

6.2.1. Isothermal

They are often designated as “static method” or “isothermal pTx method” and the temperature remains constant. The phase compositions are calculated through the application of a material balance. The most common application of this type of methods is in the determination of solubilities of gases in condensed phases [21].

Solubility of boldine (antioxidant compound from boldo leafs) in sub- and supercritical CO_2 was measured at 298, 308, 313, 323 and 333 K, and over a pressure range from 8 to 40 MPa [105].

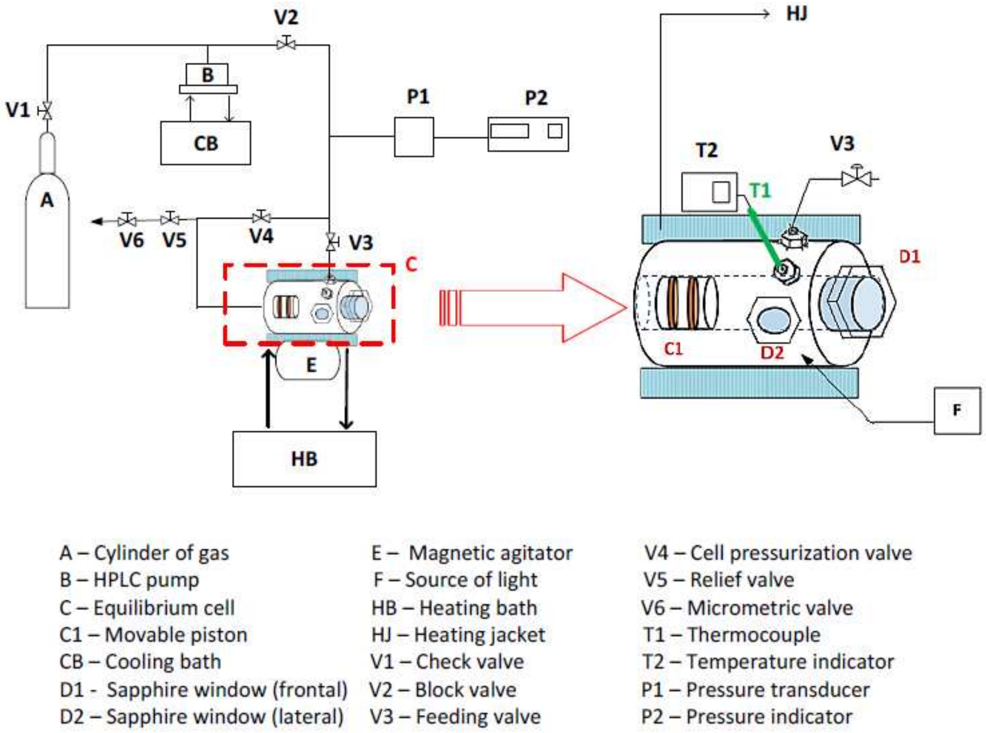

Figure 4. Schematic diagram of the experimental apparatus, adapted from Ndiaye et al. [103]

Table 4. Food systems and their used phase equilibrium measurements

System	Transition Type	Method	Reference
α-β-Ar-Turmerones (from turmeric volatile oil) + CO_2	VLE	Analytical with sampling Isothermal	[110]
α-humulene + CO_2	VLE, LLE, VLLE	Synthetic with phase transition Visual	[111]
α-humulene + Trans-caryophyllene + CO_2	VLE, LLE, VLLE	Synthetic with phase transition Visual	[111]
β-caryophyllene + CO_2	VLE	Analytical with Sampling Isothermal	[78]
β-Carotene + Organic Solvent +CO_2	VLE	Synthetic with phase transition Visual	[112]
δ-tocopherol + CO_2	VLE, VLLE	Analytical without sampling Spectroscopic	[113]
Borage Oil + CO_2	VLE	Analytical with sampling Isothermal	[114]
Brazil nut oil + CO_2	VLE	Analytical with sampling Isothermal	[115]
Camphor (from anethole) + CO_2	VLE	Synthetic with phase transition Visual	[116]
Camphor (from anethole) + CO_2 + Propane	VLE	Synthetic with phase transition Visual	[116]
Camphor (from anethole) + Propane	VLE	Synthetic with phase transition Visual	[116]
Capsaicin + Water + Ethanol + CO_2	VLE	Synthetic with phase transition Visual	[117]
Cashew Nut Shell Liquid + CO_2	VLE	Synthetic with phase transition Visual	[7]
Cinnamaldehyde + Benzaldehyde	VLE	Analytical with sampling Isobaric	[81]
Citral + CO_2	VLE	Analytical with sampling Isothermal	[118]
Clove Oil + CO_2	VLE, LLE, VLLE	Analytical with sampling Isothermal	[56]
Cocoa butter + CO_2	VLE	Analytical with sampling Isothermal	[119]
Corn Germ Oil + CO_2	VLE	Analytical with sampling Isothermal	[114]
Curcumin (from turmeric oleoresin) + CO_2 + Ethanol	VLE	Analytical with sampling Isothermal	[120]
Ethanol (from whiskey) + Water + CO_2	VLE	Analytical with sampling Isothermal	[41]
DL-α-tocopherol + Methanol	VLE	Analytical with sampling Isothermal	[121]
DL-γ-tocopherol + Methanol	VLE	Analytical with sampling Isothermal	[122]
Free Fatty Acids +Triglycerides + Squalene + CO_2	VLE	Analytical with sampling Isothermal	[123]
Fennel extract + CO_2	VLE, LLE, VLLE	Synthetic with phase transition Visual	[124]
Fish Oil Ethyl Esters +CO_2	VLE	Analytical with sampling Isothermal Continuous flow	[125]
Fish Oil Ethyl Esters + CO_2	LLE	Analytical with sampling Isothermal	[126]
Glycerol + Olive Oil + Propane + Sodium (bis-2-ethyl-hexyl) sulfosuccinate	VLE, LLE, VLLE	Synthetic with phase transitions Visual	[125]
Grape Seed Oil + CO_2+ Ethanol	VLE, LLE, VLLE	Synthetic with phase transition Visual	[101]
l-lactic acid + CO_2 + Ethanol	LLE VLLE,	Synthetic with phase transition Visual	[102]
Lemon essential oil + CO_2	VLE	Synthetic with phase transition Visual	[127]
Lemon essential oil + C_2H_6	VLE	Synthetic with phase transition Visual	[127]
Lemon essential oil + CO_2	VLE	Analytical with sampling Isothermal	[6]
Lemon and Bergamot peel oils + CO_2	VLE, LLE, VLLE	Synthetic with phase transition Visual	[128]
Limonene + Citral + CO_2	VLE	Synthetic with phase transition Visual	[85]
Limonene + Linalool+ CO_2	VLE	Synthetic with phase transition Visual	[85]
Limonene + Polystyrene +CO_2	LLE	Analytical with sampling Isothermal	[129]
Linoleic Acid (from banana peel oil) + CO_2	VLE, LLE, VLLE	Synthetic with phase transition Visual	[31]
Low-Molecular Weight Triglycerides + CO_2	VLE, LLE, VLLE	Synthetic with phase transition Visual	[130]
Menthol + CO_2	VLE	Analytical without sampling Isothermal	[131]
Menthol + Ethanol + CO_2	VLE	Analytical without sampling Spectroscopic	[132]
Oleate + Squalene (from olive oil residues) + CO_2	VLE	Analytical with sampling - Isothermal-Continuous Flow	[133]
Oleic Acid (from palm oil) + CO_2	VLE	Analytical without sampling Spectroscopic	[134]
Oleoresin Capsicum+ CO_2	VLE	Analytical with sampling Isothermal	[135]
Orange Peel Oil + Ethane	VLE	Synthetic with phase transition Visual	[135]

Orange Peel Oil + CO_2	VLE, LLE, VLLE	Synthetic with phase transition Visual	[136]
Palmitic Acid + Ethanol + CO_2	VLE, SLE	Synthetic with phase transition Visual	[137]
Palm Kernel Oil + CO_2	VLE	Analytical without sampling Spectroscopic	[134]
Palm Oil + CO_2	VLE	Analytical without sampling Spectroscopic	[134]
Propane + Chloroform + Oryzanol	VLE, SVLE, LLE, VLLE	Synthetic with phase transition Visual	[138]
Propionic acid + Caproic acid	VLE	Analytical without sampling Spectroscopic	[138]
Rapessed Oil + CO_2	VLE	Analytical with sampling Isothermal	[114]
Sunflower oil + Propane	VLE	Analytical with sampling Isothermal	[139]
Tripalmitin + CO_2	SLE	Synthetic with phase transition Visual	[140]
Ubiquinone + CO_2	SLE	Synthetic with phase transition Visual	[140]
Valeric Acid + Caproic acid	VLE	Analytical with sampling Isothermal	[141]
Vanillins (from vanilla beans) + CO_2	SLE	Analytical with sampling Isothermal	[142]
Vitamin D_2 + CO_2	SLE	Analytical with sampling Isothermal	[143]
Vitamin D_3 + CO_2	SLE	Analytical with sampling Isothermal	[143]
Vitamin K_2 + CO_2	SLE	Analytical with sampling Isothermal	[143]
Water + 2-Propanol + α-pinene	LLE	Analytical with sampling Isothermal	[144]
Water + 2-Propanol + β-pinene	LLE	Analytical with sampling Isothermal	[144]

Glass liquid–liquid equilibrium cells were used to measure LLE of fatty systems with emphasis on the distribution of tocopherols and tocotrienols, which samples of both phases were carefully collected with syringes with the observation of phases for quantification of the components [105].

6.2.2. Isobaric

In these methods, the boiling temperature of a synthetized mixture is measured at isobaric conditions, and the phase compositions are calculated by means of a material balance. This method is used to measure low-pressure data.

Isobaric VLE data for the mixture in the whole composition range constant pressure using an all-glass, dynamic re-circulating still, equipped with a Cottrell pump. The composition of liquid and vapor samples for the binary mixtures was determined by measuring the density whose dependence on composition at 298.15 K [106].

Similarly to analytical isobaric methods, ebulliometry is employed. Advantages of ebulliometric methods, include: data can be determined more quickly, degassing is not required, and simple apparatus and straightforward procedures are used. Specialized uses of ebulliometry include: high-pressure measurement (up to 2 MPa), measurement of infinite-dilution activity coefficients, screening of azeotropic systems, and measurement of solubility limits [107].

The corresponding disadvantages are the considerable demands on thermometry, the solubility of the buffer gas at high pressures, and thermal gradients due to pressure heads. But the greatest advantage is speed of measurement; typically, a pressure–temperature point can be obtained in an hour [23].

6.2.3. Others

Properties measured in the homogenous or heterogeneous region can be used in the calculation of phase boundaries. Here, a sample of known overall composition is placed in a vessel with constant volume, and the pressure is recorded as a function of temperature

A phase transition can be recognized from a change of the slope of the p(T) isochore [108]. Isochoric method, used for the determination of hydrate equilibrium phase diagrams, is based on a cooling/heating cycle at constant volume.

This method can be also coupled with visual observation. The advantage of isochoric method for pure gas systems in utilizing a section of hydrate phase diagram instead of the distinctive condition, at which the last piece of hydrate disappears [109]. Some food systems and their used phase equilibrium measurements are registered in Table 4.

7. Thermodynamic Modeling to Predict Phase Equilibrium Data

The development of models that can predict the behavior of thermodynamic systems is necessary to improvement and optimization of high-pressure process.

Foods are treated as aqueous mixtures that contains a wide variety of components in different phases which modeling requires a homogenous treatment for all physical (SLE, LLE, VLE) and chemical equilibria (dissociation, hydration, complexation and redox). For this purpose, it is necessary to generalize the existing models up to the prediction of equilibrium properties in a chosen reference state (generally the infinite dilution in water), and the prediction of the non−ideality (i.e., the deviation from Raoult's law) for concentrated solutions [145].

Among the many techniques of phase equilibrium calculations, the analytic combined methods (γ-ϕ and ϕ- ϕ approach) and the analytic direct methods (equation of state approach) are more widely used for performing practical fluid phase calculations than the other existing techniques [146].

Thermodynamic models can help to reduce the number of experimental data points needed for a special design problem, but very often, at least some experimental data points are needed to adjust interaction parameters of the model [22].

In the γ-φ is used the definition of the fugacity coefficient to describe the vapor phase and definition of the activity coefficient is used to describe the liquid phase. This method can be applied to a wide variety of mixtures and is accurate for low to moderate pressure calculations. As a result, applications of this method for critical and supercritical pressures become rather difficult and inaccurate [146].

In φ- φ approach is found better performance near the critical region, there is no dependence of density. When this method is used, computed solubilities are found to be sensitive to the temperature dependence of parameters in the equation of state [147].

The equation of state is a relationship between two or more functions associated with the matter (temperature, pressure, volume, or internal energy).

Equations of state are basically developed for pure components, but can be applied to multicomponent systems by employing some mixing rules to determine their parameters for mixtures. The mixing rules are considered to describe the prevailing forces between molecules of different substances forming the mixture [148].

The major advantage of this technique is its applicability for the ranges of pressures including critical and supercritical pressures. However, phase equilibrium calculations by this method will be rather lengthy except for simple equations of state. Another problem with the use of the equation of state technique is the insufficiency of information about the exact form of the equation of state of mixtures and inaccuracy of the existing mixing rules for mixtures consisting of polar and hydrogen bonding components and components with large molecular size and shape differences [146].

The van der Waals equation of state was the first equation to predict vapor-liquid coexistence. Later, the Redlich-Kwong [149] improved the accuracy of the van der Waals equation by proposing a temperature dependence for the attractive term. Soave [150] and Peng and Robinson [151] proposed additional modifications of the Redlich-Kwong [149] equation to more accurately predict the vapor pressure, liquid density, and equilibria ratios.

The virial equation of state is a power series, which expansion is, in principle, an infinite series, and such should be valid for all isotropic substances. In this case, the expansion permits to correct the ideal gas compressibility factor. However, in practice, terms above the third virial coefficient are rarely used.

8. Conclusions

Future trends for fluid properties and their phase equilibria involve research and development of convincing technologies, as for example supercritical fluid extraction, that ensures an innocuous separation process both to human health and to the environment.

Phase equilibrium data is of interest for applications to food systems in separation processes such as separating ethanol from water during distillation, the recovery of essential oils by liquid–vapor extraction or using supercritical fluids or even in liquid–liquid separation processes and there is a variety of experimental equipment and techniques designed to measure these kind of data. Phase equilibria are traditionally measured using two main approaches, depending on how composition is determined: analytical and synthetic.

In analytical method, the compositions of coexisting bulk phases are determined (often by sampling and chromatographic analysis) whereas, in the synthetic method, only the overall composition is determined experimentally (usually by metering the amounts of each pure substance introduced into the apparatus).

Each method possess its advantages and disadvantages. Therefore, there is no one ideal method, however, a specifically procedure to be used for each situation to be studied.

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- CAPÍTULO 7 –

High-pressure phase behavior of turmeric waste and extracts in the presence of carbon dioxide, ethanol and dimethylsulfoxide

O artigo apresentado neste capítulo relata as etapas de validação da unidade de equilíbrio de fases construída e adaptada à realidade do Lasefi. Além disso o trabalho fornece dados inéditos do comportamento de fases de sistemas multicomponentes compostos dos óleos voláteis de cúrcuma, o resíduo parcialmente hidrolisado, CO_2, etanol e dimetilsulfóxido.

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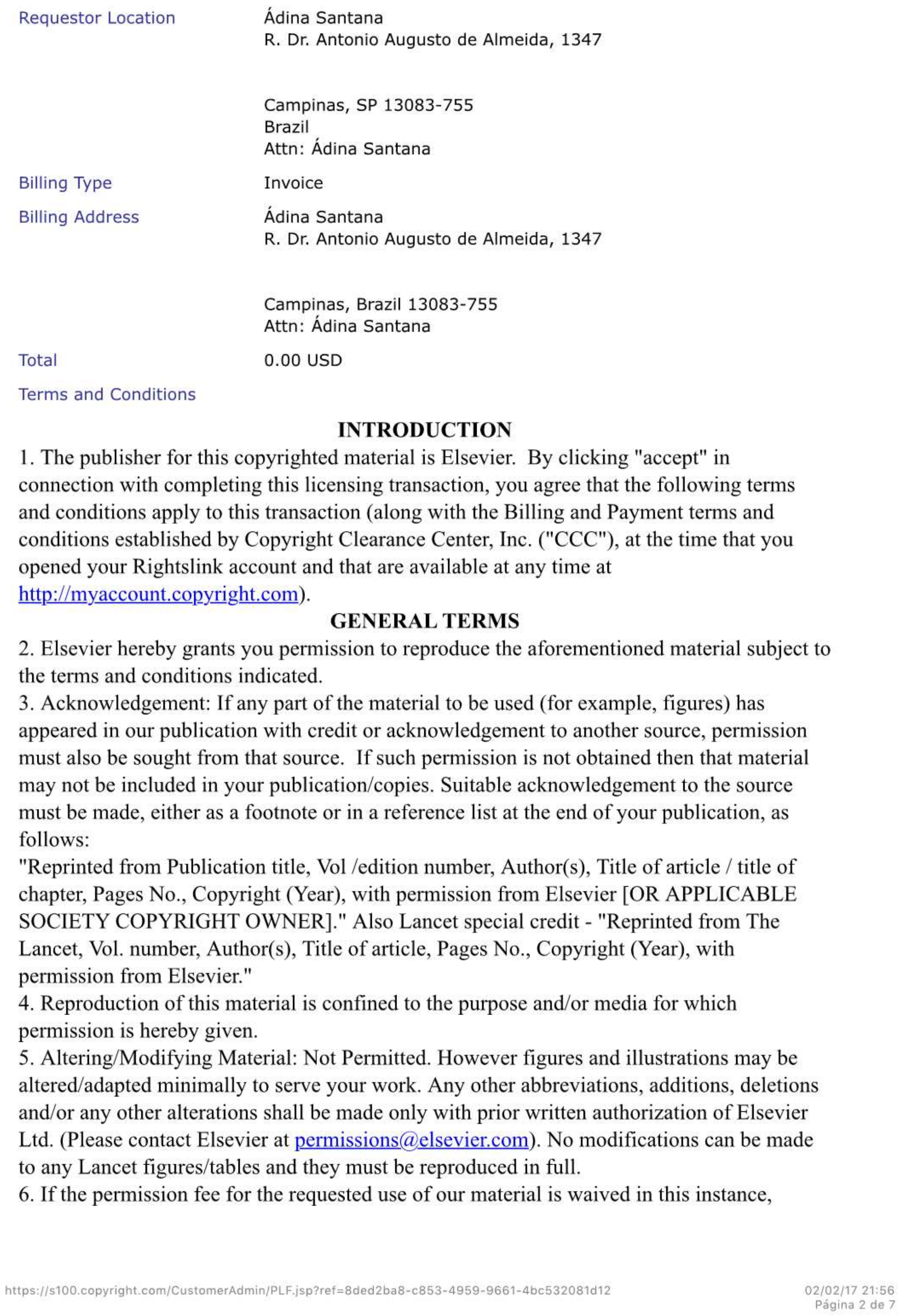

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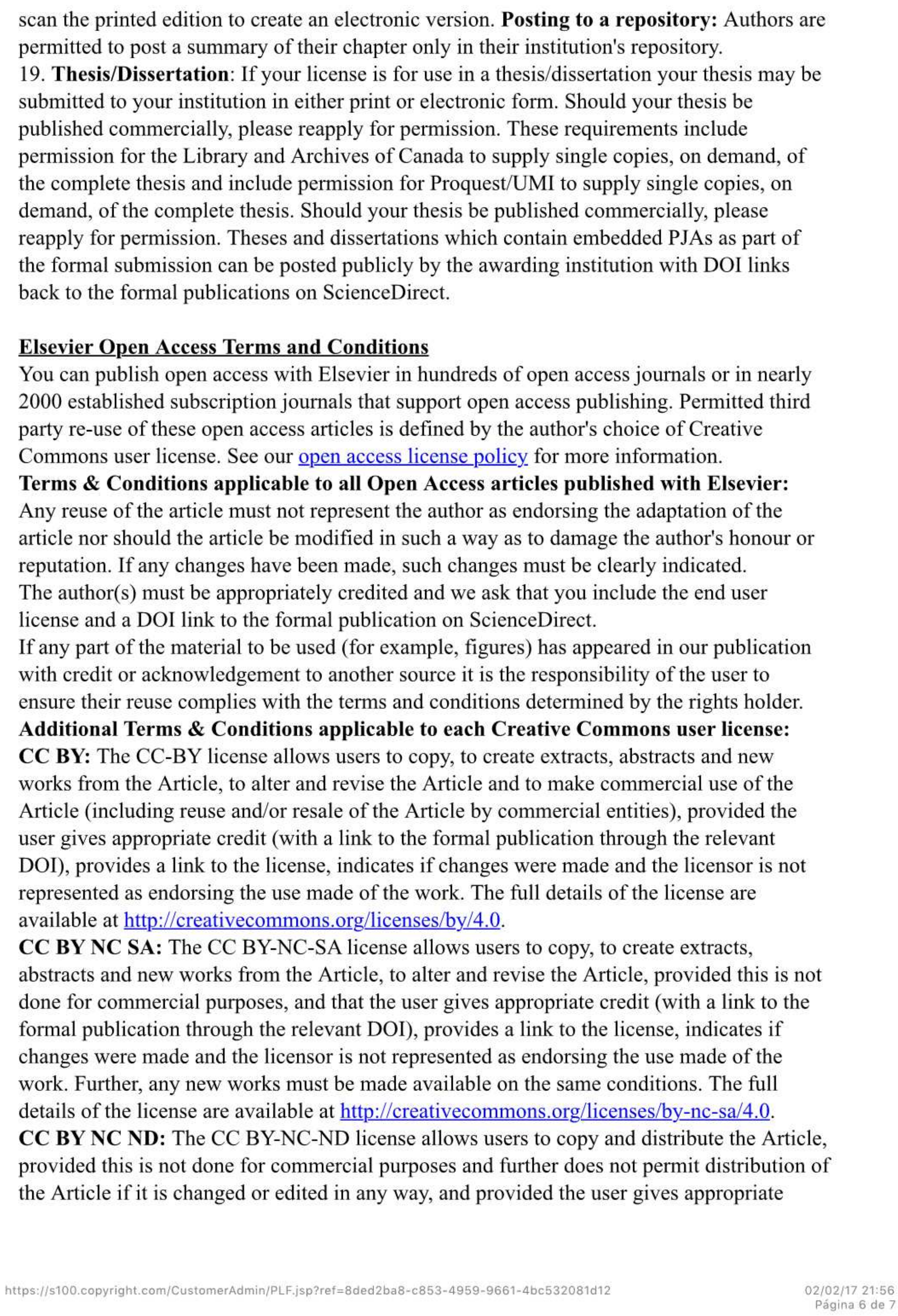

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High-pressure phase behavior of turmeric waste and extracts in the presence of carbon dioxide, ethanol and dimethylsulfoxide

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ABSTRACT

This work reports the validation of a phase equilibrium apparatus followed by the presentation of new high-pressure phase equilibrium data on systems containing turmeric waste and extracts, derived from processes that employs supercritical fluids and pressurized liquids, in the presence of carbon dioxide, ethanol and dimethylsulfoxide. In order to provide reliable information for further turmeric processing, experimental phase transition data were obtained using ten levels of temperature (303–348 K) and pressures up to 23 MPa. Results indicate the existence of complex phase behavior for the systems containing turmeric extracts and waste, with the occurrence of solid-vapor-liquid, solid-vapor-liquid-liquid, vapor–liquid, liquid–liquid and vapor–liquid–liquid phase transitions.

