Chemical Industry & Chemical Engineering Quarterly

Available online at
Association of the Chemical Engineers of Serbia *AChE*
www.ache.org.rs/CICEQ

Chem. Ind. Chem. Eng. Q. 29 (4) 263–271 (2023) CI&CEQ

VANDERLEI RODRIGUES COSTA[1]
LUANA MARCELE CHIARELLO[1]
VANDERLEIA BOTTON[1]
EDÉSIO LUIZ SIMIONATTO[2]
VINICYUS RODOLFO WIGGERS[1]
HENRY FRANÇA MEIER[1]
LAÉRCIO ENDER[1]

[1]Chemical Engineering Department, University of Blumenau - FURB, Blumenau, SC, Brazil

[2]Chemistry Department, University of Blumenau - FURB, Blumenau, SC, Brazil

SCIENTIFIC PAPER

UDC 66.092-997:665.33

GREEN CHEMICAL PRODUCTION BASED ON THERMAL CRACKING OF INEDIBLE VEGETABLE OIL

Article Highlights

- Heptaldehyde, undecylenic acid and methyl undecenoate production from castor oil
- Different feed materials were tested to compare the yields of the desired products
- Methyl ester yields a higher concentration of heptaldehyde and methyl undecenoate

Abstract

This work evaluated the process for heptaldehyde, undecylenic acid, and methyl undecenoate production from castor oil, methyl ester of castor oil, and ricinoleic acid. Experiments were performed in a continuous pilot-plant scale pyrolysis reactor. Those are very important green chemical products that the thermal cracking of castor oil might produce. Transesterification of castor oil produces methyl ricinoleate, and its thermal cracking generates methyl undecenoate and heptaldehyde. The pyrolysis temperatures tested were 530 °C, 545 °C, 560 °C, and 575 °C, with residence time from 17 s to 32 s and mass flow at 400 g/h of the mixture of materials with 25% distilled water. It was observed that the temperature influenced the bio-oil yield in different degree for each material. The bio-oil was characterized by iodine index, acid number, and mass, and the contents of its compounds were obtained by GC-FID chromatography. The best result for the undecylenic acid mass yield of the desired compounds occurred at 530 °C, achieving 17.8% from ricinoleic acid and 16.5% from castor oil. For the heptaldehyde, the highest production was also obtained at 530 °C, with a value of 20.7% from methyl ester and 15.2% from ricinoleic acid.

Keywords: triglyceride pyrolysis, castor oil, ricinoleic acid, heptaldehyde, undecylenic acid, methyl undecenoate.

Heptaldehyde and undecylenic acid can be obtained by the thermal cracking of castor oil, its methyl ester, or ricinoleic acid [1,2]. They are among the most important green chemicals obtained from castor oil, known as vital intermediates for products within medicine, fuels, perfumes, polymers, plastics, rubbers, and flavors [3–5]. Ricinoleic acid, sebacic acid, and γ-decalactone are castor oil derivatives produced at a larger scale [6]. Castor bean (*Ricinus communis L.*) is an abundant oleaginous plant in tropical and subtropical regions. It has been cultivated mainly in India, China, Brazil, and Mozambique from 2007 to 2017 [7]. The castor bean seed has an oil percentage of 40% to 55% with approximately 90% of ricinoleic acid (12-hydroxy-9-cis-octodecenoic acid) in its composition [8]. Due to the presence of ricin, a toxic substance to humans, it is not used for food, thus making it inedible oil interesting for producing green chemicals. Other than that, its applications as a precursor of green chemicals are due to its molecule having three functional groups: double bound, hydroxyl, and carboxyl groups, increasing the possibilities of chemical reactions.

Correspondence: V. Botton, Chemical Engineering Department, University of Blumenau - FURB, Rua São Paulo 3250, Blumenau, SC, 89030-000, Brazil.
E-mail: vanderleiabotton@furb.br
Paper received: 14 January, 2022
Paper revised: 29 October, 2022
Paper accepted: 28 December, 2022