1. Introduction

The predominant bioactive constituents in turmeric rhizomes are curcuminoids (yellow colorants) and volatile oil. The major volatile constituent of turmeric oil, ar-turmerone (2-methyl- 6-(4-methylphenyl)-2-hepten-4-one), is known to be a character impact compound, contributing to dry turmeric aroma and is used in pharmacy for its antibacterial, antifungal, antioxidant, antimutagenic and anticarcinogenic properties [1].

The extraction of volatile oils and curcuminoids generate a waste composed by substances with relevant level of antioxidant effects and carbohydrates, from which polymer matrix was attributed promising industry applications as edible film [2], encapsulating agent [3], and biomass applied to hydrolysis assays for further production of fermentable sugars [4] and ethanol [5]. Furthermore, the effective reuse of waste materials is a perspective for industry application in food and non-food processing, in order to improve the functionality of end-use products.

Supercritical carbon dioxide is a feasible solvent, which is applied to obtain phase equilibrium data of various systems due to the fact that its solvent power is similar to that of light hydrocarbons with most of solutes [6]. Dimethylsulfoxide (DMSO) has the ability to dissolve many kinds of compounds, including carbohydrates [7], and resinous materials [8]. Ethanol (EtOH) is a used as cosolvent in extraction and fractionation processes due to the enhancement of product yields [9].

For the design and operation of high-pressure technological processes, a large amount of reliable data on the equilibrium properties of materials is necessary [10]. Knowledgement of phase change phenomena involving substances of biological origin, like lipids and carbohydrates, is of great importance for the still emerging high-pressure technologies in order to allow adequate selection of conditions to achieve the homogeneous phase during processing.

In this context, this work provides the built and validation of a high-pressure phase equilibrium apparatus that employs the visual synthetic method. In addition, novel information regarding high-pressure phase behavior of the extracts and the solid wastes from turmeric with presence of CO_2 and cosolvents are presented.

2. Material and methods

2.1. Reagents

For validation of phase equilibrium apparatus, acetonitrile (JT Baker, Center Valley, USA) and dichloromethane (Synth, Diadema, Brazil) were used. Ethanol (99.5%, Hortolandia, Brazil) and dimethylsulfoxide (Dinâmica, Diadema, Brazil) were used as cosolvents for the experimental assays. Carbon dioxide (99.9% pure) was purchased from White Martins (Campinas, Brazil).

2.2. Turmeric extracts and powder wastes

Crude raw material was purchased from the Oficina de Ervas Farmácia de Manipulação Ltda (lot 065DM, Ribeirão Preto, Brazil).

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List of Symbols

x_i	Molar fraction of component i (–).
Greek letters	
ρ	Density of material (g/mL)
σ	Standard deviation calculated from repetition measurements
ω_i	Overall mass fraction of component i (–)

Turmeric volatile oils, in light (LTO) and heavy (HTO) fractions, were obtained using supercritical fluid extraction (SFE) at 333 K and 25 MPa [11]. In the first minutes of SFE, the LTO, an oil with low viscosity and light-yellow coloration, was collected, while in the final periods of extraction of the HTO, a highly viscous oil, with presence of solids and aqueous fractions, was collected.

Deflavored and depigmented turmeric (DDT) was obtained from the SFE deflavored turmeric using pressurized EtOH at 333 K and 10 MPa [12]. Afterward, the DDT was subjected to partial hydrolysis using pressurized water at 313 K and 1 MPa [4], which waste was identified as partial-hydrolyzed deflavored and depigmented turmeric (PHT).

Phase equilibrium data of systems including PHT were obtained from solutions formulated with this material. In encapsulation processes involving, it is necessary that the polymer material is solubilized in a solvent in order to avoid damage to the experimental apparatus in which clogging is most common. In this context, PHT was solubilized in DMSO with the aid of a 13 mm ultrasonic diameter probe, 19 kHz and 400 W of nominal power (Unique, Indaiatuba, Brazil) for 1 min forming a solution with a concentration of 10 mg/mL, which was identified as the component (DMSO + PHT). At higher concentrations of PHT it was observed the formation of precipitates. For each system, five compositions were tested due to the poor availability of material to perform the assays.

2.3. *Chemical composition of turmeric products*

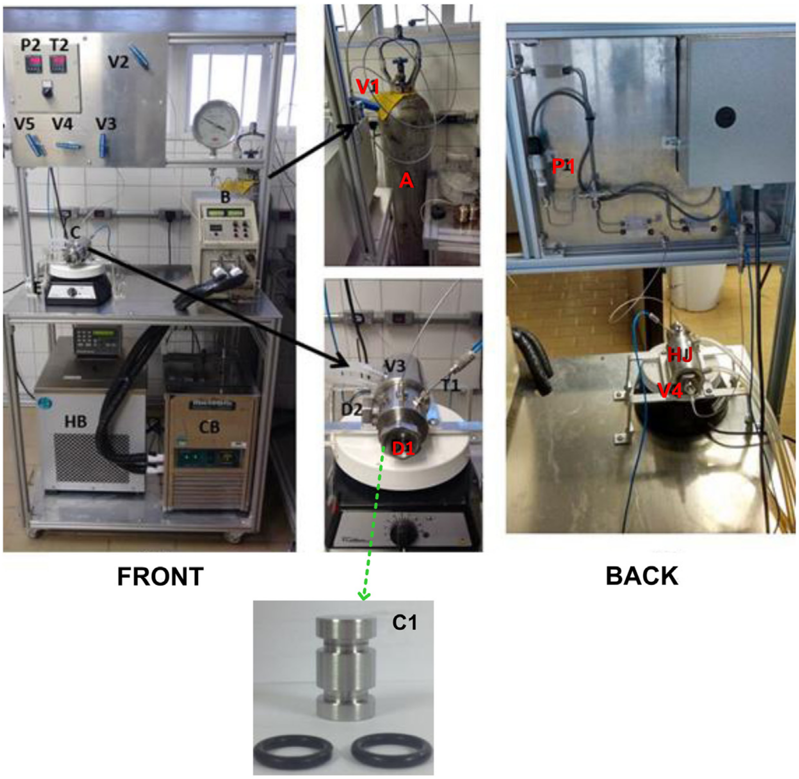
2.3.1. *Extracts*

Volatile constituents were evaluated by gas chromatograph coupled to a mass spectrometer (GC–MS). The analysis was performed in a gas chromatograph (7890 A, Agilent, USA) equipped with a capillary column DB-D (5% diphenyl, 95% dimethylpolysiloxane) fused silica 30 m × 0.25 mm × 0.25 μm thick film stationary phase (HP-5MS 19091S-433, Agilent, USA), coupled to a mass spectrometer (5975C, Agilent, USA) equipped with an injector system (Split/Splitless). The flow rate of the carrier gas Helium was 1 mL/min. The injection volume was 1 μL and the sample splitting rate was 50:1 and flow rate of 1 mL/min. The system of data acquisition was performed according to the database of spectra contained in the National Institute of Standards and Technology (NIST) library [13].

The temperature of the injector and detector was 533 K. The initial temperature of the column was 473 K for 2 min, programmed to increase to 513 K by 298 K/min, and then to 553 K by 278 K/min; the column remained at this temperature for 10 min. The temperature of the transfer line between GC–MS was 553 K.

For the quantification of fatty acids, moisture and lipids official methods were used [14–16]. Curcuminoids were determined with HPLC according to the method described previously [12] at a flow rate of 1.25 mL/min, a Waters Alliance separation module (269SD, Milford, USA), a diode array detector (2998), and a C18 column (150 × 4.6 nm, id., 2.6 μm, Phenomenex, Torrance, USA) that was maintained at 323 K.

Antioxidant activity (AA) expressed as % protection against oxidation, was obtained according to the methodology of Hammerschmidt and Pratt [17] adapted by Leal et al. [18]. The density of



A – Cylinder of gas
B – HPLC pump
C – Equilibrium cell
C1 – Movable piston
CB – Cooling bath
D1 – Saphire window (frontal)
D2 – Saphire window (lateral)
E – Magnetic agitator
HB – Heating bath
HJ – Heating jacket
T1 – Temocouple
T2 – Temperature indicator
V1 – Check valve
V2 – Blocking valve
V3 – Feeding valve
V4 – Cell pressurization valve
V5 – Relief valve
P1 – Pressure transducer
P2 – Pressure indicator

Fig. 1. Experimental high-pressure phase equilibrium experimental apparatus.

Table 1
Volatiles profile of turmeric extracts.

Retention time (min)	Compound	Peak areas (%)	
		LTO	HTO
3.700	Isooctane	3.860	4.650
40.390	α-curcumene	2.170	2.510
41.020	α-zingiberene	1.990	1.730
42.340	β-Sesquiphellandrene	1.690	2.380
44.950	NI	0.690	0.710
46.060	NI	0.680	–
47.430	NI	0.520	–
48.850	Ar-turmerone	30.510	37.730
49.020	Turmerone	30.970	21.690
50.370	Curlone	21.870	22.170
52.230	NI	0.510	0.720
52.620	NI	0.520	0.660
52.960	NI	0.560	0.810
53.110	NI	0.960	1.410
53.410	NI	1.150	1.860
54.890	NI	0.790	0.980
57.760	NI	0.550	–

NI – Non identified.

Table 2
Fatty acids profile, lipids, moisture and density of turmeric extracts.

Fatty acids		**(%)**	
		LTO	**HTO**
C11:0	Undecanoic	2.860	2.720
C18:0	Stearic	20.860	24.950
C18:2n6t	Linolelaidic	21.810	21.780
C18:2ω6	Linoleic	38.060	31.380
C18:3ω3	Linolenic	1.770	1.970
C21:0	Heneicosylic	4.180	3.720
C20:0	Arachidic	0.000	2.970
C20:2	Eicosadienoic	4.960	4.010
	Saturated	***28.200***	***27.500***
	Monounsaturated	***2.600***	***0.800***
	Polyunsaturated	***53.600***	***47.200***
	Trans	***24.000***	***18.200***
	LTO	**HTO**	
Lipids (%)	84.480	75.510	
Moisture (%)	15.520	24.490	
	Density (g/mL)		
Temperature (K)	**LTO**	**HTO**	
298	0.940	0.944	
303	0.940	0.949	
313	0.932	0.945	
323	0.925	0.939	
333	0.917	0.922	
343	0.908	0.888	

turmeric extracts was obtained using a digital densimeter (Anton-Paar, DMA 4500, São Paulo, Brazil) at atmospheric pressure.

2.3.2. *Solid waste*

Solid DDT was characterized previously [19] as starch using an enzymatic kit purchased from Megazyme® (Bray Business Park, Bray, Co. Wicklow, Ireland), method number 996.11 [20]. The following analysis were carried out using standard methods [21]: protein (method 976.05), ash (method 923.03), fibers (method 991.43, using a Megazyme® enzymatic kit), lipids (method 920.39), and moisture content (method 976.05). Curcuminoids and antioxidant activity were obtained using the same methods applied for the extracts. The density of the solid waste 0.838 g/mL was determined previously by Osorio-Tobón et al. [12]

2.4. *Phase equilibrium apparatus: validation and procedure*

Phase equilibrium experiments were performed adopting the synthetic method with phase transition visualization using in a high-pressure variable-volume cell. The experimental apparatus (Fig. 1) used in this work is an adaptation from the one which was extensively used and validated [22–26].

The system consists of a view cell (Fig. 1C.) containing two sapphire windows (Figs. 1.D1 and 1.D2), which is connected with a pressure transducer (Novus, Huba 511, Porto Alegre, Brazil), a high-performance liquid chromatography (HPLC) pump (Constametric, 3200 P/F, Thermoseparation Products), a type J thermocouple (Maqnágua, Campinas, Brazil), one indicator of temperature and one indicator of pressure (Novus, N1040i, Porto Alegre, Brazil), a CO_2 cylinder, a manometer (Record, 1438, Porto Alegre, Brazil), blocking and micrometering valves (Autoclave Engineers, Huntsville, USA) [10].

The equilibrium cell has a maximum internal volume of 27 mL and contains a movable piston (Fig. 1C1) which permits the variation of volume inside the cell. The piston has two o-rings, which allow the selling of the cell, preventing possible leaks. The safety volume adopted for composition calculations was 12 mL.

The cell was provided by a heating jacket, which was connected to a heating bath (PolyScience, Cotia, Brazil) in order to maintain the desired temperature into the cell, which was registered by the temperature indicator, connected to the thermocouple.

Table 3
Phase equilibrium data used to validate the experimental apparatus.

	CO_2 (1)/Acetonitrile (2)						CO_2 (1)/Dichloromethane (2)				
T (K)	x_1	P (MPa)	P (MPa) [25]	σ (MPa)	Phase Transition	T (K)	x_1	P (MPa)	P (MPa) [25]	σ (MPa)	Phase Transition
313	0.5925	6.273	5.640	3.363	VLE + BP	313	0.5686	4.780	4.650	0.650	VLE + BP
323		7.055	6.680	1.775	VLE + BP	323		5.772	5.630	0.710	VLE + BP
333		8.222	7.780	2.211	VLE + BP	333		6.618	6.470	0.740	VLE + BP
343		9.070	8.840	1.500	VLE + BP	343		7.136	7.330	0.970	VLE + BP
313	0.7385	7.185	6.700	2.425	VLE + BP	313	0.6580	5.338	5.390	0.262	VLE + BP
323		8.125	8.120	0.125	VLE + BP	323		6.272	6.370	0.490	VLE + BP
333		9.435	9.380	0.175	VLE + BP	333		7.028	7.300	1.360	VLE + BP
343		10.698	10.660	0.013	VLE + BP	343		8.424	8.380	0.220	VLE + BP
313	0.8844	7.673	7.570	0.362	VLE + BP	313	0.7437	5.99	5.940	0.250	VLE + BP
323		9.118	9.190	0.413	VLE + BP	323		6.818	7.040	1.110	VLE + BP
333		10.543	10.610	0.288	VLE + BP	333		8.066	8.140	0.370	VLE + BP
343		12.025	11.700	1.625	VLE + BP	343		9.208	9.170	0.190	VLE + BP
313	0.9426	8.030	8.010	0.150	VLE + BP	313	0.8522	6.516	6.810	1.470	VLE + BP
323		9.120	9.050	0.100	VLE + BP	323		8.175	8.260	0.425	VLE + BP
333		10.023	10.080	0.388	VLE + DP	333		8.783	9.290	2.533	VLE + BP
343		11.075	10.990	0.375	VLE + DP	343		9.87	10.190	1.600	VLE + BP

T = temperature (K); P = pressure (MPa); x = molar fraction of components 1 and 2 (–); σ = standard deviation of the repetition measurements (MPa); L = liquid phase; V = vapor phase; E = equilibrium = BP = bubble point = DP = dew point.

Table 4
Phase equilibrium data for the system CO_2 (1)/LTO (2).

T (K)	P (MPa)	σ (MPa)	Transition	T (K)	P (MPa)	σ (MPa)	Transition	T (K)	P (MPa)	σ (MPa)	Transition
$\omega_1 = 0.989$		$\omega_2 = 0.011$		$\omega_1 = 0.838$		$\omega_2 = 0.162$		$\omega_1 = 0.719$		$\omega_2 = 0.445$	
303	8.452	0.747	LLE	303	21.278	0.708	LLE	303	13.497	0.776	LLE
308	8.710	1.158	LLE	308	21.540	0.588	LLE	308	14.290	0.698	LLE
313	11.110	0.829	LLE	313	21.933	1.204	LLE	313	15.160	0.141	LLE
318	11.028	0.476	LLE	318	22.203	0.339	LLE	318	16.080	0.620	LLE
323	14.148	0.726	LLE	323	23.033	0.471	LLE	323	17.228	0.482	LLE
328	14.420	0.510	LLE	328	23.327	1.158	LLE	328	18.275	0.610	LLE
333	15.447	0.899	LLE	333	23.833	0.471	LLE	333	19.320	0.212	LLE
338	16.253	0.944	LLE	338	24.433	1.247	LLE	338	21.060	0.394	LLE
343	17.247	0.189	LLE	343	25.078	0.762	LLE	343	21.867	0.471	LLE
348	17.610	1.070	LLE	348	26.110	0.141	LLE	348	22.883	0.179	LLE
$\omega_1 = 0.555$		$\omega_2 = 0.445$		$\omega_1 = 0.417$		$\omega_2 = 0.583$					
303	12.260	0.432	VLLE	303	8.433	0.857	VLE				
308	12.600	0.572	LLE	308	8.914	0.801	LLE				
313	13.997	1.799	LLE	313	9.067	0.205	LLE				
318	14.933	0.287	LLE	318	11.466	0.588	VLLE				
323	15.945	0.610	LLE		10.183	0.047	VLE				
328	17.123	0.148	LLE	323	11.416	0.804	VLLE				
333	18.148	0.498	LLE		11.076	1.049	VLE				
338	19.218	0.585	LLE	328	12.418	1.030	VLLE				
343	20.148	0.109	LLE		12.124	0.709	VLE				
348	21.258	0.402	LLE	333	13.568	0.840	VLLE				
					13.230	0.422	VLE				
				338	16.616	1.991	VLLE				
					14.170	1.375	VLE				
				343	16.613	1.139	VLLE				
					15.120	0.904	VLE				
				348	17.970	0.329	VLLE				
					15.867	0.497	VLE				

T = temperature (K); P = pressure (MPa); ω = mass fraction of components 1 and 2 (–); σ = standard deviation of the repetition measurements (MPa); L = liquid phase; V = vapor phase; E = equilibrium.

Table 5
Phase equilibrium data for the system CO_2 (1)/HTO (2).

T (K)	P (MPa)	σ (MPa)	Transition	T (K)	P (MPa)	σ (MPa)	Transition	T (K)	P (MPa)	σ (MPa)	Transition
$\omega_1 = 0.990$		$\omega_2 = 0.010$		$\omega_1 = 0.957$		$\omega_2 = 0.043$		$\omega_1 = 0.792$		$\omega_2 = 0.208$	
303	6.983	0.311	VLE	303	8.377	0.492	LLE	303	17.175	1.423	LLE
308	7.760	0.589	LLE	308	9.415	0.350	LLE	308	17.783	0.624	LLE
313	8.995	0.250	LLE	313	11.007	0.249	LLE	313	18.237	0.591	LLE
318	9.920	0.367	LLE	318	11.416	0.624	LLE	318	19.103	0.531	LLE
323	10.870	0.141	LLE	323	12.58	0.455	LLE	323	19.793	0.591	LLE
328	11.510	0.489	LLE	328	13.793	0.736	LLE	328	20.890	0.659	LLE
333	11.793	0.665	LLE	333	14.713	0.984	LLE	333	21.555	0.249	LLE
338	12.453	0.410	LLE	338	16.300	0.579	LLE	338	22.590	0.793	LLE
343	12.733	0.471	LLE	343	16.973	0.976	LLE	343	–	–	–
348	13.026	0.377	LLE	348	18.483	0.849	LLE	348	–	–	–
$\omega_1 = 0.708$		$\omega_2 = 0.292$		$\omega_1 = 0.583$		$\omega_2 = 0.417$		$\omega_1 = 0.417$		$\omega_2 = 0.583$	
303	13.910	0.141	LLE	303	12.067	0.679	LLE	303	12.038	0.557	LLE
308	14.480	0.339	LLE	308	13.080	0.864	LLE	308	13.080	0.808	LLE
313	15.638	0.944	LLE	313	14.148	0.286	LLE	313	13.158	0.929	LLE
318	16.54	0.464	LLE	318	15.340	0.849	LLE	318	14.175	2.401	LLE
323	17.498	0.545	LLE	323	16.467	0.403	LLE	323	14.978	1.332	LLE
328	18.953	0.369	LLE	328	17.383	0.339	LLE	328	15.775	2.193	LLE
333	19.573	0.832	LLE	333	18.300	0.408	LLE	333	18.258	0.513	LLE
338	20.670	0.755	LLE	338	19.690	1.157	LLE	338	19.105	1.537	LLE
343	21.725	0.829	LLE	343	20.855	0.449	LLE	343	20.128	0.624	LLE
348	23.070	0.966	LLE	348	22.115	0.659	LLE	348	20.773	1.473	LLE

T = temperature (K); P = pressure (MPa); ω = mass fraction of components 1 and 2 (–); σ = standard deviation of the repetition measurements (MPa); L = liquid phase; V = vapor phase; E = equilibrium.

A cooling bath (Marconi, MA184, Piracicaba, Brazil) was connected to the HPLC pump and the CO_2 cylinder in order to guarantee the entrance of liquid CO_2 (268 K) inside the cell. A manometer was connected to the CO_2 cylinder in order to assure the initial pressure of this solvent. After established the initial pressure from the manometer, and the desired temperature, the density of CO_2 was obtained according to the NIST library [13]. The density of CO_2 was used to calculate the necessary quantity of CO_2 to be inserted inside the cell until reach the desired composition to be studied.

Depending on the overall composition to be investigated, an amount of sample was weighted with the aid of a high-precision scale balance (Sartorius, A200S, Berkeley, USA) with 1×10^{-4} g of accuracy and inserted into the cell. Phase transitions were observed through variation of the pressure behind the piston by opening the first cell pressurization valve and CO_2 injection from the HPLC pump.

Reached the desired temperature, the blocking valve (Fig. 1V2, which implies on the isolation of the cell from the CO_2 cylinder) was opened, followed by the opening of the feeding valve (Fig. 1V3) and

Table 6
Phase equilibrium data for the system CO_2 (1)/EtOH (2).

T (K)	P (MPa)	σ (MPa)	Transition	T (K)	P (MPa)	σ (MPa)	Transition	T (K)	P (MPa)	σ (MPa)	Transition
$\omega_1 = 0.861$	$\omega_2 = 0.139$			$\omega_1 = 0.787$	$\omega_2 = 0.213$			$\omega_1 = 0.712$	$\omega_2 = 0.288$		
303	6.360	0.361	VLE	303	6.297	0.551	VLE	303	5.627	0.153	VLE
308	6.920	0.436	VLE	308	7.067	0.814	VLE	308	6.023	1.050	VLE
313	7.507	0.208	VLE	313	7.803	0.231	VLE	313	6.983	1.818	VLE
318	8.280	0.100	VLE	318	8.420	0.557	VLE	318	8.057	2.695	VLE
323	9.203	0.153	VLE	323	9.037	1.662	VLE	323	8.293	0.961	VLE
328	9.950	0.458	VLE	328	9.663	0.252	VLE	328	8.887	1.501	VLE
333	10.493	0.058	VLE	333	10.283	0.802	VLE	333	9.857	3.402	VLE
338	10.967	0.404	VLE	338	10.900	1.058	VLE	338	10.137	0.635	VLE
343	11.447	0.416	VLE	343	12.023	1.159	VLE	343	10.457	1.686	VLE
348	12.180	0.889	VLE	348	12.187	0.643	VLE	348	10.733	1.172	VLE
$\omega_1 = 0.633$	$\omega_2 = 0.633$			$\omega_1 = 0.553$	$\omega_2 = 0.447$						
303	5.953	0.708	VLE	303	5.200	0.200	VLE				
308	6.657	0.588	VLE	308	5.637	0.379	VLE				
313	7.207	1.204	VLE	313	5.793	0.850	VLE				
318	8.040	0.339	VLE	318	6.143	1.150	VLE				
323	8.590	0.471	VLE	323	6.977	1.328	VLE				
328	8.643	1.158	VLE	328	8.003	1.097	VLE				
333	9.627	0.471	VLE	333	8.193	0.902	VLE				
338	9.533	1.247	VLE	338	8.697	1.050	VLE				
343	10.033	0.762	VLE	343	9.197	0.751	VLE				
348	10.947	0.141	VLE	348	9.747	0.907	VLE				

T = temperature (K); P = pressure (MPa); ω = mass fraction of components 1 and 2 (–); σ = standard deviation of the repetition measurements (MPa); L = liquid phase; V = vapor phase; E = equilibrium.

Table 7
Phase equilibrium data for the system CO_2 (1)/EtOH (2)/LTO (3).

T (K)	P (MPa)	σ (MPa)	Transition	T (K)	P (MPa)	σ (MPa)	Transition	T (K)	P (MPa)	σ (MPa)	Transition
$\omega_1 = 0.810$	$\omega_2 = 0.186$	$\omega_3 = 0.004$		$\omega_1 = 0.562$	$\omega_2 = 0.422$	$\omega_3 = 0.016$		$\omega_1 = 0.529$	$\omega_2 = 0.214$	$\omega_3 = 0.266$	
303	6.293	0.554	VLLE	303	6.520	0.082	VLLE	303	6.290	0.561	VLE
	6.168	0.389	VLE		6.233	0.205	VLE	308	7.400	0.354	VLE
308	7.043	0.936	VLLE	308	6.740	0.779	VLLE	313	7.553	0.369	VLE
	6.855	0.415	VLE		6.583	0.238	VLE	318	8.120	0.216	VLE
313	7.550	0.640	VLLE	313	7.260	0.942	VLLE	323	9.130	0.712	VLE
	7.268	0.492	VLE		7.030	0.100	VLE	328	10.108	0.849	VLE
318	8.295	0.856	VLLE	318	8.088	0.536	VLLE	333	10.657	0.613	VLE
	8.080	0.367	VLE		7.598	0.228	VLE	338	11.577	1.078	VLE
323	9.050	0.188	LLE	323	8.790	0.942	VLLE		12.520	0.432	VLLE
328	–	–	–		8.233	0.311	VLE		11.955	0.659	VLE
333	–	–	–	328	9.263	0.759	VLLE	343	13.553	0.411	VLLE
338	–	–	–		8.893	0.268	VLE		13.240	0.432	VLE
343	–	–	–	333	10.087	0.525	VLLE	348	–	–	–
348	–	–	–		9.588	0.487	VLE	$\omega_1 = 0.385$	$\omega_2 = 0.609$		$\omega_3 = 0.006$
$\omega_1 = 0.478$	$\omega_2 = 0.520$	$\omega_3 = 0.002$		338	10.878	0.867	VLLE	303	5.878	0.531	VLLE
303	5.823	0.205	VLE		10.467	0.574	VLE		5.775	0.396	VLE
308	6.183	0.124	VLE	343	11.320	0.681	VLLE	308	6.388	0.227	VLLE
313	7.040	0.999	VLE		11.095	0.550	VLE	313	7.093	1.461	VLLE
318	7.753	0.776	VLE	348	11.980	0.864	VLLE		6.800	0.210	VLE
323	8.270	0.638	VLE		11.890	0.804	VLE	318	7.603	1.155	VLLE
328	8.835	0.779	VLE						7.350	0.245	VLE
333	9.650	0.872	VLE					323	8.477	0.309	VLLE
338	10.273	1.558	VLE						8.105	0.287	VLE
343	10.997	0.329	VLE					328	9.027	0.659	VLLE
348	11.613	0.386	VLE						8.733	0.411	VLE
								333	9.463	0.501	VLLE
								338	10.423	0.235	VLLE
									10.023	0.975	VLE
								343	10.977	0.433	VLLE
									10.737	0.722	VLE
								348	16.647	0.485	VLLE
									11.407	1.057	VLE

T = temperature (K); P = pressure (MPa); ω = mass fraction of components 1, 2 and 3 (–); σ = standard deviation of the repetition measurements (MPa); L = liquid phase=; V = vapor phase; E = equilibrium.

CO_2 feed the cell with the desired composition with the aid of HPLC pump. Reached the pre-established composition of CO_2, the feeding valve was closed, the cell pressurization valve (Fig. 1V4) was opened and the pressure of the cell was increased by pumping CO_2 on the back of the piston until the observation of a single phase. The mixture was kept in continuous agitation with the aid of a magnetic agitator (Fisatom, 753, Perdizes, Brazil) and a teflon-coated agitation bar.

Afterward, the cell pressurization valve was closed and the relief valve was opened followed by the mild opening and manipulation of micrometering valve in order to decrease the pressure until incipient formation of a new phase. The definitive equilibrium pressure was recorded after repetition of the experimental procedure

Table 8
Phase equilibrium data for the system CO_2 (1)/EtOH (2)/HTO (3).

T (K)	P (MPa)	σ (MPa)	Transition	T (K)	P (MPa)	σ (MPa)	Transition	T (K)	P (MPa)	σ (MPa)	Transition
$\omega_1 = 0.693$	$\omega_2 = 0.139$	$\omega_3 = 0.168$		$\omega_1 = 0.552$	$\omega_2 = 0.346$	$\omega_3 = 0.102$		$\omega_1 = 0.457$	$\omega_2 = 0.367$	$\omega_3 = 0.176$	
303	6.475	0.050	SVLE	303	6.067	0.125	VLE	303	6.125	0.206	SVLE
308	7.090	0.308	SVLE	308	6.900	0.748	VLE	308	6.703	0.329	VLE
313	7.853	0.579	SVLE	313	7.195	1.620	VLE	313	7.643	0.822	VLE
318	8.910	0.169	VLE	318	7.937	0.865	VLE	318	8.328	0.249	VLE
323	9.860	0.309	VLE	323	8.708	0.978	VLE	323	9.143	0.616	VLE
328	10.935	0.952	VLE	328	9.133	0.943	VLE	328	9.618	0.613	VLE
333	12.033	0.843	VLE	333	10.120	0.652	VLE	333	10.610	1.532	VLLE
338	13.005	0.180	VLE	338	10.763	0.189	VLE		10.228	0.411	VLE
343	13.820	0.741	VLE	343	11.330	0.469	VLE	338	11.123	0.881	VLLE
348	14.643	1.034	VLE	348	12.050	0.500	VLE		10.920	0.282	VLE
$\omega_1 = 0.377$	$\omega_2 = 0.531$	$\omega_3 = 0.092$		$\omega_1 = 0.330$	$\omega_2 = 0.358$	$\omega_3 = 0.312$		343	12.167	1.699	VLLE
303	5.943	0.169	VLE	303	6.157	0.125	VLLE		11.747	0.659	VLE
308	6.607	0.741	VLE		6.113	0.540	VLE	348	13.300	2.160	VLLE
313	7.437	0.988	VLLE	308	6.903	1.000	VLLE		12.963	0.408	VLE
	7.080	1.030	VLE		6.723	0.192	VLE				
318	7.983	1.369	VLLE	313	7.497	0.377	VLLE				
	7.593	0.934	VLE		7.425	0.304	VLE				
323	8.603	1.322	VLLE	318	8.150	0.294	VLLE				
	8.343	0.249	VLE		8.027	0.249	VLE				
328	9.345	0.779	VLLE	323	8.928	0.363	VLLE				
	8.966	0.094	VLE		8.853	0.129	VLE				
333	10.083	2.169	VLLE	328	9.720	0.474	VLLE				
	9.738	0.129	VLE		9.543	0.189	VLE				
338	10.693	0.694	VLLE	333	10.430	0.534	VLLE				
	10.188	0.867	VLE		10.268	0.179	VLE				
343	11.420	0.943	VLLE	338	11.073	0.613	VLLE				
	11.020	0.255	VLE		10.867	0.264	VLE				
348	12.000	0.485	VLLE	343	11.600	0.509	VLLE				
	11.710	0.158	VLE		11.478	0.303	VLE				
				348	12.410	0.566	VLLE				

T = temperature (K); P = pressure (MPa); ω = mass fraction of components 1, 2 and 3 (–); σ = standard deviation of the repetition measurements (MPa); L = liquid phase = S = solid phase; V = vapor phase; E = equilibrium.

Table 9
Phase equilibrium data for the system CO_2(1)/DMSO(2).

T (K)	P (MPa)	σ (MPa)	Transition	T (K)	P (MPa)	σ (MPa)	Transition	T (K)	P (MPa)	σ (MPa)	Transition
$\omega_1 = 0.907$	$\omega_2 = 0.093$			$\omega_1 = 0.862$	$\omega_2 = 0.184$			$\omega_1 = 0.727$	$\omega_2 = 0.273$		
303	6.684	0.950	VLE	303	7.040	1.735	VLE	303	6.453	0.351	VLE
308	7.203	1.159	VLE	308	7.877	1.504	VLE	308	7.353	1.079	VLE
313	–	–	–	313	8.630	0.608	VLE	313	8.387	0.586	VLE
318	–	–	–	318	9.813	0.231	VLE	318	9.503	0.681	VLE
323	–	–	–	323	10.887	0.153	VLE	323	11.047	0.751	VLE
328	–	–	–	328	–	–	–	328	11.763	1.222	VLE
333	–	–	–	333	–	–	–	333	13.083	1.518	VLE
338	–	–	–	338	–	–	–	338	14.317	1.387	VLE
343	–	–	–	343	–	–	–	343	15.630	0.361	VLE
348	–	–	–	348	–	–	–	348	17.360	1.442	VLE
$\omega_1 = 0.554$	$\omega_2 = 0.446$			$\omega_1 = 0.471$	$\omega_2 = 0.529$						
303	6.097	0.586	VLE	303	5.617	0.351	VLE				
308	6.523	0.551	VLE	308	5.920	0.624	VLE				
313	8.056	0.451	VLE	313	7.057	2.255	VLE				
318	8.816	0.681	VLE	318	8.040	1.411	VLE				
323	9.073	1.079	VLE	323	8.297	3.421	VLE				
328	10.480	0.529	VLE	328	9.463	0.379	VLE				
333	10.720	0.300	VLE	333	9.957	2.113	VLE				
338	11.597	0.709	VLE	338	11.170	2.252	VLE				
343	12.387	0.577	VLE	343	11.733	2.715	VLE				
348	14.037	1.185	VLE	348	12.053	1.595	VLE				

T = temperature (K); P = pressure (MPa); ω = mass fraction of components 1 and 2 (–); σ = standard deviation of the repetition measurements (MPa); L = liquid phase; V = vapor phase; E = equilibrium.

at least three times. After completing the measurement at a determined temperature, the cell temperature was established at a new value and the experimental procedure was repeated.

The validation of the experimental apparatus was performed using the systems CO_2 (1)/acetonitrile (2) and CO_2 (1)/dichloromethane (2), in terms of molar fractions (x_i), which resulted data were compared to those performed using the same methodology and type of equipment [27].

After confirmed reliability of the apparatus, experimental phase equilibrium procedures were applied for the multicomponent systems containing turmeric extracts and waste (LTO, HTO and PHT) in the presence of CO_2, EtOH and DMSO for the temperature levels ranging between 303 K and 348 K.

The studied overall compositions in terms of mass fractions (ω_i) were approximately between 0.330 and 0.990 for CO_2 (ω_1), 0.100

Table 10
Phase equilibrium data for the system CO_2 (1)/(DMSO/PHT) (2).

T (K)	P (MPa)	σ (MPa)	Transition	T (K)	P (MPa)	σ (MPa)	Transition	T (K)	P (MPa)	σ (MPa)	Transition
$\omega_1 = 0.907$	$\omega_2 = 0.093$			$\omega_1 = 0.816$	$\omega_2 = 0.184$			$\omega_1 = 0.728$	$\omega_2 = 0.272$		
303	6.693	0.757	SVLE	303	7.027	0.709	SVLE	303	6.807	0.351	SVLE
308	–	–	–	308	8.020	1.389	SVLE	308	7.710	0.458	SVLE
313	–	–	–	313	8.580	0.265	SVLE	313	8.297	0.058	SVLE
318	–	–	–	318	10.497	0.850	SVLE	318	8.997	0.451	SVLE
323	–	–	–	323	11.893	0.902	SVLE	323	10.043	1.021	SVLE
328	–	–	–	328	12.677	0.208	SVLE	328	11.690	0.173	SVLE
333	–	–	–	333	13.767	1.041	SVLE	333	12.923	0.666	SVLE
338	–	–	–	338	14.840	0.529	SVLE	338	14.170	0.200	SVLE
343	–	–	–	343	15.800	0.900	SVLE	343	15.790	0.854	SVLE
348	–	–	–	348	16.833	1.050	SVLE	348	17.123	1.305	SVLE
$\omega_1 = 0.555$	$\omega_2 = 0.445$			$\omega_1 = 0.471$	$\omega_2 = 0.529$						
303	6.200	0.265	SVLE	303	6.327	0.379	SVLE				
308	6.937	0.351	SVLE	308	6.937	0.306	SVLE				
313	7.703	0.058	SVLE	313	7.597	0.058	SVLE				
318	8.487	0.289	SVLE	318	8.570	0.200	SVLE				
323	9.783	0.289	SVLE	323	9.393	0.115	SVLE				
328	11.097	0.643	SVLE	328	11.133	1.155	SVLE				
333	12.237	0.586	SVLE	333	12.413	0.416	SVLE				
338	13.557	0.981	SVLE	338	13.023	0.681	SVLE				
343	14.727	0.462	SVLE	343	14.730	1.127	SVLE				
348	16.177	1.662	SVLE	348	16.267	0.577	SVLE				

T = temperature (K); P = pressure (MPa); ω= mass fraction of components 1 and 2 (—); σ= standard deviation of the repetition measurements (MPa); L = liquid phase; V = vapor phase; E = equilibrium.

Table 11
Phase equilibrium data for the system CO_2 (1)/(DMSO + PHT) (2)/LTO (3).

T (K)	P (MPa)	σ (MPa)	Transition	T (K)	P (MPa)	σ (MPa)	Transition	T (K)	P (MPa)	σ (MPa)	Transition
$\omega_1 = 0.648$	$\omega_2 = 0.273$	$\omega_3 = 0.078$		$\omega_1 = 0.558$	$\omega_2 = 0.403$	$\omega_3 = 0.038$		$\omega_1 = 0.555$	$\omega_2 = 0.441$	$\omega_3 = 0.004$	
303	6.617	0.569	SVLE	303	6.050	1.179	SVLE	303	6.887	0.950	SVLLE
308	7.640	0.458	SVLE	308	7.887	0.551	SVLE	308	7.330	0.781	SVLLE
313	7.810	0.265	SVLE	313	8.193	0.503	SVLE	313	8.053	0.473	SVLLE
318	8.623	0.907	SVLE	318	9.043	0.833	SVLE	318	8.907	1.041	SVLE
323	9.783	0.971	SVLE	323	–	–		323	9.460	0.964	SVLE
328	11.497	0.058	SVLE	328	–	–		328	10.517	0.503	SVLE
333	12.140	0.700	SVLE	333	–	–	–	333	12.127	3.107	SVLE
338	14.193	0.493	SVLE	338	–	–	–	338	13.083	0.839	SVLE
343	15.367	0.208	SVLE	343	–	–	–	343	14.057	0.603	SVLE
348	16.820	0.346	SVLE	348	–	–	–	348	16.157	2.312	SVLE
$\omega_1 = 0.555$	$\omega_2 = 0.445$	$\omega_3 = 0.001$		$\omega_1 = 0.477$	$\omega_2 = 0.447$	$\omega_3 = 0.077$					
303	7.017	0.321	SVLE	303	6.613	1.801	SVLE				
308	6.897	1.026	SVLE	308	7.957	0.351	SVLE				
313	8.210	0.529	SVLE	313	8.370	0.854	SVLE				
318	9.049	1.212	SVLE	318	10.403	1.550	SVLE				
323	10.043	1.801	SVLE	323	–	–	–				
328	11.230	0.819	SVLE	328	–	–	–				
333	12.290	1.572	SVLE	333	–	–	–				
338	13.020	2.307	SVLE	338	–	–	–				
343	13.813	0.709	SVLE	343	–	–	–				
348	15.740	0.608	SVLE	348	–	–	–				

T = temperature (K); P = pressure (MPa); ω= mass fraction of components 1 and 2 (—); σ= standard deviation of the repetition measurements (MPa); L = liquid phase; V = vapor phase; E = equilibrium.

and 0.530 for EtOH or DMSO or PHT/DMSO (ω_2) and ranging from 0.001 to 0.580 for HTO or LTO (ω_3).

3. Results and discussion

3.1. Chemical composition of turmeric products

The extracts presented similar volatile chromatographic profile, in which ar-turmerone, turmerone and curlone prevail (Table 1). Other minor components were also detected, but their identification was not possible due to their low intensity. The quantity of turmerones present in HTO and LTO represent respectively 59.420% and 61.480%, of the volatile fraction of the extracts, which is slightly lower than the 67.7% reported elsewhere for turmeric volatile oil obtained by SFE [1].

Table 2 shows the results for fatty acids composition, lipids, moisture and density of the extracts. Linolelaidic (C18:2n6t) and linoleic (C18:2ω6) were the main fatty acids present in the HTO and LTO, differently from the results reported previously for turmeric volatile oils obtained with steam distillation [28], in which oleic (C18:1) was the main fatty acid. The highest content of moisture of 24.490% was attributed to HTO. Density measurements of the extracts with temperature variation at constant pressure differed from each other because of differences in chemical composition, showing that the difference between the extracts is relevant, and may result in different phase behaviors by applying pressure (Table 2). The densities for each extract obtained at 298 K were used to calculate the quantity of extract used to feed the equilibrium cell, according to the pre-established compositions (Table 2).

The composition of solid turmeric waste resulted on moisture value of 5%, protein content of 3.100%, ashes of 4.400% and lipids of

Table 12
Phase equilibrium data for the system CO_2 (1)/(DMSO + PHT) (2)/HTO (3).

T (K)	P (MPa)	σ (MPa)	Transition	T (K)	P (MPa)	σ (MPa)	Transition	T (K)	P (MPa)	σ (MPa)	Transition
$\omega_1 = 0.558$	$\omega_2 = 0.403$	$\omega_3 = 0.039$		$\omega_1 = 0.555$	$\omega_2 = 0.441$	$\omega_3 = 0.004$		$\omega_1 = 0.554$	$\omega_2 = 0.445$	$\omega_3 = 0.001$	
303	6.667	0.551	SVLE	303	6.170	0.200	SVLE	303	6.107	0.643	SVLE
308	7.503	0.289	SVLE	308	6.893	0.462	SVLE	308	6.930	0.557	SVLE
313	7.893	0.153	SVLE	313	7.443	0.416	SVLE	313	7.443	0.416	SVLE
318	8.300	0.361	SVLE	318	8.300	0.361	SVLE	318	8.113	0.862	SVLE
323	9.110	0.755	SVLE	323	9.297	0.643	SVLE	323	9.183	0.351	SVLE
328	11.767	1.206	SVLE	328	11.713	0.709	SVLE	328	10.317	0.289	SVLE
333	13.117	0.666	SVLE	333	12.713	0.231	SVLE	333	11.480	0.700	SVLE
338	14.723	0.586	SVLE	338	13.540	0.361	SVLE	338	13.307	0.666	SVLE
343	16.120	0.794	SVLE	343	15.093	0.208	SVLE	343	14.363	0.850	SVLE
348	17.100	0.000	SVLE	348	–	–	–	348	15.813	1.002	SVLE
$\omega_1 = 0.481$	$\omega_2 = 0.509$	$\omega_3 = 0.010$		$\omega_1 = 0.481$	$\omega_2 = 0.447$	$\omega_3 = 0.072$					
303	6.170	0.199	SVLE	303	6.467	0.208	SVLE				
308	6.893	0.462	SVLE	308	6.947	0.513	SVLE				
313	8.140	1.217	SVLLE	313	7.523	0.416	SVLE				
	7.480	1.058	SVLE	318	8.750	0.458	SVLE				
318	8.833	0.651	SVLLE	323	9.777	0.666	SVLE				
	8.317	0.643	SVLE	328	11.847	0.503	SVLE				
323	10.553	1.361	SVLLE	333	12.820	1.997	SVLE				
	9.297	0.643	SVLE	338	13.837	0.709	SVLE				
328	11.303	0.635	SVLLE	343	16.117	1.021	SVLE				
333	11.713	0.709	SVLLE	348	16.923	0.681	SVLE				
338	12.713	0.231	SVLLE								
343	13.540	0.361	SVLLE								
348	15.070	0.608	SVLLE								

T = temperature (K); P = pressure (MPa); ω = mass fraction of components 1 and 2 (–); σ = standard deviation of the repetition measurements (MPa); L = liquid phase; V = vapor phase; E = equilibrium.

0.500%. From the total carbohydrates content of 86.900%, were analyzed total fiber (28.400%) and starch (36%) [19]. The composition was similar from those registered from powder turmeric [29].

Curcuminoids are promising natural compound with a large variety of therapeutic properties, particularly biological targets and interactions, linked to numerous disease [30]. Total curcuminoids detected in turmeric products were 0.200% for LTO, 0.580% for HTO and 3.630% for PHT. Antioxidant activity (AA) values were 63.650% for LTO, 81.610% for HTO and 9.760% for PHT after 3 h of reaction. The presence of volatile constituents and curcuminoids in turmeric extracts justify the highest values of AA. Although PHT is a waste from extraction processes, it contains antioxidant functionality which can assign applications for its reuse.

3.2. Phase equilibrium apparatus: validation and procedure

Table 3 presents the validation of the phase equilibrium apparatus, through comparison of phase transition pressure for the systems CO_2 (1)/acetonitrile (2) and CO_2 (1)/dichloromethane (2). The associated experimental error for each condition was represented by the standard deviation of the repetition measurements (σ). The data obtained in this work corroborates to those from literature [27,31].

3.3. Phase equilibrium experimental data

The experimental measurements for the systems containing the products from turmeric revealed a complex phase behavior, consisting of five types of phase equilibrium: vapor-liquid (VLE), vapor-liquid–liquid (VLLE), liquid–liquid (LLE), solid-vapor-liquid (SVLE), and solid-vapor-liquid–liquid (SVLLE), according to the results expressed on Tables 4, 5, 7, 8, 10–12. Some of these systems showed varied behavior in a same temperature according to the mass fractions proportions (Tables 4, 5, 7, 8, 11 and 12). In addition, turmeric extracts and waste are multicomponent substances, i.e., the large differences between the chemical and structural nature of the constituents present in these products may cause complex phase behavior, therefore, multiples solubilities may happen, in spite of not visually detected in the used apparatus [32]. According to Raeissi et al. [33] this complexity may increase even more when we are dealing with mixtures of interest for supercritical fluid technology, i.e., mixtures where carbon dioxide is used as the near-critical solvent.

As shown in Fig. 2 the behavior of the studied systems is characteristic of LCST (Lower Critical Solution Temperature), in which an increase in the temperature clearly leads to an increase in the pressure transition values, similarly to those reported to the pseudobinary system (propane + ethanol) (1)/l-lactic acid (2) for the mass fractions of the (propane + ethanol) compound between 0.960 and 0.990 [23].

The particular visualization for each investigated system is reported on Fig. 3. Unusual behaviors could be visualized for the multicomponent systems, like foaming (Fig. 3F), droplets (Fig. 3H.), solid particles (Fig. 3J and K) and turbidity (Fig. 3K and I.).