https://doi.org/10.2298/CICEQ220114033C

Das *et al.* [9] reported a process where the castor oil was thermally cracked in a stainless steel tubular vertical reactor 76.2 cm height by 2.5 cm internal diameter, filled with steel balls in the preheating section, 0.5% benzoyl peroxide was added as cracking initiator at 45 mmHg of pressure, with yields of 24.8% of heptaldehyde and 35.4% of undecylenic acid at 550 °C. The authors observed that castor oil, when cracked at lower temperatures, favored the occurrence of polymerization of the formed products, making it difficult to analyze their composition. It also hinders the formation of major products by reducing their yields and increasing secondary reactions in the form of acrolein, ketone compounds, and other fatty acids. Botton *et al.* [8] performed the thermal cracking of methyl esters in castor oil (65% of methyl ricinoleate) under steady-state and isothermal conditions in stainless steel auger reactor. They obtained yield values of 17.7% for heptaldehyde and 11.9% for methyl undecenoate with a mass flow of 280 g h^{-1} residence time of 44 s at 525 °C. It is important to say that thermal cracking of the methyl ester in castor oil has an intermediate compound, i.e., methyl undecenoate, which needs to be subsequently converted to the undecylenic acid by alkaline hydrolysis followed by acid hydrolysis [9,10]. As a contribution, this work proposed a simplified reaction mechanism, demonstrating one route for the desired products and another for the undesired products, such as methyl esters with 7 to 11 carbons in the chain, methanol, water, 1-decene, and 1,9-decadiene.

Some researchers have used water in thermal cracking reactions to obtain heptaldehyde, methyl undecenoate, and undecylenic acid, dealing with the performance increase of the process [11,12]. Wetroff *et al.* [11] described in USPTO 2807 633 the thermal cracking of castor oil, methyl ricinoleate, and ricinoleic acid in different conditions and reactor specifications for each material. They focused on the production of heptaldehyde and undecylenic acid with acrolein formation. At the same time, Guobin *et al.* [12] studied the kinetics of the thermal cracking reaction in the methyl ricinoleate and water mixture. According to the authors, the advantage of this route is that in the thermal cracking of methyl ricinoleate to obtain heptaldehyde and methyl undecenoate, it generates less harmful gases since no acrolein formation depends on the glycerol portion present in the triacylglycerol molecule, as well as the fact that viscosity of methyl ricinoleate is lower and easier to work with.

Recently, based on the work of Botton *et al.* [8] and samples of bio-oil produced by thermal cracking of methyl ester in castor oil under isothermal conditions (525 °C) and different residence times, Menshhein *et al.* [13,14] evaluated a process for separation and purification of heptaldehyde and methyl undecenoate with distillation as downstream operation, with an absolute characterization of the products using gas chromatography (GC). As a result, it was possible to concentrate the products in fractions with heptaldehyde and methyl undecenoate in atmospheric distillation. It is the first step for the technical viability and up-scaling of the thermal cracking of the inedible oil process for producing green chemicals.

Literature revision shows the same doubts about which raw material is better for producing a green chemical in terms of heptaldehyde and undecenoate acid (or methyl undecenoate) by thermal cracking. Thus, the main objective of the present work was to evaluate the continuous production of undecylenic acid, heptaldehyde, and methyl undecenoate from thermal cracking in a pilot-plant scale reactor of different materials (castor oil, methyl ester of castor oil, and ricinoleic acid) under different temperatures and residence times. Furthermore, the effects of the residence time and temperature on the product yields, the composition of the non-condensable gases, and the physical-chemical properties of the bio-oil produced, such as density and acid index, were considered.

MATERIALS AND METHODS

Materials

The materials used in experiments of thermal cracking were castor oil from Campestre Vegetable Oils (São Paulo/SP, Brazil), ricinoleic acid from A. Azevedo Oils Industry (São Paulo/SP, Brazil), while the methyl esters were obtained by methylic transesterification of castor oil (MECO) at 65 °C for 2h (FURB, Blumenau/SC, Brazil). The other reagents were obtained from Brazilian suppliers with the purity specifications recommended by the methods and used without any treatment. These materials were analyzed using gas chromatography (GC), whereas the bio-oil produced was analyzed according to standard methods such as density ASTM D4052, acidity index ASTM D664 and iodine index EN 14111.