Lipids are the most pressure-sensitive biological components, since lipid assemblies are governed by hydrophobic interactions [34]. In the systems containing turmeric extracts in the presence of CO_2 the presence of LLE phase transitions were observed for most of the compositions (Table 4 and 5), differently from the VLE transtions observed for the isolated turmerones in the presence of CO_2, which data were obtained from an analytical isothermal apparatus provided with measurements of densities from the coexisting phases [1].

In addition, due to the chemical composition variability possibly encountered for a determined volatile oil, associated to the type of experimental methodology used to measure phase equilibrium data, it may not be surprising to found discrepancies in the phase behavior thus justifying the necessity of additional measurements as it was the case of the system CO_2 (1)/lemon peel volatile oil (2), decribed by Gironi and Maschietti [35] who used an analytical isothermal method with measurements of the liquid and vapor fractions from the coexisting phases, and by Francheschi et al. [36] who used the same method used in this work.

For some systems containing turmeric extracts, there is the appearance of a vapor-liquid-liquid above the vapor-liquid transition for lower CO_2 overall compositions (Tables 4 and 7–8) with

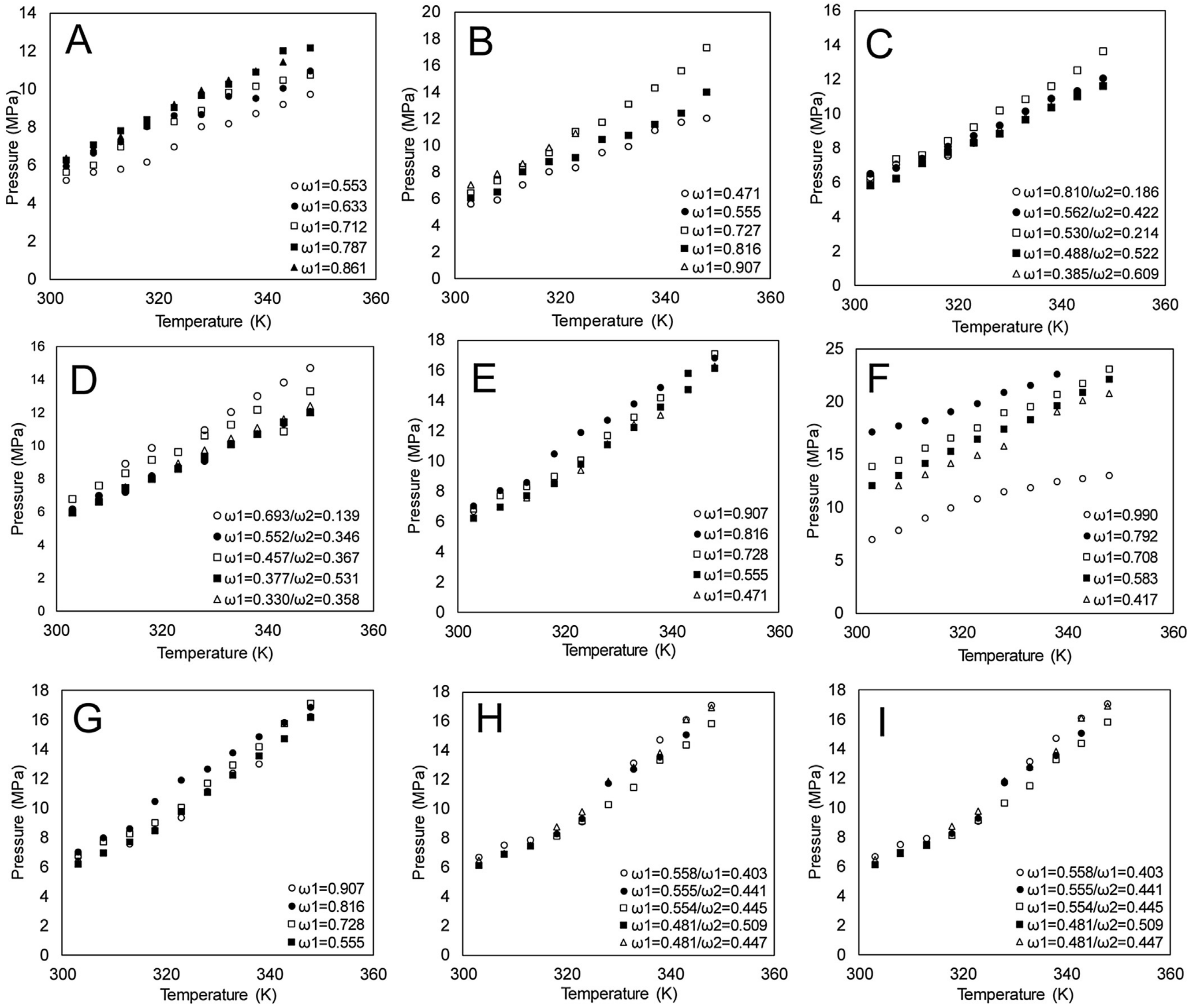


Fig. 2. Vapor-liquid equilibria phase transitions of CO_2 (1) in the binaries containing EtOH (A), DMSO (B). Vapor-liquid–liquid phase transitions of CO_2 in the pseudoternaries containing EtOH (2)/LTO (3) (C) and EtOH (2)/HTO (3) (D). Liquid-liquid equilibria phase transitions of CO_2 (1) in the pseudobinaries containing LTO (E) and HTO (F). Solid-vapor-liquid equilibria phase transitions of CO_2(1) in the pseudobinary system containing (DMSO + PHT) (G), pseudoternaries (DMSO + PHT) (2)/LTO (3) (H) and (DMSO + PHT) (2)/HTO(3) (I).

bubble cloud point transitions. Moreover, some scattering in the VLLE data is expected because of the multicomponent nature of the mixture and due to uncertainties in the pressure measurements. Perhaps, the phase behavior differences between LTO and HTO in the presence of CO_2 were related to the water content, expressed in terms of moisture (Table 2) that exerted influence on the liquid–liquid behavior of the mixture, since under the conditions performed in this work, water is liquid.

The phase transitions observed in the pseudoternaries CO_2 (1)/EtOH (2)/LTO (3) (Table 7) and CO_2 (1)/EtOH (2)/HTO (3) (Table 8), except SVLE, were similar to those registered for the pseudoternaries CO_2 (1)/EtOH (2)/banana peel oil (3) [24] and CO_2 (1)/methanol (2)/lauric acid (3) [37].

Besides that, the inclusion of cosolvent EtOH to the mixtures CO_2 (1)/LTO (2) and CO_2 (1)/HTO (2) contributed to the decreasing of the pressure transition, which is attributed to the improvement of solubility of the fatty acids content in the extracts in the primary solvent CO_2, similarly to those reported to grape seed oil in the presence of CO_2 and EtOH [38], and to the interaction between varied types of fatty acids in the presence of CO_2 and cosolvents with similar polarity [37].

The pseudoternary CO_2 (1)/EtOH (2)/LTO (3) presented VLE and VLLE phase transitions (Table 7), similarly to that reported previously for the systems CO_2 (1)/palmitic acid (2) [39] and CO_2 (1)/annatto extracts (2) [32].

Nevertheless, the pseudoternary CO_2 (1)/EtOH (2)/HTO (3) presented solid-vapor-liquid equilibria (SVLE) phase transition, characterized by the presence of solid particles on the lowest temperature conditions at $\omega_1 = 0.693$ and $\omega_1 = 0.457$ (Table 8), which appearance is attributed to the proximity of the organic solution saturation, similar to that reported for the system CO_2 (1)/EtOH (2)/guaçatonga extracts (3) [26]. The presence of solid phase occurs for highly asymmetric mixtures where the limited solubility of the light component in the liquid phase of the nonvolatile component results in relatively small freezing-point depressions at high pressures [23].

Furthermore, the magnitude and rate of pressure application influences the mechanism of lipid crystallization under pressure.

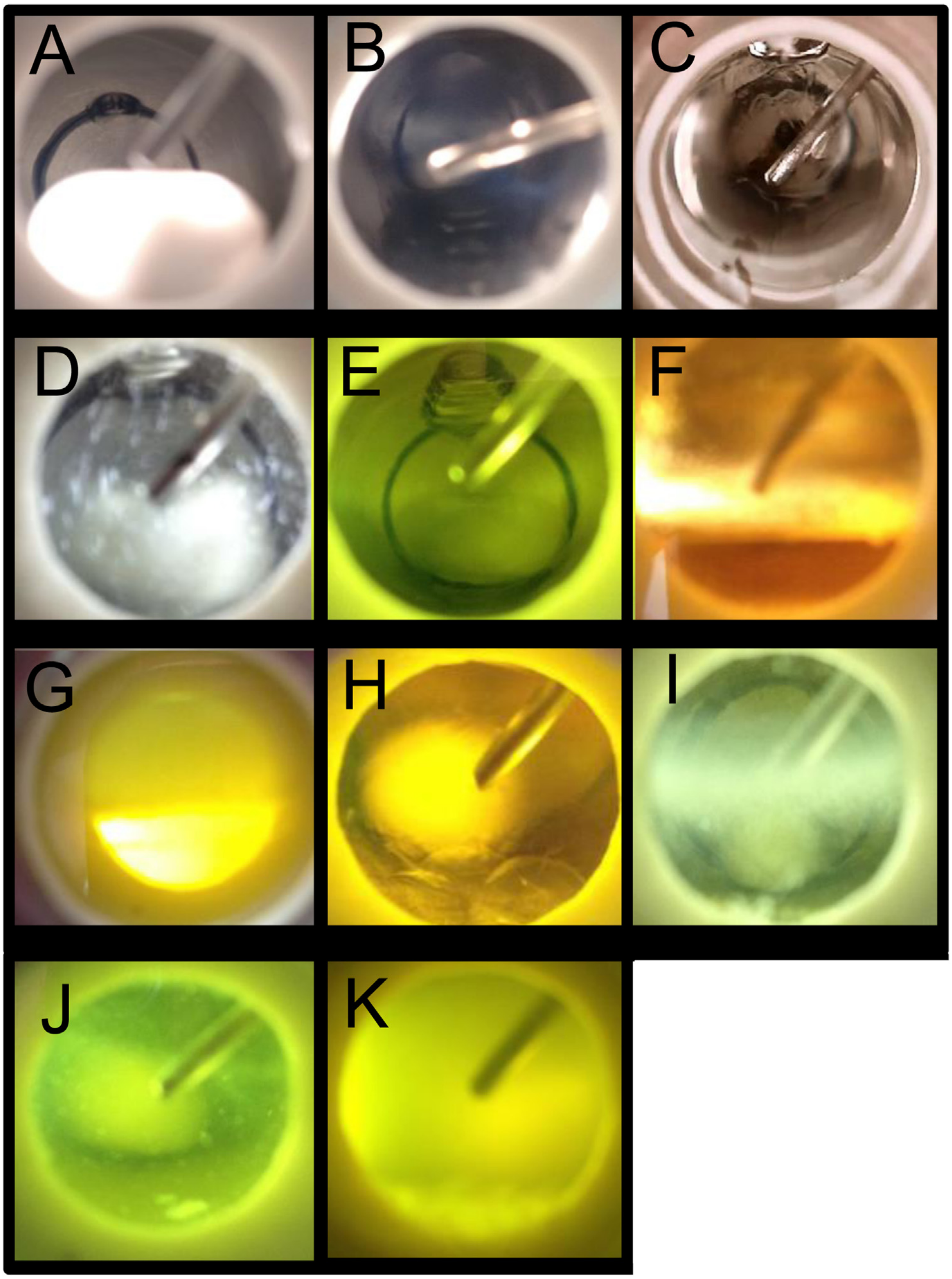


Fig. 3. High-pressure Phase equilibrium visualization of CO_2 (1) in the presence of dichloromethane (A), acetonitrile (B), EtOH (C), DMSO (D), LTO (E), HTO (F), EtOH (2)/LTO(3) (G), EtOH (2)/HTO(3) (H) (DMSO + PHT) (I), (DMSO + PHT) (2)/LTO(3) (J) and (DMSO + PHT) (1)/HTO (2) (K).

For example, high-pressure significantly alters interatomic distance between molecules thus influences physical or chemical reactions involving volumetric changes including phase transition reaction of lipids from liquid to solid. The equilibrium of the liquid state shifts toward the solid state and increases the melting temperature of lipids nonlinearly with pressure [34]. Vapor-liquid equilibria (VLE) was predominantly visualized on the system containing CO_2 (1)/EtOH (2), as observed in Table 6. The phase transition data were next to those obtained using a combination of the visual and the acoustic method [40].

Table 9 report VLE phase transitions for the binary CO_2 (1)/DMSO (2), which data were next from those obtained by Andreatta et al. [41] who measured phase equilibrium data for the same system using a Cailettet apparatus, which operates according to the synthetic method. Similar results were also registered for the ternary CO_2 (1)/DMSO (2)/EtOH (3) which data were obtained from an apparatus that employed the same experimental method used in this work [42].

The systems containing the pseudocomponent (DMSO+ PHT) exhibited SVLE behavior (Tables 10, 11 and 12) with presence of gelatinized particles (Fig. 3I, 3J and 3 K) which started to appear from the contact with CO_2 in the moment of feeding the equilibrium cell. This phenomenon shows that PHT solubilized in DMSO became insoluble in the presence of CO_2. In addition, PHT is a complex lignocellulosic biomass composed of 86.900% of carbohydrates, from which starch content was gelatinized induced by pressure increasing as the same way to those reported to the starches of potato [43], barley [44], corn, and wheat [45].

Besides the inclusion of turmeric extracts increased the pressure phase transition of the systems containing the compounds

CO_2 and (DMSO + PHT) (Tables 11 and 12) they contributed to difficult the visualization of phase transitions by causing large turbity in the systems attributed to the increasing of solid particles (Figs.3J and 3K.). A probable justification of this behavior is the formation of starch-lipid complexes that implied on the physical modification of the starchy structure of PHT that took place in the non-heterogeneous system. In addition, the literature reports that the relation of between DMSO and these compounds contributes for the increasing of complex indexes [46].

4. Conclusions

Turmeric is an important plant due to its wide range of application in food and non-food industry and much work has been performed with respect to the composition and promising applications of this material. The acquisition of reliable high-pressure phase equilibrium data is of interest in food and non-food purposes in terms of equipment design and selection of adequate conditions for separation processes.

In this work a synthetic-visual phase equilibrium apparatus was validated. In addition, we provided new phase equilibrium experimental results for systems containing waste and extracts from turmeric in the presence of carbon dioxide, ethanol and dimethylsulfoxide over the temperature ranging between 303 and 348 K and pressures above 4 MPa, with observed solid-vapor-liquid, solid-vapor-liquid-liquid, vapor–liquid, liquid–liquid and vapor–liquid–liquid phase transitions.

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- CAPÍTULO 8 –

Coprecipitation of turmeric extracts and polyethylene glycol with compressed carbon dioxide

Neste capítulo foi avaliada a qualidade dos coprecipitados de extratos de cúrcuma e polietilenoglicol, através do emprego dos solventes diclorometano e dimetilsulfóxido em presença do antisolvente CO_2 comprimido.

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Coprecipitation of turmeric extracts and polyethylene glycol with compressed carbon dioxide

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ABSTRACT

Low bioavailability and poor absorption of turmeric bioactives in human body limit their application. In order to propose products with improved stability we investigate the quality of coprecipitated microparticles of polyethyleneglycol (PEG) and turmeric extracts, which were obtained using dichloromethane (DCM) and dimethylsulfoxide (DMSO) as solvents and compressed carbon dioxide as antisolvent. The effects of pressure, antisolvent flow, concentration of extract and solvent proportion were investigated. The mean size of microparticles varied between 20.52 and 182.74 μm. Particle size distribution indicate irregularities that were confirmed by polydispersive index (PDI) values, and by the images obtained with scanning electron microscopy. The profile of bioactives was analyzed using two approaches, i.e., a qualitative (Thin-Layer Chromatography), which indicated weak presence and a quantitative (Antioxidant Activity), which indicated relevant contribution of these substances present in coprecipitates for the inhibition of β-carotene oxidation, besides evidence the efficiency of PEG as wall material.

Symbols

d_P	Mean particle diameter (μm)
OCY	Overall coprecipitation yield (%)
PDI	Polydipispersity index (–)
Q_{CO2}	Mass flow of carbon dioxide (kg/h)

1. Introduction

The expanding demand for natural bioactive constituents increased the optimization of separation technologies that maximize their usability. Global natural colorants consumption is projected to reach 40,500.00 metric tons by 2020 [1], while the global pharmaceutical excipients market is projected to reach US$ 8.1 billion in 2021 at a compound annual growth rate (CAGR) of 6.1% in the forecast period 2016–2021 [2].

Turmeric (*Curcuma longa* L.) and its commercial extracts are employed in a number of innovative products for food and non-food industries, due to the colorant power with antioxidant effects [3], followed by anticancer [4–6], anti-inflamatory [7] and antimicrobial [8] properties. The major biologically active components in turmeric are curcuminoids, which are yellow phenolic pigments, and volatile oil, an extract composed by turmerones and sesquiterpene alcohols [9–11].

Brazil has favorable conditions for turmeric cultivation and is considered the 14th producer of this crop worldwide [12]. The levels at dry basis of curcuminoid pigments in turmeric cultivated in Brazil ranged from 1.4 to 6.1 g/100 g, while the volatile oil fraction was between 1.0 and 7.6 mL/100 g [13]. Nevertheless, the poor absorption of bioactives from turmeric in human intestine [14], associated to the low water solubility and low bioavailability limit their wide application [15].

Supercritical and compressed fluids-based particle formation techniques have been successfully applied to enhance stability of these ingredients with the employment of biodegradable and biocompatible polymers as carrier agents, such as polyethylene glycol (PEG) [16], which have been widely studied for coprecipitation of extracts with relevant content of bioactives [17–20].

In this context, the goal of this work is to investigate the effects of process conditions on coprecipitation of turmeric extracts in PEG using compressed carbon dioxide as antisolvent with the purpose to provide stable substances for food and non-food applications.

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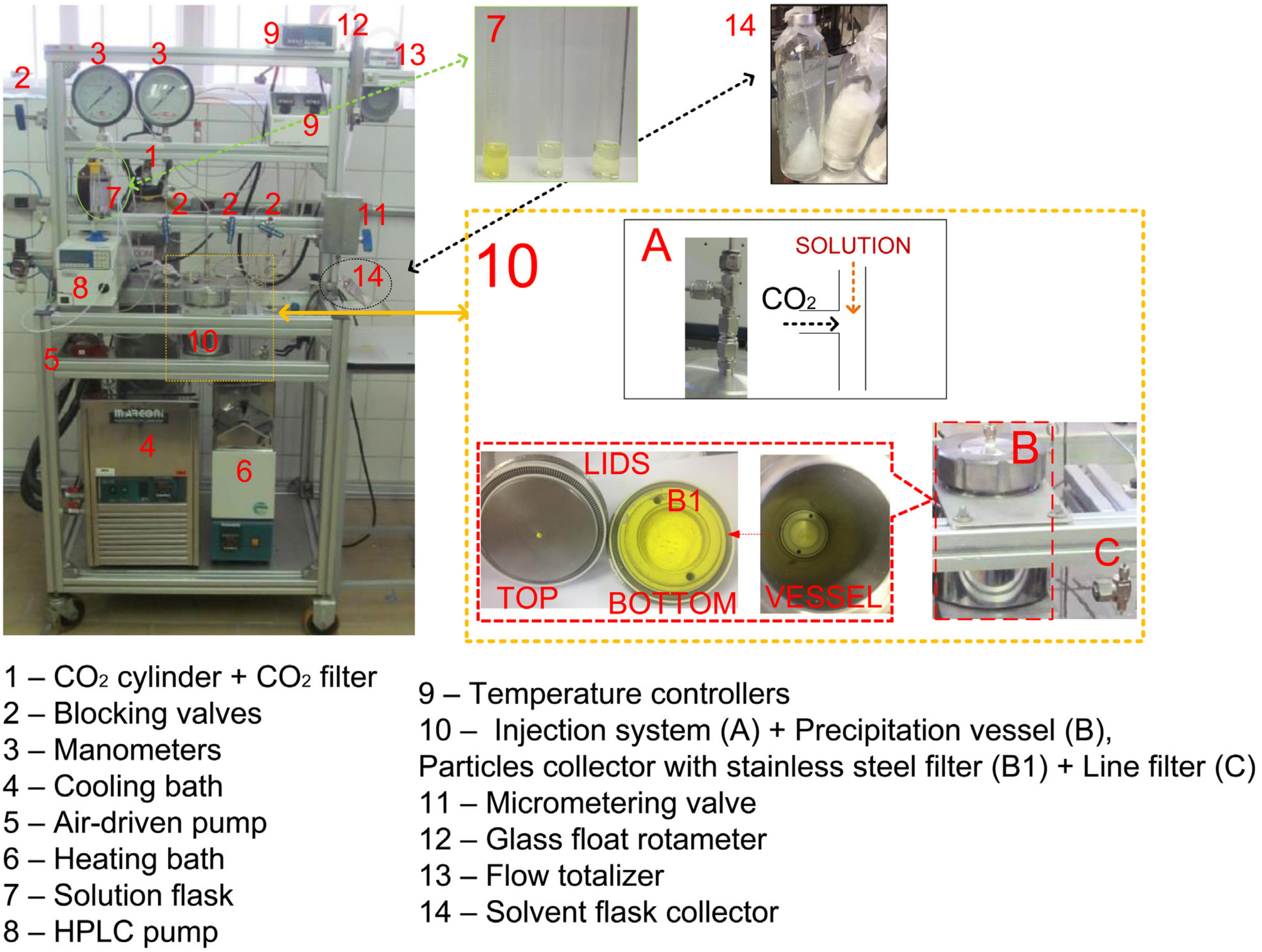

Fig. 1. Schematic diagram of apparatus used in this work.

2. Material and methods

2.1. Materials

Polyethylene glycol (PEG) with a mean molecular weight of 10,000 g/mol (Sigma–Aldrich, Darmstadt, Germany) was used as wall material. Turmeric extracts used in this work were: curcuminoids ethanolic extract (CEE), obtained using pressurized liquid ethanol at 333 K and 10 MPa [21] and turmeric volatile oils in light fraction (LTO) and heavy fraction (HTO), which were obtained using supercritical carbon dioxide at 333 K and 25 MPa [22].

Dichloromethane (DCM), purchased from Synth (99.9% pure, Diadema, Brazil), and dimethylsulfoxide (DMSO), obtained from Dinâmica (99.9% purity, Diadema, Brazil) were selected as solvents because both turmeric extracts and the PEG are soluble.

Carbon dioxide (99% purity) was purchased from White Martins (Campinas, Brazil). For the preparation of the bioactives solutions, PEG was diluted in the solvents until the concentration of 10 mg/mL. Turmeric extracts were diluted in the solution containing PEG until the concentrations of 1 mg/mL (ratio 1/10, w/w) and 5 mg/mL (ratio 5/10, w/w).

Table 1
Summary of operating conditions and experimental results.

Experiment	Substance (s)	Pressure (MPa)	Solvent	Q_{CO2} (kg/h)	OCY (%)	d_P (μm)	PDI (–)
1	PEG	8	DCM	0.5	30.05 ± 9	182.74 ± 1	1.66 ± 0
2	PEG	8	DCM	1	74.75 ± 5	127.51 ± 0	2.37 ± 0
3	PEG	10	DCM	1	74.73 ± 5	26.59 ± 0	3.70 ± 0
4	CEE/PEG (1/10, w/w)	10	DCM	1	70.42 ± 1	21.64 ± 0	3.16 ± 0
5	LTO/PEG (1/10, w/w)	10	DCM	1	59.61 ± 7	20.52 ± 0	3.70 ± 0
6	HTO/PEG (1/10, w/w)	10	DCM	1	55.45 ± 0	25.24 ± 0	3.80 ± 0
7	CEE/PEG (5/10, w/w)	10	DCM	1	52.68 ± 7	30.72 ± 0	3.06 ± 0
8	LTO/PEG (5/10, w/w)	10	DCM	1	50.06 ± 4	23.64 ± 0	2.98 ± 0
9	HTO/PEG (5/10, w/w)	10	DCM	1	51.67 ± 2	23.73 ± 0	2.74 ± 0
10	PEG	10	DCM/DMSO (50/50, v/v)	1	32.05 ± 3	32.98 ± 0	3.17 ± 0
11	PEG	10	DCM/DMSO (90/10, v/v)	1	57.30 ± 4	46.02 ± 1	3.73 ± 0
12	PEG	10	DCM/DMSO (10/90, v/v)	1	5.28 ± 1	*	*
13	PEG	10	DMSO	1	–	–	–

*Unavailability of sample.

2.2. Experimental

The coprecipitation experiments of PEG and turmeric extracts were performed in a homemade Supercritical Antisolvent (SAS) apparatus (Fig. 1) at 293 K employing dichloromethane (DCM) and dimethylsulfoxide (DMSO) as solvents and compressed carbon dioxide as antisolvent.

The temperature of 293 K was applied because of plasticization effects induced from the contact of the polymer with CO_2 at supercritical conditions, which did not yielded precipitated particles, but the formation of a film that caused clogging in the pipes and the line filter, which would result in serious damages to the solvent injection system. Similar behavior was reported elsewhere with PEG (molecular weight of 20,000 g/mol), in which a film of polymer covered the filter and the walls of the precipitation vessel at typical conditions for SAS processes of 10 MPa and 313 K [17].

In addition to PEG, modified corn starch (Hi-cap 100, DBI-6644, Ingredion, Mogi-Guaçu, Brazil) was tested in preliminary assays. Because of the natural phenomenon of gelatinization of the starch granules caused by the increase in temperature or pressure, problems with clogging were predominant and there was no particle formation.

At first, a cooling bath (MA-184, Marconi, Piracicaba, Brazil) was used to ensure the liquefaction of gas CO_2 from the cylinder. Afterward, liquid CO_2 was pumped until the desired pressure with the aid of an air-driven liquid pump (Maximator, PP 111, Zorge, Germany), and heated to 293 K using a heating bath (MA-126, Marconi, Piracicaba, Brazil), before inserting into the precipitation vessel (500 mL, 6.8 cm inner diameter). The precipitation vessel was fitted with an electric heating jacket (Autic, Campinas, Brazil). The desired conditions of pressure, temperature and CO_2 flow rate were achieved and stabilized by holding them constant for 10 min.

Then, the solution containing polymer was introduced into the precipitation vessel with the aid of a high-performance liquid chromatography (HPLC) pump (Jasco, PU-2080, Japan) at a constant flow rate of 1 mL/min for 20 min.

When the desired amount (20 mL) of solution has been injected, which enabled the collection of sufficient amount of precipitated particles for analysis, the HPLC pump was stopped and only pure CO_2 was injected into the precipitation vessel at constant flow rate during 15 min for the complete drying of particles, with subsequent removal of the solvent from the precipitation vessel.

The injection system is composed of a T-mixer nozzle (Fig. 1.10.A), which is a 1/8 in. tube (inner diameter of 3.17 mm), through which the solution and the CO_2 entered simultaneously. The particles were collected using a stainless steel porous filter (AISE, 316, screen size of 2 μm) fixed at the bottom of the precipitation vessel, followed by a line filter (Fig. 1.10.C) used to retain part of the solids that were not precipitated.

The CO_2 flow rate was measured using a glass float rotameter (16/286A/2, ABB, Warminster, USA), coupled with a flow totalizer (LAO, G0. 6, Osasco, Brazil).

The effluent solvent was recovered in a 100 mL glass flask collector (Fig. 1.14) connected to a micrometering valve. This valve was

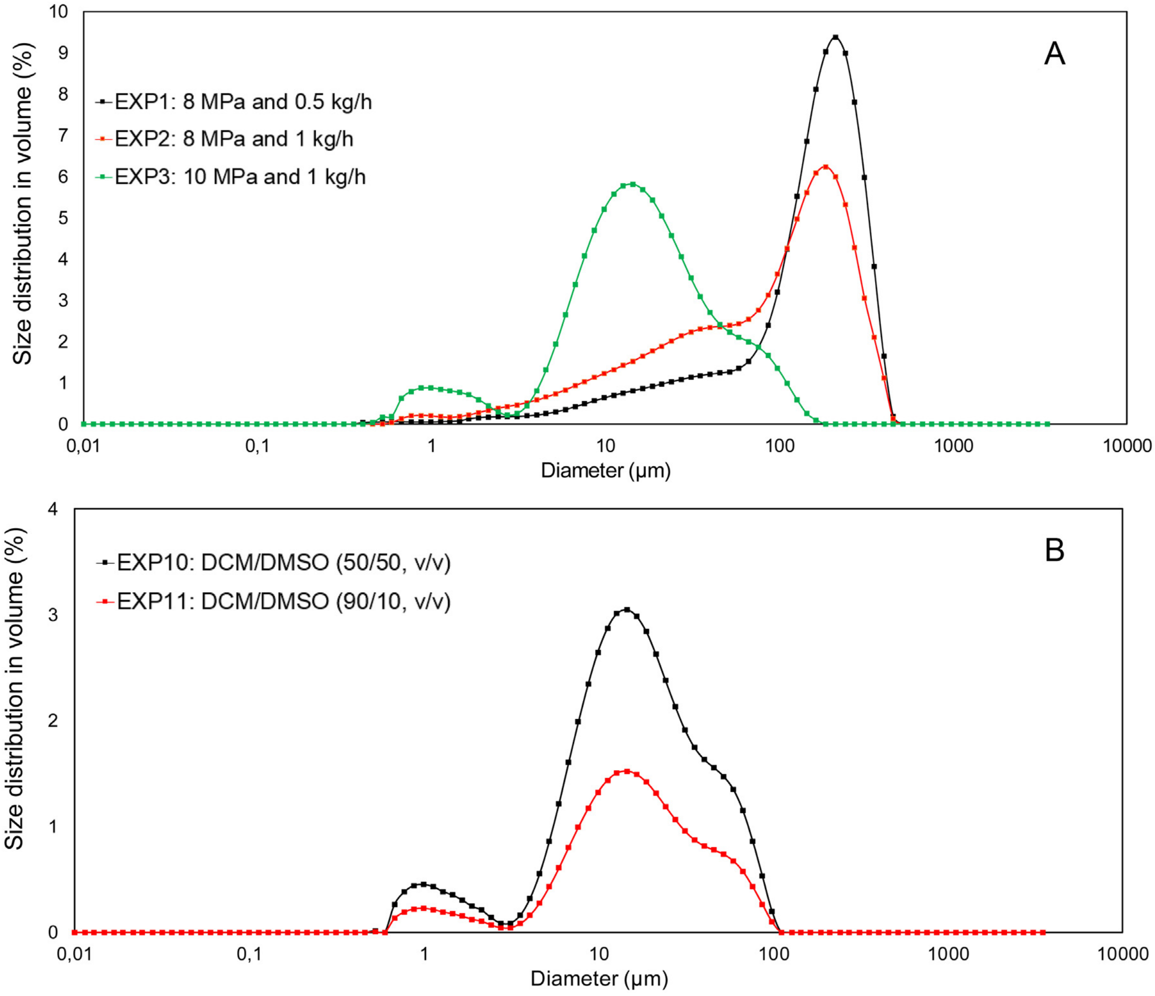

Fig. 2. Particle size distribution of PEG coprecipitates: influence of pressure and antisolvent flow (A), and influence of solvent (B).

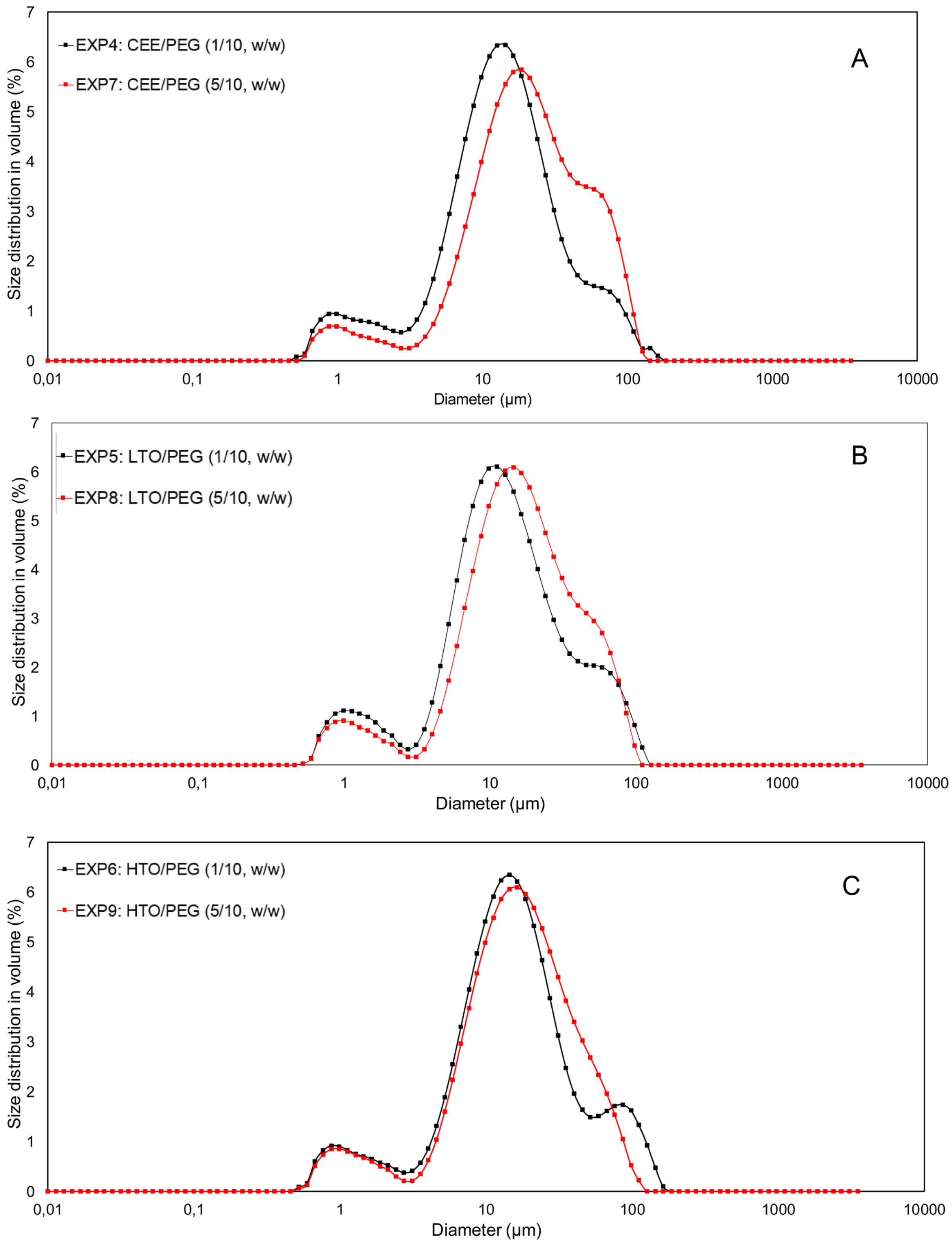

Fig. 3. Particle size distribution of PEG and turmeric extracts coprecipitates: CEE (A), LTO (B) and HTO (C).

maintained at 393 K to avoid freezing and subsequent blocking of the outlet caused by the Joule–Thompson effect, attributed to the expansion of CO_2.

Finally, the precipitation vessel was slowly depressurized until atmospheric pressure, and the particles were carefully collected with a soft brush and were stored at 275 K in the dark, until further analysis.

2.3. Particle characterization

2.3.1. Overall coprecipitation yield

The overall coprecipitation yield (OCY) or global yield of solids (%) was calculated using the following equation.

$$OCY(\%) = \left(\frac{W_{CP}}{W_T}\right) \times 100 \quad (1)$$

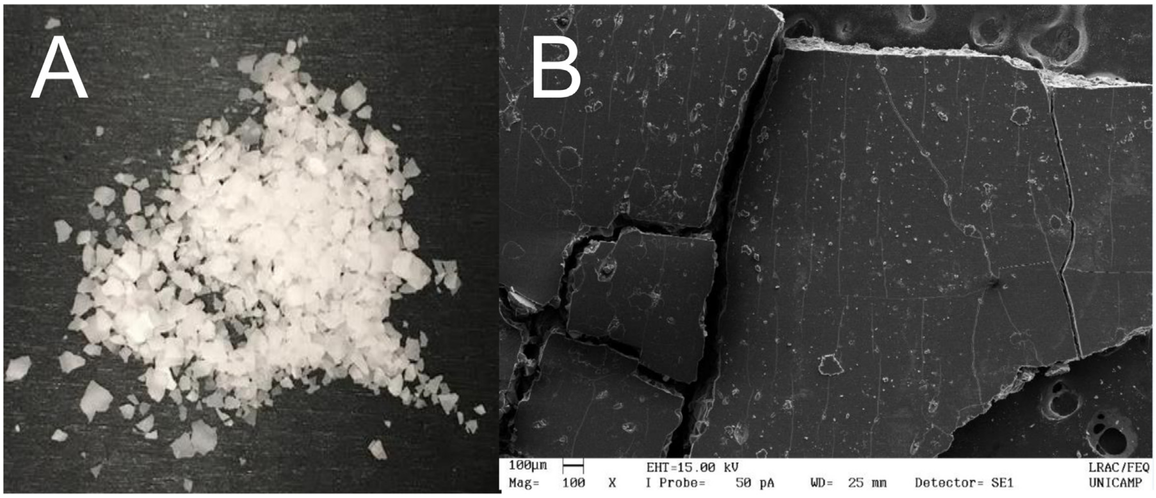

Fig. 4. Crude PEG (A) and the subsequent SEM image (B).

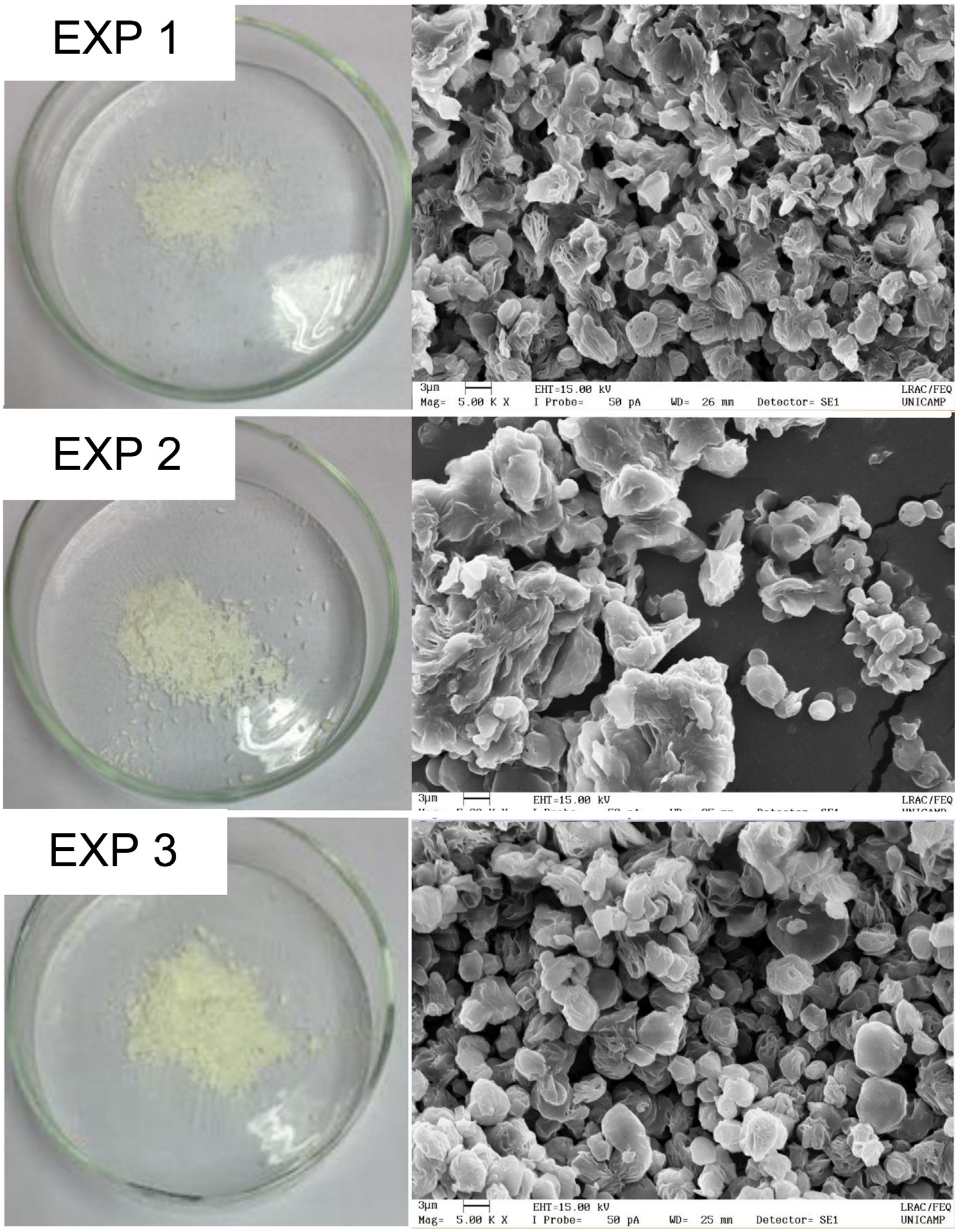

Fig. 5. PEG precipitates and the subsequent SEM images: influence of pressure and antisolvent flow.

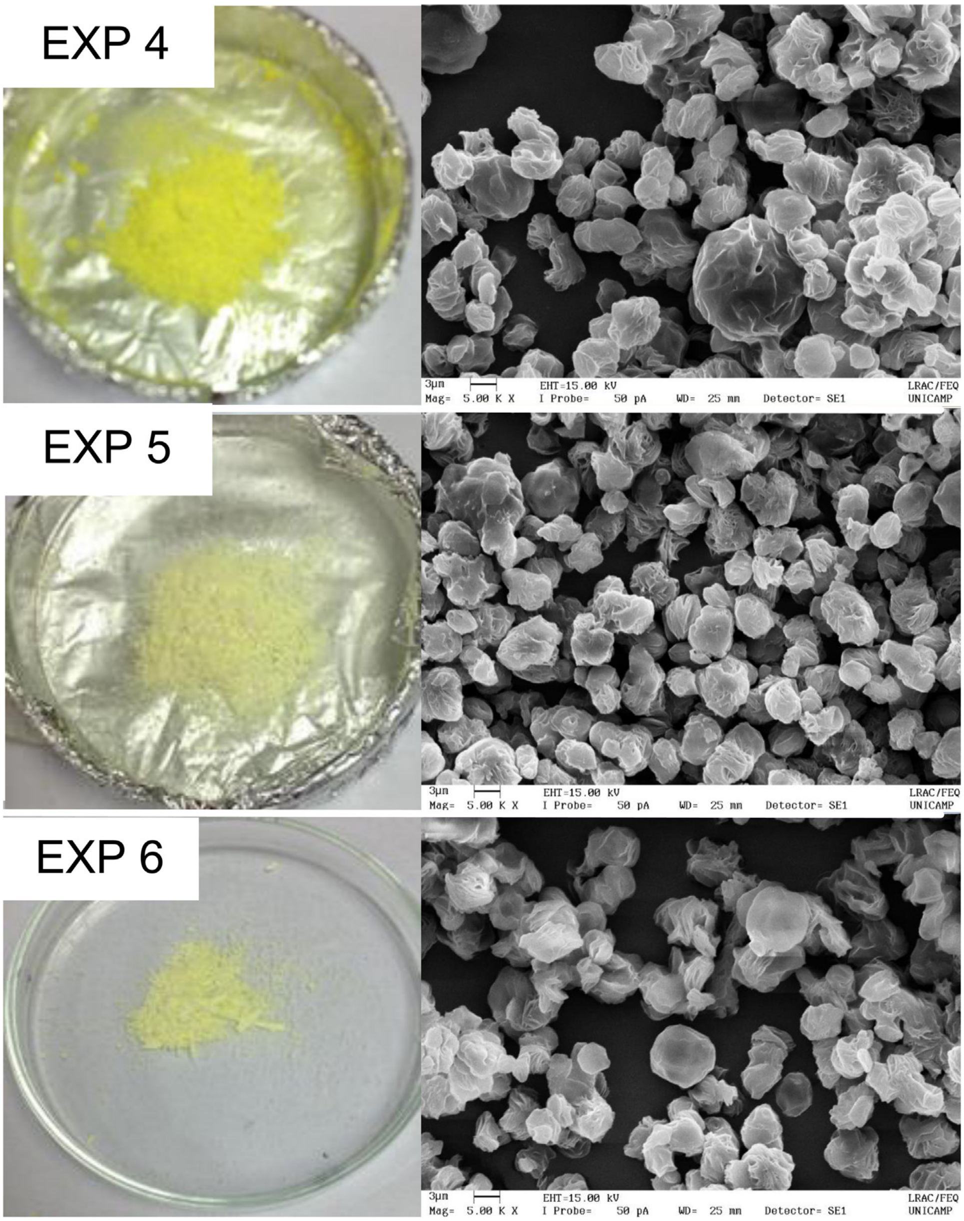

Fig. 6. PEG and turmeric extracts coprecipitates and the subsequent SEM images at 1/10 (w/w) ratio.

Where W_{CP} = weight of coprecipitated particles (mg), W_T = Theorical content of polymer and extract from the bioactives solution (mg).

2.3.2. Polydispersity index

Dimensionless polydispersity index (PDI) was calculated as follows:

$$PDI = \frac{d_{90} - d_{10}}{d_{50}} \quad (2)$$

Where d_{10}, d_{50} and d_{90} are the particle diameters at the 10th, 50th and 90th percentile of particles undersized, respectively.

2.3.3. Particle size distribution

Size distribution and mean diameter (d_P) of particles were determined by light scattering technique using laser diffraction (Mastersizer 3000, MAZ3000, Malvern Instruments, Worcesteshire, United Kingdom). The samples were analyzed by wet method, with dispersion in ethanol under 3500 rpm using ultrasound at 40 kHz for 1 min. Particle size distribution was calculated using the theory of Mie [23], assuming a volume equivalent sphere model.

2.3.4. Scanning electron microscopy

Scanning Electron Microscopy (SEM) was applied to examine the structure of the particles. The samples were applied on circular aluminum stubs with double carbon sticky tape and coated with 200 Å of gold on the Sputter Coater (EMITECH, K450, Kent, United Kingdom). The micrographies were obtained using a scanning electron microscope (Leo 440i, Cambridge, England), accelerating potential of 15 kV, and current of 50 pA.

2.3.5. Thin-layer chromatography

Thin layer chromatography (TLC) was performed using silica gel plates with aluminum backs (Alugram®, Xtra SIL G, Macherey-Nagel, Germany) as stationary phase. The mobile was composed by chloroform (Merck, Darmstadt, Germany), ethanol (Chemco, Hortolandia, Brazil) and glacial acetic acid (Synth, Diadema, Brazil), in the proportion of 95/05/01, v/v/v [24].

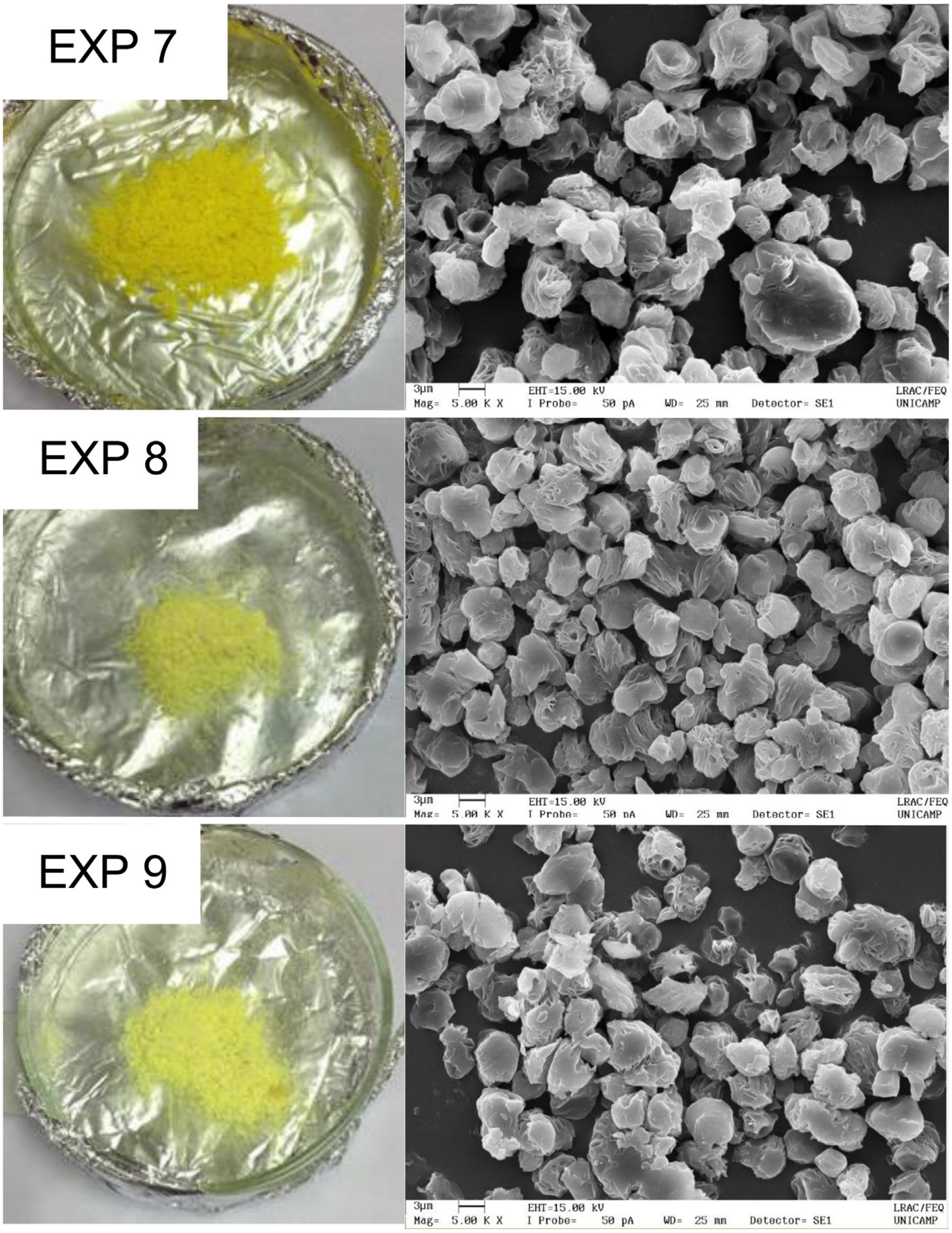

Fig. 7. PEG and turmeric extracts coprecipitates and the subsequent SEM images at 5/10 (w/w) ratio.

The bands of compounds generated by the constituents that could not be detected in the visible region were visualized using a UV lamp (Multiband UV – 254–366 nm, UVGL-58, Mineralight® Lamp, Upland, CA, USA) equipped with a cabinet (UVP-Chromato-VUE, CC-10, Upland, CA, USA), in which long wavelength (366 nm) was adopted.

The *p*-anisaldehyde (Sigma-Aldrich, Darmstadt, Germany) and sulfuric acid (Exodo, Hortolandia, Brazil) were used to formulate the *p*-anisaldehyde-sulfuric acid spray reagent [25] with the aim to identify the compounds of interest. In order to facilitate the identification of the probable constituents, the standards ar-turmerone, curcumin (≥94% curcuminoids; ≥80% curcumin), demethoxycurcumin and bisdemethoxycurcumin (Sigma-Aldrich, Darmstadt, Germany) were used.

2.3.6. Antioxidant activity

The antioxidant activity (AA) of coprecipitated turmeric extracts was investigated through behavior of the coupled reaction of linoleic acid and β-carotene, according to the methodology of Marco [26], followed by adaptations of Miller [27], and Leal et al. [28]. Antioxidant activity was calculated using Eq. (3), as proposed elsewhere [29].

$$AA(\%) = 100 \times \left\{ 1 - \left[\frac{\left(ABS^{t=0}_{SAMPLE} - ABS^{t}_{SAMPLE}\right)}{\left(ABS^{t=0}_{CONTROL} - ABS^{t}_{CONTROL}\right)} \right] \right\} \qquad (3)$$

Where AA is antioxidant activity, $ABS^{t=0}_{SAMPLE}$ is the absorbance of the sample at t = 0 h, $ABS^{t=0}_{CONTROL}$ is the absorbance of control sample at t = 0 min, ABS^{t}_{SAMPLE} is the absorbance of the sample at t = 1 h, t = 2 h and t = 3 h, and $ABS^{t}_{CONTROL}$ is the absorbance of control sample at t = 1 h, t = 2 h and t = 3 h.

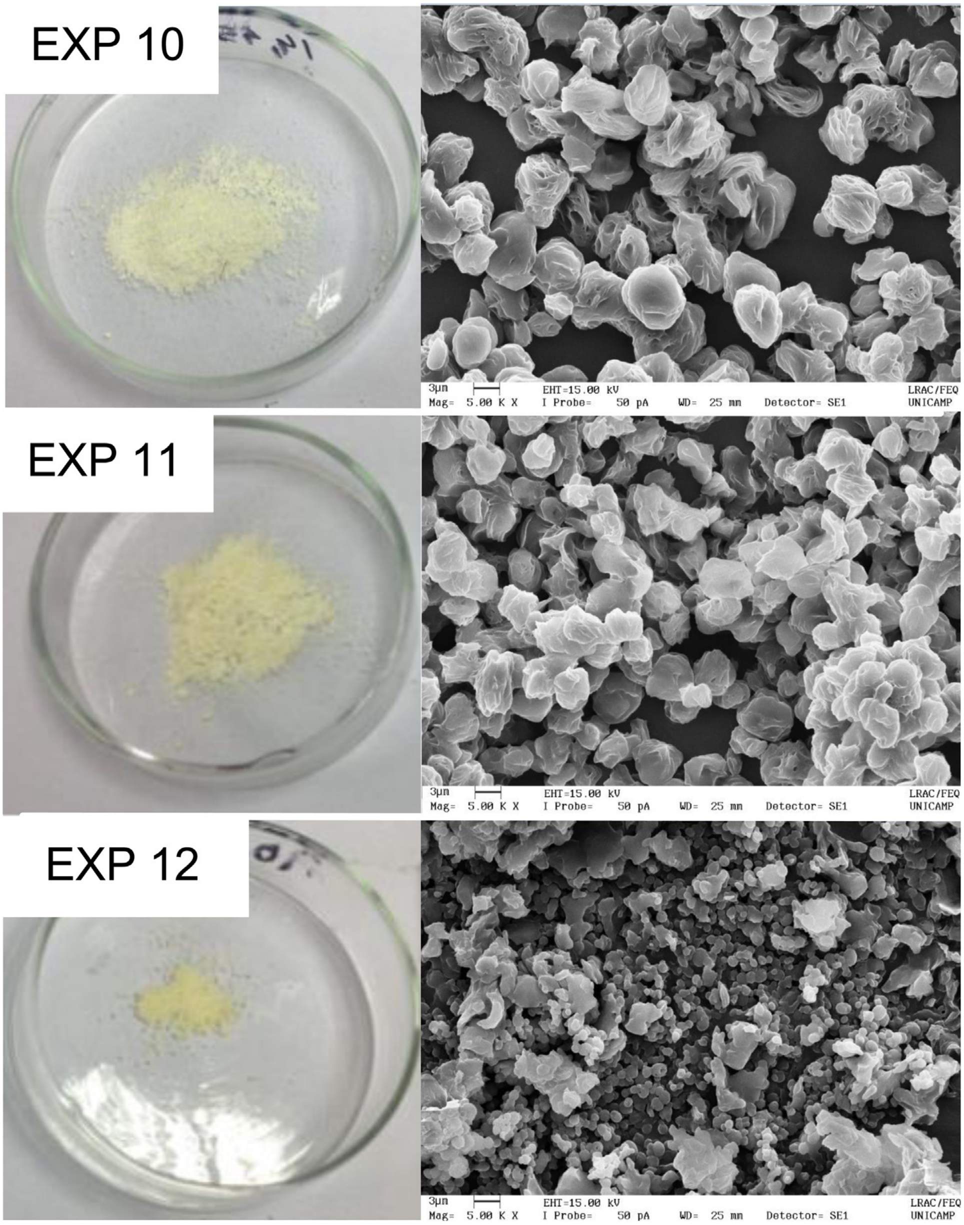

Fig. 8. PEG precipitates and the subsequent SEM images: influence of solvent.

3. Results and discussion

3.1. Overall coprecipitation yield and particle size distribution

Particles of PEG and turmeric extracts were successfully obtained, except in the presence of pure DMSO (Table 1).

The experimental assays resulted on particles with sizes between 20.52 and 182.74 μm, which were higher than coprecipitates of ampicillin and ethyl cellulose (1–3 μm) [30], lutein and poly-lactic acid (5–10 μm) [31], lower than rosemary (>200 μm) precipitates [32], and comparable to curcuminoids (111–840 μm) [33] and onion peels (119–234 μm) [34] precipitated particles.

Process performed on experiments 1–3 were conducted to analyze the effect of pressure and CO_2 flow. It is noted that an increase of CO_2 flow from the experiment 1 to the experiment 2 contributed to the decreasing of particle diameter, similarly to those reported to DLBS2347 microparticles [35] and differently as found to coprecipitates of paclitaxel and poly(L-lactic acid). Nevertheless the increasing of CO_2 flow contributed to the increasing of OCY from 31.97 to 74.75%, which value is comparable to the 70.3% obtained for medroxyprogesterone particles [36].

Particle diameter decreased with the pressure increased, while the overall coprecipitation yield was not modified (Table 1), differently to that reported for the precipitation of curcuminoids extracts, which increasing of pressure decreased the OCY, besides of the decreasing of particle diameter [33].

The effects of mass ratio between turmeric extracts and PEG on coprecipitation process were evaluated on experiments 4–9. The increase in concentration of solute resulted on the increasing in mean particle diameter in approximately 42% for CEE and 15% for LTO respectively, which corroborates to that related to the d_P of lycopene particles [37]. However, a slight decrease in mean particle of 6% occurred with the increase of HTO concentration.

Process run from experiments 10, 11, and 12 were conducted to investigate the effect of solvent. The increasing in DMSO proportion contributed to the increasing in the particle diameter, similarly to those related to the coprecipitation of paclitaxel and poly(L-lactic acid) at 308 K and 12 MPa from DCM/DMSO solutions [38], and to

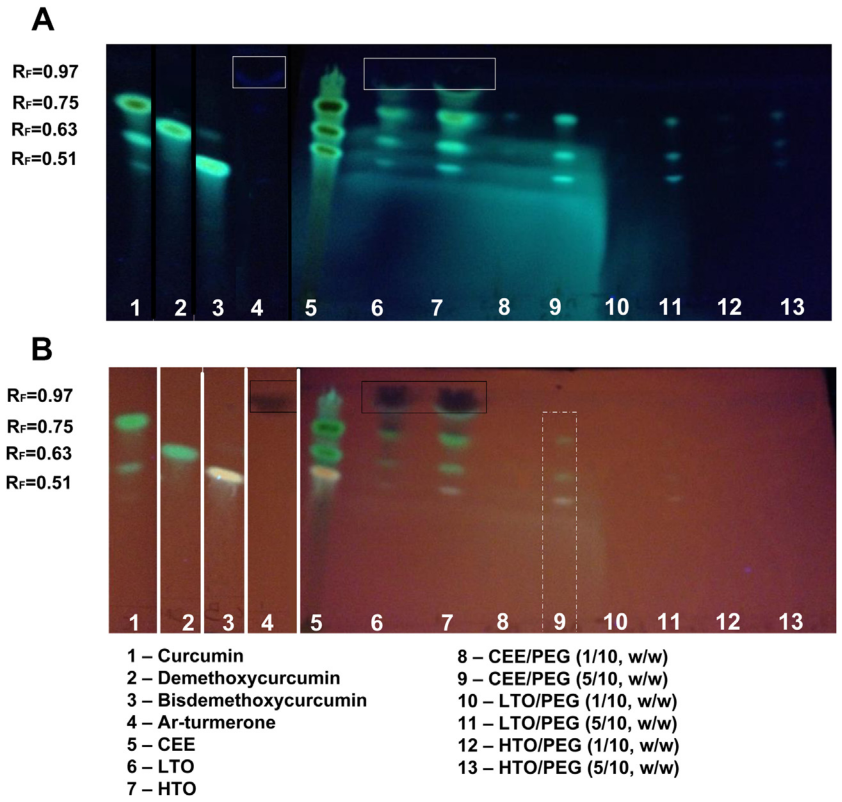

Fig. 9. Thin-layer chromatography profile of turmeric crude extracts and coprecipitates: without spray reagent (A) and after spraying with *p*-anisaldehyde-sulfuric acid reagent (B) at 366 nm.

the precipitation of polyvinylpyrrolidone (PVP) particles at 313 K and 10 MPa from acetone/DMSO solutions [39]. Nevertheless, the particle size obtained in this work using DCM/DMSO (10/90, v/v) solution is approximately 54–164 times higher than those obtained in the previously cited works [38,39]. In case of supercritical conditions for the antisolvent, precipitation occurs very fast, and much smaller particles can be obtained [40].

In addition, the increase of DMSO decrease the OCY, similarly as reported to the coprecipitates of amoxicillin and ethyl cellulose from a DCM/DMSO (85/15, v/v) solution with antisolvent CO_2 in supercritical conditions of 308 K and 10 MPa [30].

The poor solubility of DMSO in compressed CO_2 at 293 K [41], increased mass transfer resistance between solvent and antisolvent. As consequence, the supersaturation of the solutes is reached slowly, resulting in the formation of large particles, and the entrainment of a part of the polymer together with the effluent solution that leaves the precipitation vessel.

Low polydispersity index (PDI), i.e., below 2, indicate narrow and uniform distribution of particles [42]. In this work most of PDI values were higher than 2 (Table 1), which is evidenced by size distribution plotting (Figs. 2–3), wherein the majority of microparticles have irregular distribution, except for those obtained at 8 MPa and Q_{CO2} = 0.5 kg/h that showed narrow distribution (Fig. 2.A, EXP 1). Similar behavior was found for the precipitates of poly(lactic acid) [43], onion peels [34], and curcuminoids [21].

3.2. Scanning electron microscopy

Crude PEG used in this work is composed by large blocks with crystalline structure (Fig. 4). Coprecipitation of PEG with compressed carbon dioxide resulted on the formation of varied types

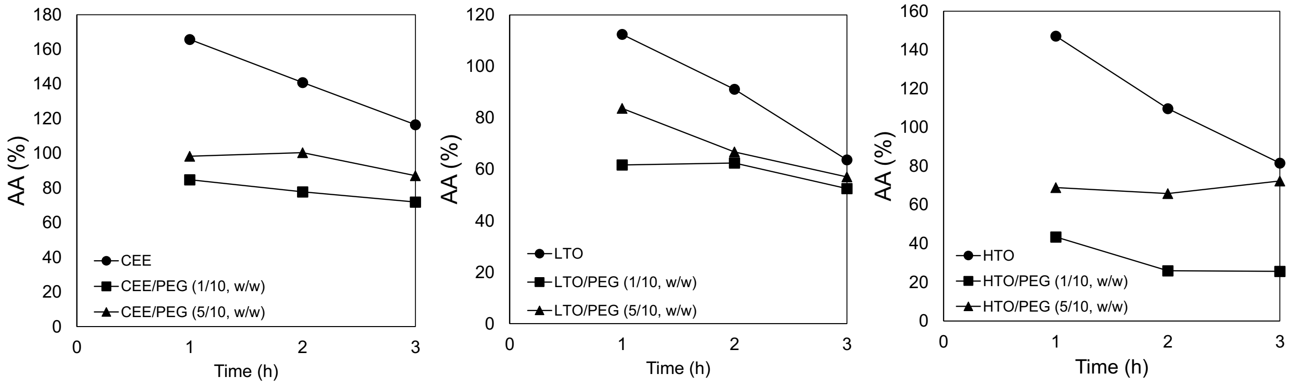

Fig. 10. Antioxidant activity of crude turmeric extracts and coprecipitates: CEE (A), LTO (B), and HTO (C).

of particles, ranging from spherical morphology to irregular blocks of aggregates (Figs. 5–8).

Particles with high aggregation and irregular shape were obtained from the experiments performed at 8 MPa (Fig. 5EXP1 and EXP2) because at low pressures mass transfer is low, and consequently particles are not dried fast enough and tend to aggregate during the precipitation. However, at 10 MPa and 1 kg/h, well separated and spherical particles are observed (Fig. 5.EXP3).

Although visible differences related to the mass ratio variation were not detected in the coprecipitated extracts (Figs. 6–7), SEM images show that a decrease in the mass ratio between core material and wall material, i.e., an increase in the polymer concentration, led to the production of less agglomerated spherical particles, as can be observed in Fig. 6 (EXP4, EXP5 and EXP6). The high agglomeration with partial loss of spherical shape from the microparticles obtained at mass ratio of 5/10 (w/w) occurred probably because the amount of polymer was not sufficient to effectively cover the amount of extract (Fig. 7.EXP7, EXP8 and EXP9).

In addition to contributing to the reduction of OCY, the increasing of DMSO proportion increased the aggregation of particles, with subsequent formation of irregular non-spherical blocks (Fig. 8.EXP10, EXP11, and EXP12). High viscosity of DMSO, associated to differences in volatility between DCM (313 K) and DMSO (464 K) makes the mass transfer more difficult and produces these kind of particles [38].

3.3. *Thin-layer chromatography*

The curcuminoids belong to a class of phenolic compounds that produce fluorescent yellow-green spots under UV before and after detection with spray reagent [44] which are clearly visualized on the crude extracts at R_F ranging between 0.51–0.75 (Fig. 9).

A prominent sesquiterpene zone is evidenced in the ar-turmerone standard, and in the extracts HTO and LTO at the solvent front in the $R_F = 0.97$ (Fig. 9), similarly as reported elsewhere for turmeric volatile oil after spraying with vanillin-sulfuric acid reagent [45]. The qualitative presence of volatile oil constituents in terms of ar-turmerone, was not detected in the coprecipitated extracts. Considering the coprecipitated extracts, only CEE (5/10, w/w) presented positive response with respect to the presence of bioactive compounds, in terms of curcuminoids (Fig. 9.B).

3.4. *Antioxidant activity*

Antioxidants play an important role in food preservation by inhibiting oxidation processes and contributing to health promotion rendered by many dietary supplements, nutraceuticals and functional food ingredients [46].

Although TLC has not demonstrated relevance in terms of presence of bioactive compounds in the coprecipitated extracts, AA show that these products have a sufficient content of these compounds for the inhibition of β-carotene oxidation (Fig. 10).

Depending on hours of reaction, there was a considerable AA reduction in turmeric crude extracts. Nevertheless, AA of coprecipitated extracts remained stable, suggesting that PEG is a potential protective carrier for turmeric extracts.

4. Conclusions

Microparticles are extensively used for industrial purposes and the coprecipitation of turmeric extracts and PEG is a promising alternative to provide stable products with functional application. The variation of pressure, antisolvent flow, concentration of extract and solvent ratio promote relevant changes in particle properties, resulting in products with irregular distribution and variations in overall coprecipitation yield and particle size.

Thin-layer chromatography of coprecipitated extracts showed very weak presence of bioactive compounds, while antioxidant activity demonstrated the presence of these substances for the inhibition of β-carotene oxidation. In addition, the stable values of AA on the coprecipitated extracts are attributed to efficient performance of the PEG as wall material.

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- CAPÍTULO 9 –

Discussão geral

DISCUSSÃO GERAL

Uma breve contextualização das temáticas que englobam esta tese foi abordada no **Capítulo 1**. Inicialmente foi exposto o cenário de produção e aplicação dos produtos derivados dos rizomas de cúrcuma e a problemática dos rejeitos sólidos, gerados após os processos de extração de óleos voláteis e curcuminóides. Em seguida, foram mostradas tecnologias de extração SFE e PLE e de formação de partículas como alternativas limpas para obtenção de produtos com maior qualidade e valor agregado em termos de compostos bioativos. Também foi abordada a importância do estudo do comportamento de fases a altas pressões aplicados a substâncias de interesse para indústria.

De acordo com o levantamento bibliográfico apresentado no **Capítulo 2**, a aplicação de novos amidos, ou amidos oriundos de matérias-primas não convencionais, é uma tendência para indústria alimentícia e não alimentícia, seja na sua forma integral, seja como complemento às fontes convencionais. A utilização matérias-primas amiláceas que são constituídas de cor, aroma e substâncias com poder antioxidante, tais como a cúrcuma e o urucum são fatores que podem agregar valor em formulação de novos produtos em que essas características são desejáveis.

O **Capítulo 2** serviu como alicerce para o **Capítulo 5**, que avalia a influência dos processos de separação SFE e PLE na recuperação dos rejeitos de cúrcuma dos processos SFE e PLE no que diz respeito à qualidade deste material e avaliação econômica do aproveitamento da matriz amilácea. Os processos SFE e PLE contribuíram para a modificação física da estrutura do amido, resultando em grânulos ásperos e resistentes à deformação, além do aumento da disponibilidade dos grânulos, cuja parte foi perdida durante as etapas de lavagem realizadas no procedimento de isolamento. O baixo rendimento em amido isolado se deve às características intrínsecas da matéria-prima, cujas condições de cultivo não foram divulgadas pelo fornecedor. A análise econômica do aproveitamento dos resíduos de extração sob a forma de amido isolado foi avaliada sobre duas perspectivas relacionadas ao rendimento em produto final obtido nesta tese (3,33%), em comparação aos 80% que se tem registrado na literatura. Obviamente em função do baixo rendimento (3,33%) em produto final, o processo para o aproveitamento da fração amilácea do rejeito de cúrcuma não é viável, visto que essa variável é a que mais interfere no preço do produto final.

Hidrólise parcial com uso de água pressurizada foi aplicada aos rejeitos de cúrcuma como uma forma de aproveitamento dessas matrizes vegetais. No caso dos **Capítulos 3 e 4**, a hidrólise parcial resultou na recuperação de compostos bioativos a partir da obtenção de dois produtos: um biopolímero misto, composto de amido e curcuminóides e um extrato líquido com curcuminóides e oligômeros de açúcar. No **Capítulo 3**, os carboidratos e curcuminóides (polifenois) foram caracterizados por uma abordagem qualitativa (cromatografia de camada delgada) e no **Capítulo 4**, por uma abordagem quantitativa (análises cromatográficas e espectrofotométricas). A maior parte dos resultados gerados pelas metodologias quantitativas não detectou influência das variáveis temperatura e pressão nos produtos obtidos (**Capítulo 4**), ao contrário da abordagem qualitativa (**Capítulo 3**), em que se percebeu claramente a influência do aumento da temperatura na alteração da qualidade das bandas de compostos emitidas.

As informações contidas no **Capítulo 6** concedem a noção da variedade de técnicas experimentais utilizadas para se avaliar o comportamento de fases a altas pressões nos mais variados tipos de sistemas que contemplam substâncias de interesse no setor alimentício. Essas técnicas são importantes por conceder um conjunto de dados teóricos que podem ser utilizados para posteriores etapas de separação.

O **Capítulo 7** aborda a validação de um aparato experimental que emprega a metodologia sintético-visual para aquisição de dados inéditos do comportamento de fases de sistemas que contemplam os óleos voláteis e o resíduo parcialmente hidrolisado de cúrcuma diante de CO_2, etanol e dimetilsulfóxido. O comportamento gerado por esses sistemas foi complexo, caracterizado por cinco tipos de transição de fases observadas. Tal comportamento se deve à natureza multicomponente dos produtos derivados de cúrcuma, cuja interação com os solventes estudados resultou nos mais variados tipos de comportamento, que contemplam o aparecimento de espumas, bolhas, e partículas sólidas gelatinizadas.

Ensaios de coprecipitação dos extratos de cúrcuma (óleos voláteis e curcuminóides) diante de CO_2 comprimido e o impacto das condições de processo na qualidade dos produtos finais foram realizados no **Capítulo 8**. Extratos coprecipitados que tiveram maior proporção do material de parede (polietilenoglicol) na solução formulada apresentaram menos agregação do que os que tiveram menor a proporção do polímero. O perfil de compostos bioativos (curcuminóides e ar-turmerona) nos extratos e nos produtos coprecipitados foram avaliados qualitativamente por cromatografia de camada delgada. Apenas na região de ultravioleta a 366 nm, com ausência de solução reveladora foi possível identificar com clareza a presença destes compostos nos produtos. Após inserção do revelador p-anisaldeído as bandas de compostos emitidas pelos coprecipitados foram ofuscadas. Os resultados mostrados pela cinética de degradação do beta-caroteno (expressos em atividade antioxidante) sugere que os compostos bioativos contidos nos coprecipitados possuem ação relevante no que diz respeito ao impedimento da degradação do beta-caroteno. Além disso, durante a cinética de 3 horas os coprecipitados mostraram comportamento estável, o que revela a eficácia do polietilenoglicol como material de parede.

- CAPÍTULO 10 –

Conclusões gerais e sugestões para trabalhos futuros

CONCLUSÕES GERAIS

O primeiro capítulo desta tese mostrou o cenário promissor do uso de tecnologias limpas para obtenção de extratos naturais visando o aproveitamento dos resíduos gerados por esses processos com o objetivo de recuperar compostos bioativos que seriam descartados visando a aquisição de novos produtos de competitividade comercial.

O **Capítulo 2** abordou uma revisão das propriedades, aplicações e perspectivas relacionadas às fontes não convencionais de amido.

A composição química dos produtos dos rejeitos de cúrcuma pós-hidrólise parcial foi estudada no **Capítulo 3** a partir de uma abordagem qualitativa, por cromatografia de camada delgada. Os resultados mostram que esses produtos possuem compostos bioativos que lhe conferem valor agregado, além de mostrar claramente a influência da temperatura de reação na qualidade dos extratos e dos rejeitos sólidos.

No **Capítulo 4** foi investigada a influência das condições de processo na hidrólise parcial nos rejeitos de cúrcuma e nos extratos com o objetivo de se obter compostos bioativos de valor agregado a partir de uma matriz residual. Além disso, foi mostrada que esse processo é economicamente viável por causa do baixo gasto de energia e materiais.

No **Capítulo 5** foi estudada a aplicação das tecnologias de fluido supercrítico e de líquidos pressurizados aplicadas aos rejeitos de cúrcuma visando a agregação de valor destes materiais para a recuperação de amido e curcuminóides, para ser usado como fonte complementar às matérias-primas amiláceas convencionais, como o milho e o arroz. Na primeira parte do trabalho foi verificado que os solventes dióxido de carbono supercrítico e etanol pressurizado contribuíram para o aumento da disponibilidade, com subsequente modificação física dos grânulos de amido presente nos resíduos, que resultaram em grânulos enrijecidos e resistentes a deformações. Na segunda parte do trabalho, a avaliação econômica para a recuperação de amido em larga escala é considerado viável apenas para um cenário de 80% de amido recuperado.

Técnicas experimentais usadas para a aquisição de dados de equilíbrio de fases em sistemas que envolvem substâncias de interesse para indústria de alimentos foram evidenciadas no **Capítulo 6.**

A construção e validação de um aparato experimental e aquisição de dados a altas pressões de sistemas envolvendo óleos voláteis e o resíduo parcialmente hidrolisado de cúrcuma na presença de CO_2, etanol e dimetilsulfóxido foram avaliados no **Capítulo 7**. Os resultados indicaram existência de comportamentos complexos com ocorrência de vários tipos de transições de fase: equilíbrios sólido-líquido-vapor, sólido-líquido-líquido-vapor, líquido-vapor, líquido-líquido-vapor e líquido-líquido.

Ensaios de coprecipitação dos extratos de cúrcuma e polietilenoglicol com uso de CO_2 comprimido como antisolvente foram realizados no **Capítulo 8** com o objetivo de se obter compostos bioativos com maior estabilidade. Diferentes solventes e condições de temperatura, pressão e vazão de antisolvente contribuíram para a formação de partículas de distribuição irregular, diâmetros e estado de agregação diversificados.

Por fim, esta tese cumpriu com os objetivos propostos no que diz respeito em propor alternativas sustentáveis para o valorização dos rejeitos de cúrcuma. Paralelamente, houve construção e validação de aparato experimental para estudo do comportamento de fases a altas pressões, seguido de novas informações referente ao comportamento dos extratos e dos rejeitos de cúrcuma. Além disso, nesta tese foram realizados ensaios de encapsulamento dos extratos, resultando em produtos com maior estabilidade.

SUGESTÕES PARA TRABALHOS FUTUROS

A lista abaixo foi elaborada a fim de se motivar novas pesquisas continuadas na temática abordada nesta tese, a saber:

1 – Inclusão dos rejeitos e dos amidos isolados de cúrcuma para formulação de produtos alimentícios e estabelecer comparação com matérias-primas convencionais no que diz respeito à qualidade final de um produto comumente aceitável sensorialmente e para comercialização;

2 – Estudar a viabilidade de aplicação dos rejeitos e dos amidos isolados de cúrcuma como material de parece a partir do uso de outras técnicas de encapsulamento;

3 – Estudar a interação que os compostos bioativos da cúrcuma possam ter com a matriz amilácea;

4 – Isolamento do amido a partir dos rejeitos de cúrcuma desaromatizado, despigmentado e parcialmente hidrolisados;

5 – Realizar ensaios de hidrólise com auxílio de ultrassom e avaliar os efeitos dos tratamentos nas matrizes sólidas e nos extratos;

6 - Realizar estudos do comportamento de fases dos extratos etanólicos de curcuminóides a altas pressões;

7 – Avaliar a quantidade de solvente residual que possa ter ficado nos extratos de cúrcuma coprecipitados em polietilenoglicol;

8 – Aplicação dos extratos coprecipitados na formulação de alimentos para atribuição de cor e estudo da vida de prateleira;

9 – Realização de estudos *in vitro* e *in vivo* dos extratos coprecipitados a fim de se avaliar a eficácia destes produtos para tratamento de enfermidades;

Memórias do doutorado

MEMÓRIAS DO DOUTORADO

Ádina Lima de Santana, candidata ao doutorado pelo programa de pós graduação em Engenharia de Alimentos (DEA/FEA) da Universidade Estadual de Campinas (Unicamp), tem realizado suas atividades de pesquisa apresentada neste projeto integrante do grupo de pesquisas do laboratório Lasefi sob auxílio financeiro da CAPES (2952/2011), com vigência de março de 2014 a outubro de 2017.

Até este momento 22 créditos foram quitados, cujas disciplinas cursadas foram Métodos Matemáticos na Engenharia de Alimentos (TP132), Fenômenos de Transporte II (TP323), Fenômenos de Transporte I (TP322), Termodinâmica (TP320), Seminários (TP199) e Tópicos em Engenharia de Alimentos – ciclo de aprendizagem PDSA (TP159).

A doutoranda participou do Programa de Estágio Docente grupo C (PED C) com atividades de apoio parcial à docência na disciplina Termodinâmica (TA 331-A), atuando como voluntária no segundo período letivo de 2015, e como bolsista no primeiro período letivo de 2016, com carga horária de 4 horas semanais.

Além disso, participou do Fórum de Debates I – Mitos e Verdades sobre o Óleo de Coco, com carga horária de 6 horas, do III Congresso Brasileiro de Reologia, com carga horária de 22 horas, do mini-curso ´´Equilíbrio de Fases em sistemas lipídicos e processos de cristalização em emulsões O/A e A/O´´, com carga horária de 6 horas e do mini-curso ´´Planejamento Experimental e Otimização de Processos´´, ministrado pela professora Dra. Maria Isabel Rodrigues, com carga horário de 8 horas.

Visando o aprimoramento de sua escrita científica a doutoranda participou de três workshops sobre escrita e publicações científicas, sendo dois promovidos pela Elsevier, com cargas horárias de 2 e 6 horas, respectivamente, e um promovido pelo Espaço da Escrita da Unicamp, em parceria com a University of Bath, em carga horária de 4 horas. Além disso, para aprimorar sua argumentação, a candidata participou do mini-curso ´´Pensamento Crítico, Lógica e Argumentação´´, ministrado pelo prof. Dr. Walter Carnielli (IFCH e CLE/Unicamp).

As pesquisas referentes ao projeto de doutorado e às parcerias com outros integrantes do Lasefi resultaram em 2 artigos publicados em anais de congresso, 2 artigos de revisão, 1 artigo experimental publicado no periódico Food and Public Health, 2 artigos publicados no periódico Journal of Supercritical Fluids, 1 artigo publicado no Journal of Food Engineering, além coautoria em um 1 artigo fruto da parceria com a Dra. Carolina Lima Cavalcanti de Albuquerque publicado no mesmo periódico e coautoria em um artigo de revisão publicado no periódico Recent Patents on Engineering.

Artigos completos publicados em periódicos

1. **Á. L. Santana**, M. A. A. Meireles, "New Starches are the Trend for Industry Applications: A Review", Food and Public Health, vol.4, no.5, pp.229-241, 2014.
2. C. L. C. Albuquerque, **Á. L. Santana**, M. A. A. Meireles, "Thin Layer Chromatographic Analysis of Annatto Extracts Obtained Using Supercritical Fluid", Food and Public Health, vol.5, no.4, pp.127-137, 2015.
3. **Á. L. Santana**, I. C. N. Debien, M. A. A. Meireles, "High-Pressure Phase Equilibrium Methodologies Applied to Food Systems", Food and Public Health, vol.5, no.5, pp.184-202, 2015.
4. **Á. L. Santana**, M. A. A. Meireles, ´´Thin-Layer Chromatographic Profile of Non-Commercial Turmeric (*Curcuma longa* L.) Products Obtained via Partial Hydrothermal Hydrolysis´´, Food and Public Health, vol. 6, no.1, pp.15-25, 2016.
5. R.A.C. Torres, **Á.L. Santana**, D.T. Santos, M. A. A. Meireles, ´´Perspectives on the Application of Supercritical Antisolvent Fractionation Process for the Purification of Plant Extracts: Effects of Operating Parameters and Patent Survey´´, Recent Patents on Engineering, vol. 10, no. 2, pp. 88-97, 2016.
6. **Á. L. Santana**, I. C. N. Debien, M. A. A. Meireles. ´´High-pressure phase behavior of turmeric waste and extracts in the presence of carbon dioxide, ethanol and dimethylsulfoxide´´. The Journal of Supercritical Fluids, vol. 124, pp. 38-49, 2017.
7. **Á. L. Santana**, G.L. Zabot, J.F. Osorio-Tobón, J.C.F. Johner, A.S. Coelho, M. Schmiele, .C.J. Steel, M. A. A. Meireles. ´´ Starch recovery from turmeric wastes. Journal of Food Engineering, vol 214, pp. 266-276 , 2017,

8. **Á. L. Santana**, M. A. A. Meireles. Coprecipitation of turmeric extracts and polyethylene glycol with compressed carbon dioxide. The Journal of Supercritical Fluids, vol. 125, pp. 31-41, 2017.

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1. **Á.L. Santana**, J.C.F. Johner, M. A. A. Meireles. ´´Thin-layer chromatography profile of annatto extracts obtained with supercritical carbon dioxide and subsequently high-pressure phase equilibrium data´´. XXV Congresso Brasileiro de Ciência e Tecnologia de Alimentos. 24.10.2016.
2. J.C.F. Johner, **Á.L. Santana**, M. A. A. Meireles. Supercritical fractionation of extracts from annatto seeds using a home-made equipment. XXV Congresso Brasileiro de Ciência e Tecnologia de Alimentos. 24.10.2016.

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Anexos

A.1 Testes preliminares dos experimentos de hidrólise na unidade PLE, variando-se a razão S/F

Os ensaios foram realizados a 70 bar, variando-se as temperaturas e as razões S/F.

Tabela A.1. Influência da razão S/F em X_0 (extrato seco).

S/F	T(ºC)	X_0(%)
2	40	3,604
4		2,339
8		1,640
10		0,805
12		0,664
2	70	1,404
4		1,205
8		0,944
10		0,662
12		0,278
2	100	0,269
4		0,237
8		0,202
10		0,012
12		0,018

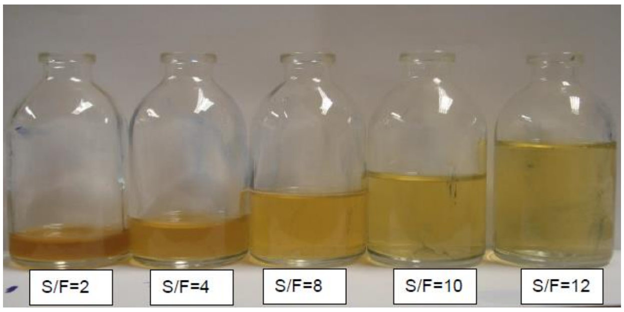

Figura A1. Testes das razões S/F nos ensaios de hidrólise de cúrcuma a 40ºC.

O X_0 foi calculando considerando a massa de hidrolisado no estado sólido, ou seja, esses hidrolisados foram liofilizados e o peso dessas mostras foi inserido no cálculo da equação 3.2

(no capítulo 3 deste exame de qualificação). Durante os ensaios, foi observado que diante de um S/F=4 houve a iniciação do esgotamento da matéria-prima ao produzir hidrolisados, portanto, o aumento de S/F contribuiu na diluição dos açúcares presentes nos hidrolisados, fato este mostrado pela diminuição de X_0. (Tabela A.1.). Por causa disso para os ensaios de hidrólise foi escolhido o S/F=4.

A.2 Açúcares totais e redutores (espectrofotômetro)

A varredura no espectrofotômetro foi feita numa amostra de hidrolisado de cúrcuma diluída na proporção 1:50 em que 0,02 ml de hidrolisados de cúrcuma foram adicionados em 0,98 ml de água deionizada, resultando numa proporção de 0,03 g de glicose diluída em 0,98 ml de água.

Tabela A.2. Varredura espectrofotométrica de hidrolisado de cúrcuma.

λ (nm)	Abs1	Abs1	$Abs_{MÉDIA}$
300	0,001	0,001	0,001
350	0,177	0,089	0,133
400	0,178	0,089	0,134
450	0,176	0,088	0,132
500	0,254	0,127	0,191
550	0,436	0,218	0,327
600	0,692	0,346	0,519
650	0,924	0,462	0,693
700	1,167	0,584	0,876
750	1,293	0,647	0,970
800	1,206	0,603	0,905

O início da curva foi a 300 nm, o pico foi a 750 nm (comprimento de onda selecionado para as leituras realizadas em cúrcuma), o ponto final foi a 800 nm e a altura do pico correspondeu a absorbância de 1,3 (Figura A.2.).

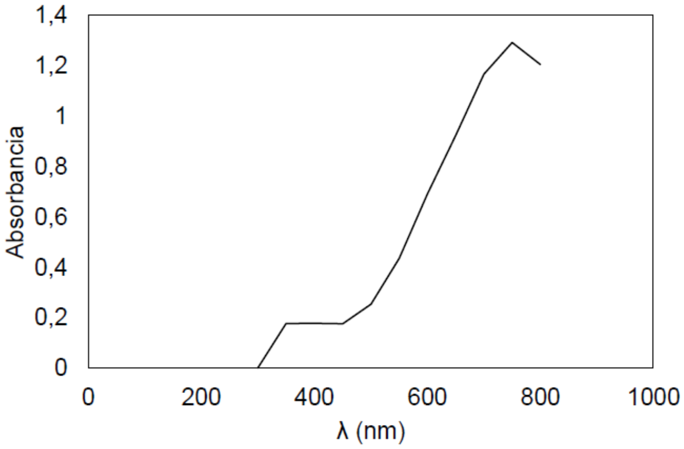

Figura A.2. Varredura do espectro para a amostra de cúrcuma hidrolisada.

Tabela A.3. Dados para a curva padrão para sacarose (determinação de açúcares totais).

[ ]	**Abs1**	**Abs2**	**Abs média**
0,06	0,017	0,017	0,017
0,08	0,037	0,034	0,036
0,10	0,081	0,083	0,082
0,12	0,104	0,106	0,105
0,14	0,167	0,168	0,168
0,16	0,178	0,178	0,178
0,20	0,256	0,257	0,257

[ ] = concentração, em g/L.

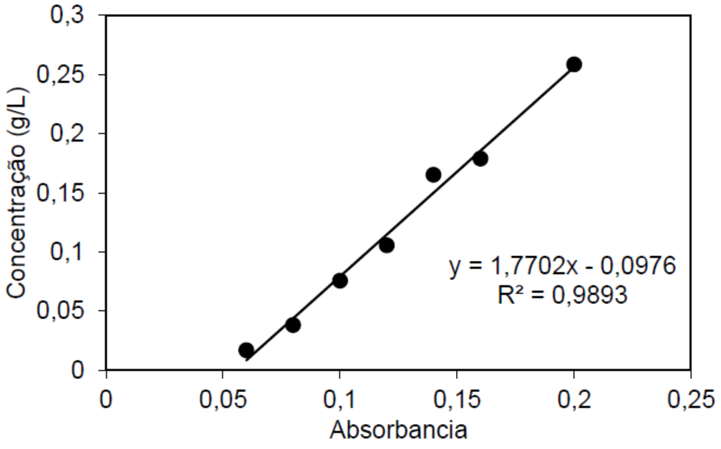

Figura A.3. Curva padrão de sacarose para determinação de açúcares totais.

Tabela A.4. Dados para a curva padrão de glicose para determinação de açúcares redutores.

[ ]	Abs1	Abs2	AbsMÉDIA
0,80	0,184	0,184	0,184
1,00	0,252	0,252	0,252
1,20	0,321	0,320	0,321
1,40	0,422	0,423	0,423
1,60	0,406	0,407	0,407
1,80	0,471	0,470	0,471
2,00	0,486	0,485	0,486

[ ] = concentração, em g/L.

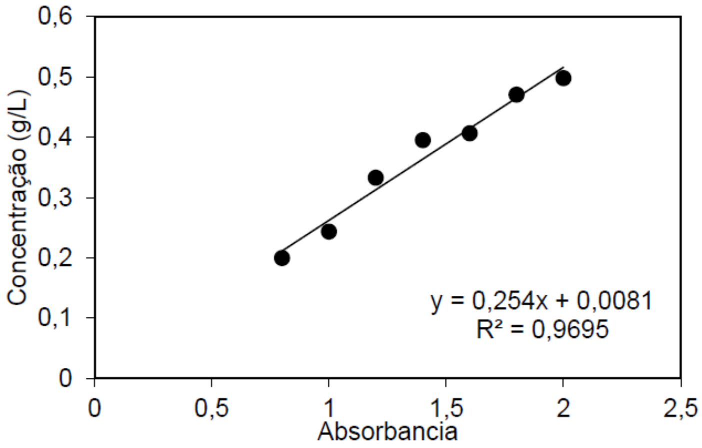

Figura A.4. Curva padrão de glicose para determinação de açúcares redutores

Figura A.5. Hidrolisados de cúrcuma em etapa anterior a leitura espectrofotométrica.

A.3 Curvas padrão utilizadas na análise de curcuminóides (HPLC)

Tabela A.5. Dados para curva de calibração de curcumina para determinação do teor de curcuminóides.

[ ]	T_R	A_1	A_2	$A_{MÉDIA}$
100	2.235	10628135	10726861	1,1E+07
50	2,231	5713704	5626447	5670076
25	2,237	2753093	2746462	2749778
10	2,223	986309	965785	976047
1	2,241	87658	91786	89722
0,5	2,239	43861	44070	43965,5
0,25	2,241	19332	21152	20242
0,1	2,255	8964	9808	9386

[ ] = concentração, em ppm; T_R=Tempo de retenção, em minutos; A_1 = Área 1, em µV. seg; A_2 = Área 2, em µV. seg;

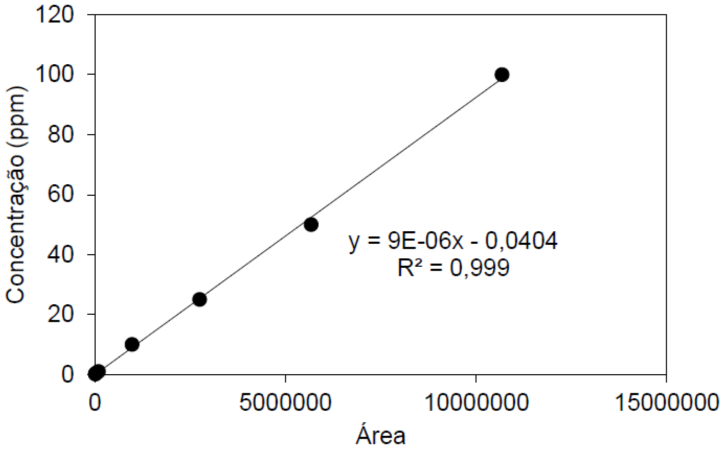

Figura A6. Curva padrão de curcumina para método de determinação do teor de curcuminóides.

Tabela A.6. Dados para curva de calibração de demetoxicurcumina para determinação do teor de curcuminóides.

[ ]	T_R	A_1	A_2	$A_{MÉDIA}$
100	2,067	10436990	10564430	10500710
50	2,079	5710516	5751210	5730863
25	2,08	2665380	2723967	2694674
10	2,077	1058906	1062648	1060777
1	2,088	98620	100614	99617
0,5	2,075	47593	48958	48275,5
0,25	2,087	25490	25553	25521,5
0,1	2,077	8891	8981	8936

[ ] = concentração, em ppm; T_R=Tempo de retenção, em minutos; A_1 = Área 1, em µV. seg; A_2 = Área 2, em µV. seg.

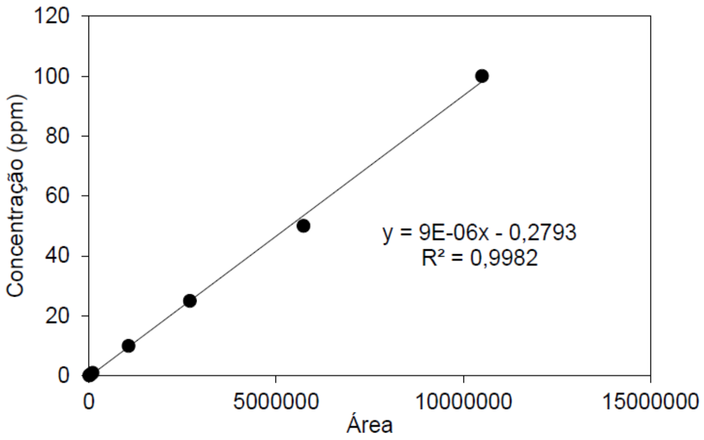

Figura A.7. Curva padrão de demetoxicurcumina para método de determinação do teor de curcuminóides.

Tabela A.7. Dados para curva de calibração de bisdemetoxicurcumina para determinação do teor de curcuminóides.

[ ]	T_R	A_1	A_2	$A_{MÉDIA}$
100	1,932	9978633	10051871	10015252
50	1,923	5444388	5426735	2296907
25	1,923	2555846	2576156	1242846
10	1,92	950644	954348	540788,5
1	1,939	92390	94397	152154,5
0,5	1,927	45257	50479	17207,5
0,25	1,933	25711	24110	7913
0,1	1,93	11772	8953	3593,5

[ ] = concentração, em ppm; T_R=Tempo de retenção, em minutos; A_1 = Área 1, em µV. seg; A_2 = Área 2, em µV. seg;

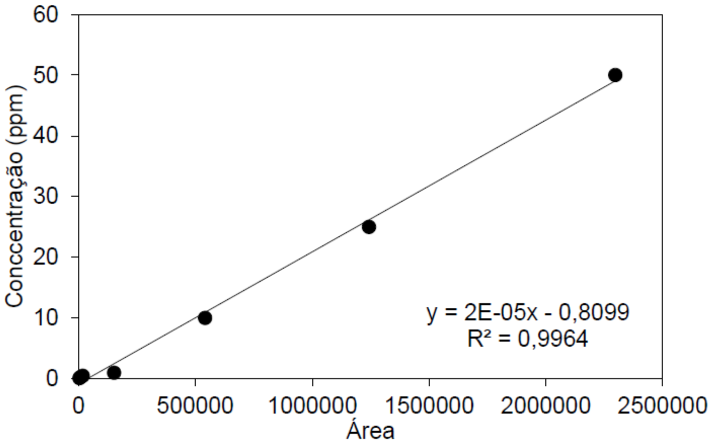

Figura A.8. Curva padrão de bisdemetoxicurcumina para método de determinação do teor de curcuminóides.

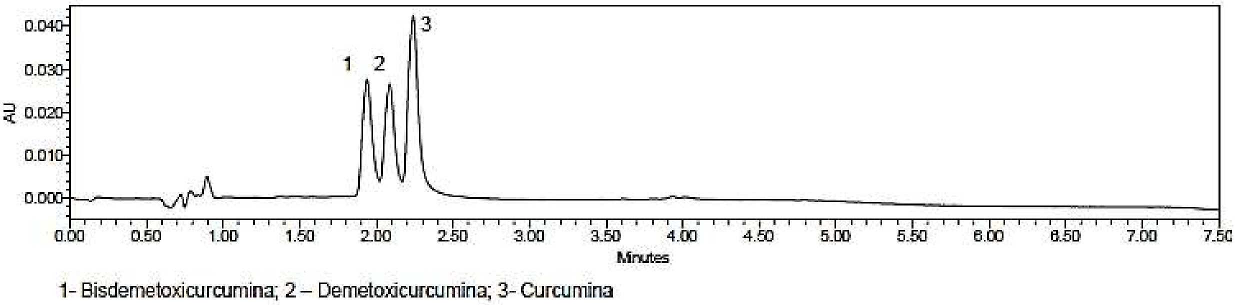

Figura A.9. Cromatograma característico.

1 Bisdemetoxicurcumina; 2- Demetoxicurcumina, 3- Curcumina.

A.4 Curva padrão utilizada na análise de fenólicos

Tabela A.8 Dados para curva de calibração de fenólicos.

[ ]	Abs1	Abs2	Abs$_{\text{MÉDIA}}$
0,000	0,000	0,000	0,000
0,050	0,015	0,019	0,017
0,100	0,022	0,021	0,022
0,150	0,038	0,024	0,031
0,250	0,041	0,034	0,038
0,500	0,040	0,048	0,044

[ ] = concentração, em g/ml.

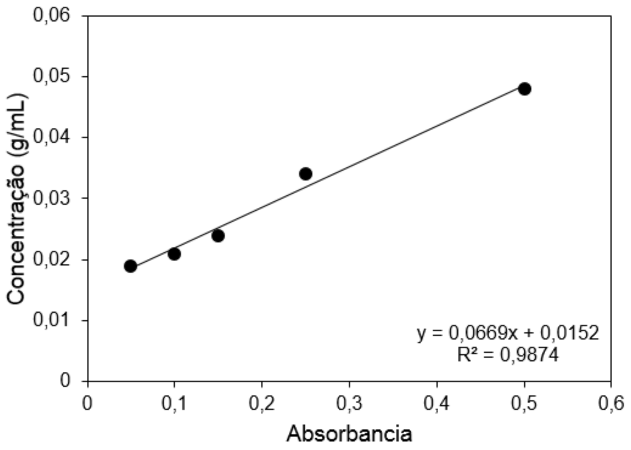

Figura A.10. Curva padrão de fenólicos a partir do reagente Folin-Ciocateau.

A.5 Análise de amido

Figura A.11. Amostras de cúrcuma desaromatizada e despigmentada após aplicação das enzimas α-amilase e amiloglucosidade.

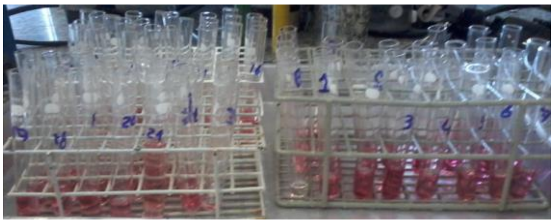

Figura A.12. Amostras de cúrcuma desaromatizada e despigmentada com reagente GOPOD.

A.6 Descrição do Aparato Experimental de Equilíbrio de Fases

A.6.1 Parte estrutural

A parte estrutural da unidade foi montada com perfilado quadrado de alumínio extrudado (Sistema – Automação e comércios de equipamento industriais, Amparo, SP) de 30 mm, que possui encaixe nas quatro laterais, onde através de cantoneiras e parafusos poder-se fixar uma barra de perfilado a outra. Esse tipo de material facilitou muito a montagem, pois dispensou qualquer tipo de solda ou furos, uma vez que requer apenas corte e montagem. A estrutura foi montada no próprio Lasefi. Foram utilizados quatro rodízios (dois fixos e dois giratórios), para facilitar o deslocamento do aparato.

A essa estrutura foram fixadas três placas de alumínio de espessura de 5 mm, duas de 85 x 58 cm para suporte dos equipamento e da célula de equilíbrio e uma de 40 × 50 cm para fixação de válvulas e indicadores.

Todos os componentes da unidade foram instalados na parte estrutural através de porcas e parafusos "cabeça de martelo" (chamados como tal por causa do formato retangular de uma das extremidades). Na caneleta do perfilado o parafuso é colocado de lado e quando se encaixa na porca vira no sulco prendendo-se na parte interna, ocorrendo sua fixação. Com este sistema é possível realizar qualquer modificação estrutural com muita facilidade.

A.6.2. Equipamentos e Materiais

A unidade de equilíbrio de fases a altas pressões foi montada de forma similar àquelas propostas por Corazza (2002), Dariva (2000) e Stuart et al. (2000). As figuras pertencentes aos capítulos 6 (Figura 6.1) e 7 (Figura 7.1) desta tese mostram o diagrama esquemático do aparato experimental, que consiste basicamente nos seguintes itens com as respectivas funções:

A) Cilindro de Solvente. Armazenamento do solvente empregado nos experimentos. Foi utilizado dióxido de carbono (Gama Gases Especiais, Campinas, SP) com pureza de 99,5%, em cilindros com capacidade de 31 kg a uma pressão de 70 bar a 25 ºC, provido com um tubo pescador para a coleta da fase líquida (parte inferior do cilindro);

V1) Válvula de bloqueio (Autoclave Engineers, modelo 10V2071 15000 psi, Erie, EUA): Isola o cilindro de solvente, quando aberta permite o fluxo de solvente do cilindro para a bomba;

B) Bomba HPLC: bomba de alta pressão (Thermo Separation Products, modelo 3200 P/F, Flórida, EUA). É necessário um equipamento que permita a quantificação da massa de fluido deslocada e que sirva para manipular a pressão do sistema, como a bomba HPLC .opera com controle de vazão é possível realizar esse controle. O cabeçote da bomba é encamisado, o que possibilita a manutenção da temperatura em um valor pré-determinado com auxílio de um banho de recirculação (CB);

CB) Banho de resfriamento: Banho termostático de recirculação (MARCONI, modelo Ma-184, Piracicaba, SP) utilizado para manter a temperatura do cabeçote da bomba constante à -10°C. Para garantir que o dióxido de carbono vai entrar na bomba no estado líquido foi construída uma serpentina de 7,5 metros de comprimento com um tubo de aço inox 316 (sem costura, 1 mm de espessura e 1/8 polegada). Essa serpentina foi instalada no interior do banho de recirculação, ficando submersa na solução (50 % água e 50 % etileno glicol) para refrigeração, conforme Figura A. 13.

Figura A.13. Serpentina submersa no banho de resfriamento.

V2) Válvula de bloqueio (Autoclave Engineers, modelo 10V2071 15000psi, Erie, EUA): Utilizada para isolar a unidade da bomba de alta pressão durante a montagem e desmontagem da célula de equilíbrio;

C) Célula de equilíbrio (Figura 1, capítulo 7): Consiste em um cilindro de aço inox 316, com capacidade máxima de 27 mL, possuindo um diâmetro interno de 17,2 mm e comprimento de 176 mm. A célula possui três entradas superiores: uma para conexão com o termopar (T1), outra com a válvula V3 e uma fechada por segurança; uma entrada lateral onde é fixada a janela de safira lateral (D2) e entradas frontal (Janela de safira frontal – D1) e traseira (fechamento da célula e conexão com a válvula V4). A célula é envolta por uma camisa conectada a um banho térmico cuja função é manter a temperatura desejada.

Figura A14. Célula de equilíbrio e camisa de aquecimento. A) Vista superior: entradas para conexão e termopar; B) Vista lateral: janela de safira lateral.

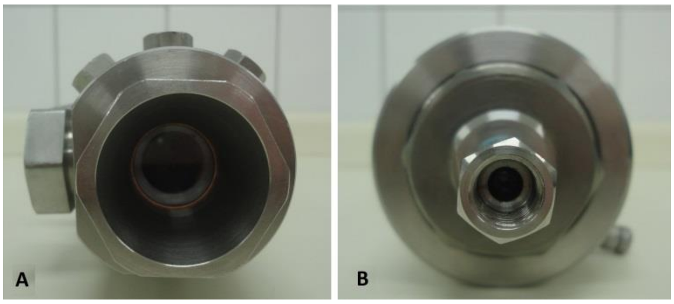

Figura A15. Célula de equilíbrio. A) Vista frontal: janela de safira frontal; B) Vista traseira: fundo da célula.

C1) Pistão (Figura 1, capítulo 7). No interior da célula foi inserido um pistão de aço inox 316 de 28 x 17 mm que tem por objetivo controlar o volume e, consequentemente, a pressão do sistema. Ele possui dois anéis de BUNA N90 localizados em suas extremidades, que o permitem deslizar pelo interior da célula e garantem a vedação entre o fundo e a frente da célula. Através da manipulação deste pistão controla-se a pressão dentro da célula.

D1) Janela de safira frontal: A célula possui uma janela de safira (Swiss Jewel Company, Philadelphia, EUA) frontal possuindo um diâmetro de 25,4 mm e espessura de 9,52 mm, que permite a visualização do interior da célula (Figura A16).

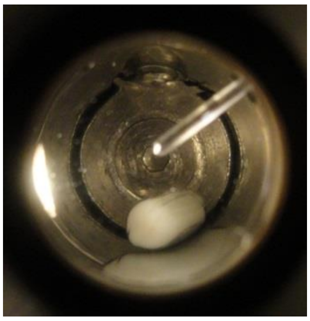

Figura A16. Janela de safira frontal mostrando o interior da célula: pistão ao fundo, na parte interior a barra magnética e na parte superior o termopar.

D2) Janela de safira lateral: A célula também possui uma janela de safira (Swiss Jewel Company, Philadelphia, EUA) lateral possuindo um diâmetro de 15,87 mm e espessura de 4,76 mm, que permite a entrada de luz, o que facilita a visualização no interior da célula;

As janelas frontal e lateral são fixadas à célula conforme apresenta a Figura A14. Tanto para a janela frontal quanto para a janela lateral foi utilizado um anel de teflon na posição do anel de vedação 1 e um anel de cobre na posição do anel de vedação 2 (Figura A17).

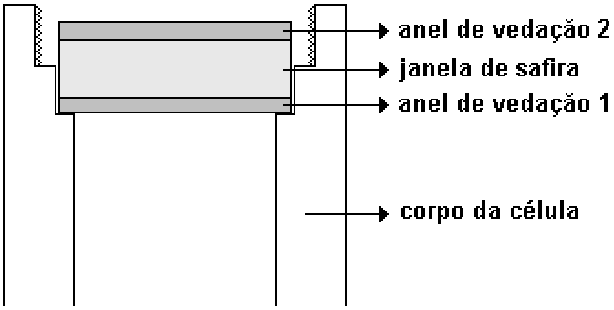

Figura A17. Posicionamento da janela de safira na célula de equilíbrio.

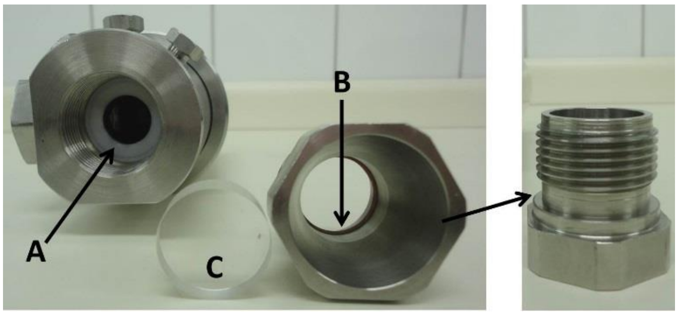

Figura A18. Vista frontal da célula de equilíbrio. A) Anel de vedação 1 de teflon; B) Anel de vedação 2 de cobre; C) Safira.

E) Agitador magnético: O sistema de agitação tem como objetivo agilizar o alcance do equilíbrio. Para tal foi inserido dentro da célula uma barra magnética ("peixinho"), acionada pelo agitador magnético que foi inserido logo abaixo da célula de equilíbrio;

F) Fonte de luz: Feixe de luz branca na janela de safira lateral para iluminar o interior da célula e assim facilitar a visualização das transições de fases.

HB) Banho de aquecimento: Banho termostático de recirculação (Marconi, modelo MA 159/300, Piracicaba, SP) conectado a uma camisa em volta da célula de equilíbrio que tem como objetivo manter a temperatura no interior da célula constante;

HJ) Camisa de aquecimento: Camisa de aço inox 316 em volta da célula;

V3) Válvula de bloqueio (Autoclave Engineers, modelo 10V2071 15000psi, Erie, EUA): Válvula de alimentação do sistema, permite a entrada do líquido comprimido (solvente) no interior da célula;

V4) Válvula de bloqueio (Autoclave Engineers, modelo 10V2071 15000psi, Erie, EUA):

Válvula cuja função é impedir a passagem de fluxo para o fundo da célula durante o processo de carga do solvente ao sistema e também para permitir a pressurização do fundo da célula através da passagem do líquido comprimido até o fundo do pistão;

V5) Válvula de bloqueio (Autoclave Engineers, modelo 10V2071 15000psi, Erie, EUA): Válvula de descarga do sistema e despressurização do fundo da célula;

V6) Válvula micrométrica (Autoclave Engineers, modelo 10VRMM 11000PSI, Erie, USA): Essa válvula foi inserida com o objetivo de controlar a despressurização do sistema. A despressurização deve ser lenta, o que facilita a visualização do momento exato em que ocorre a transição de fases;

P1) Transdutor de pressão (Huba Control, modelo 511, 0 a 400 bar, Würenlos, Dinamarca): É conectado à linha proveniente da bomba para verificar a real pressão do sistema;

P2) Indicador de pressão (Novus, modelo N1040i, Porto Alegre, RS): Recebe um sinal digital do P1 indicando a pressão da linha. Esse modelo de indicador precisou ser adaptado pelo fornecedor para ser compatível com o transdutor de pressão, foi colocada uma fonte auxiliar de 24V mais rele de alarme SPDT;

T1) Termopar tipo J: Sensor de temperatura usado para medir o valor real da temperatura na solução no interior da célula;

T2) Indicador de temperatura (Novus, modelo N1040i, Porto Alegre, RS): Recebe um sinal digital do T1 indicando a temperatura real da solução no interior da célula;

Uma vista geral da unidade de equilíbrio de fases a altas pressões é apresentada na Figura 7.1. desta tese, na qual é possível visualizar todos os equipamentos e materiais descritos acima.

Filtro de linha: Logo após a válvula de bloqueio que isola o cilindro de solvente do sistema (V1) foi colocado um filtro de linha (Swagelok, EUA) de aço inox série F para retenção de partículas com poros de 0,5 micra. Esse filtro tem como objetivo reter partículas de sujeira provenientes do fundo do cilindro de solvente, para evitar a obstrução de tubulações, válvulas e o cabeçote da bomba.

Manômetro: Também logo após a válvula V1 foi instalado um manômetro (Record, tipo Bourdom, São Paulo, SP) de 150 mm de diâmetro, com corpo de aço inox e escala de 0 a 250 bar com precisão aproximada de ± 0,25 %. Esse manômetro foi utilizado para indicar a pressão inicial do cilindro de solvente.

Tubulações: Em toda unidade foram utilizadas tubulações de aço inox 316 que suportam pressões de trabalho de até 880 bar, fornecidas pela Fopil – Tecnologia em condução de fluidos, Campinas, SP. Foram adquiridas tubulações de 1/8 e 1/16 polegadas. A tubulação de 1/8 foi utilizada na saída do cilindro de solvente e após a válvula micrométrica para a descarga do sistema, para a alimentação da célula de equilíbrio bem como para sua pressurização e despressurização foi utilizada a tubulação de 1/16.

Conexões: Todas as conexões (cruzetas, tês, cotovelos, conectores macho para termopar, conectores para manômetro e uniões redutoras) utilizadas são de aço inox 316 fabricadas pela Parker Hannifin (Cleveland, EUA) também fornecidas pela Fopil – Tecnologia em condução de fluidos, Campinas, SP. Essas conexões são de alta resistência a pressão e temperatura, possibilitando boa vedação e facilitando a montagem e manutenção da unidade.

A.6.3 Procedimento experimental

O método utilizado foi o sintético-visual, cuja principal característica baseia-se no fato da composição das fases em equilíbrio ser determinada indiretamente, ou seja, quantidades pré-determinadas são introduzidas na célula de equilíbrio, de tal forma que a composição global da mistura no início do experimento seja conhecida.

Em síntese, a ideia principal desse método consiste em preparar uma mistura com uma composição global conhecida e observar seu comportamento à medida que se varia a pressão, mantendo-se a temperatura constante ou vice versa.

O procedimento experimental adotado para medidas de equilíbrio de fases a altas pressões inicia com o ajuste da temperatura do banho de resfriamento (CB), em torno de 263 K, para manter a temperatura do cabeçote da bomba constante. Até que essa temperatura seja alcançada, é realizada montagem da célula de equilíbrio (C) obedecendo a passos cuidadosos. Primeiramente o pistão (C1) é introduzido no interior da célula de forma que ele possa deslizar e não permitir a passagem de fluido do fundo para frente e vice-versa, e por fim a célula é então fechada (manipulação das roscas de fechamento).

Em seguida a célula é posicionada adequadamente na unidade e as linhas que contém as válvulas V3 e V4 são conectadas a ela. As válvulas V1 e V2 são então abertas para permitir o fluxo de solvente do cilindro (A) para a bomba (B) e da bomba (B) para a unidade. Na metodologia estática sintética aqui empregada, deve-se conhecer a composição global do sistema em estudo, assim quantidades pré-determinadas de todos os compostos do sistema são colocados no interior da célula, seja no momento da montagem ou após por meio de uma seringa através do orifício onde posteriormente será colocado o termopar. A temperatura e pressão do solvente na bomba foram mantidas constantes durante a carga e a massa de solvente adicionada foi calculada com base em sua densidade.

Desta forma, a célula foi carregada com composição global conhecida. A válvula V4 será aberta lentamente, permitindo a entrada de solvente na célula, até o volume desejado Durante o processo de carga do solvente, nenhuma pressão foi aplicada no fundo do pistão, para permitir que o experimento comece com a célula em seu volume máximo. Após a alimentação, o sistema é continuamente agitado por meio do agitador magnético (E) e o aquecimento (HB) é acionado.

Com a válvula V4 fechada e a temperatura do sistema estabilizada, a válvula de esfera V5 foi aberta para permitir a entrada do solvente no fundo da célula ocasionando a movimentação do pistão e, assim, um aumento gradativo da pressão no interior da célula até o sistema atingir uma condição monofásica. Mantendo-se a temperatura constante e a solução sob agitação, inicia-se a despressurização lenta do sistema. A despressurização foi mantida até o surgimento incipiente de uma segunda fase, sendo que ao menor sinal da transição de fases a ação foi interrompida para identificação do tipo de transição e da interface entre as fases segregadas. Após estabilizar a oscilação da pressão neste ponto, anota-se o valor dessa e em seguida o sistema é pressurizado novamente para repetir o procedimento.

Esse procedimento é repetido (aumento de pressão até que se forme uma fase e posterior redução da pressão até o surgimento da transição de fases) diversas vezes (no mínimo 3) para avaliar a repetibilidade da metodologia experimental e obter um valor médio da pressão de transição à temperatura e composição global constantes. Após a medida experimental em uma temperatura, a temperatura do sistema é modificada e o processo descrito anteriormente repetido outras vezes. Desta forma, para uma composição global constante, é possível obter a curva P-T para o sistema em estudo.