Methyl ester production

Methyl ester of castor oil was obtained by homogeneous transesterification with the following conditions: reactions were carried out in a 3 L batch reactor; castor oil and methanol were used as reagents in 1:6 and 1:9 stoichiometric excess (i.e., castor oil to methanol) [15]; and with 1% (oil basis) potassium hydroxide (KOH) as a catalyst. The transesterification reaction started by adding methoxide (methanol with potassium hydroxide) to castor oil at 65 °C, 120 rpm for 2 h. Samples were collected for gas chromatography to determine their esters contents according to European Standard EN 14103. In addition, esters obtained from different reactions were well mixed to form a standard sample for thermal cracking experiments.

Thermal cracking to bio-oil production

Thermal cracking experiments in a continuous pilot-plant scale reactor (Figure 1) to produce bio-oils were conducted using the same reactor with a cylindrical tube and an internal screw and operation procedure as described in Botton *et al.* [8,16]. For the three materials emulsified with 25% distilled water, the mass flow rate was 400 g/h at several temperatures of 530 °C, 545 °C, 560 °C, and 575 °C under steady and isothermal conditions. All the experiments were carried out in triplicate to confirm the reproducibility of the thermal cracking procedure.

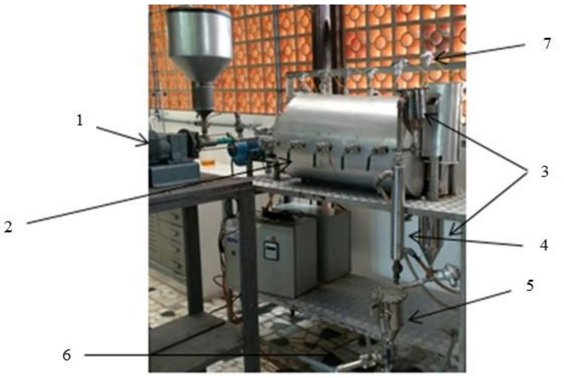


Figure 1. Reactor unit: 1 - Feeding, 2 - Reaction section, 3 - Expansion tanks, 4 - Condensing system, 5 - Flash: the collection of condensable gases occurs, 6 - Collection of non-condensable gases, 7 - Type "K" thermocouples, 8 - SCADA System (Supervisory Control and Data Acquisition).

The products yields (bio-oil and non-condensable gases) were calculated as follows: for the yield of bio-oil, it was considered the mass obtained at the end of the reactor divided by the mass fed; for the gas yield, the mass of the gas produced was divided by the mass of material fed into the reactor. Otherwise, the residence time was calculated as a function of the compositions of the bio-oil and non-condensable gas coupled with the thermal cracking temperature and pressure (atmosphere pressure), using the ideal gas model for density prediction and assuming a plug flow inside the reactor, following previous publications from the research group [8,17].

Gas chromatography analysis

The fatty acid content in the castor oil was esterified with methanolic sulfuric acid before submission to gas chromatography/mass spectrometry (Shimadzu GCMS-QP2010 Plus), according to Botton *et al.* [8]. The fatty acids were identified by comparison of the NIST 08 Mass Spectral Database.

Methyl ester content, obtained from methanolysis of castor oil, was determined using a GC- 7890B (Agilent, Santa Clara, EUA) equipped with flame ionization detector analysis (GC-FID) and Stabilwax capillary column according to Menshhein et al. [13,14] however with a split ratio of 1:50. The ester content (in mass percentage) was determined relative to the peak area of the internal standard (EN, 2003).

The non-condensable gas contents were determined by gas chromatography-flame ionization detection/thermal conductivity detection (GC-FID/TCD) using a Shimadzu GC-17A (Agilent, Santa Clara, EUA) according to Beims *et al.* [18]. The quantified components of non-condensable gases were CO, CO_2, methane, hydrogen and light hydrocarbons in the C_2–C_4 range.

Bio-oil samples obtained by thermal cracking of castor oil, ricinoleic acid and methyl esters were analyzed using the same GC-FID equipment with a split ratio of 1:200, according to Menshhein *et al.* [13,14]. The compounds were identified by comparison of their retention times with those of heptaldehyde, undecylenic acid, and methyl undecenoate standards (Sigma Aldrich). The color maps with yield information as a function of temperature and residence time for the different raw materials were constructed from numerical interpolation of experimental data.

RESULTS AND DISCUSSION

Composition of the feed materials

The fatty acid composition of castor oil obtained by GC-MS was 89.72%, 5.12%, 3.86%, 0.88%, and 0.42% for ricinoleic, oleic, linoleic, stearic and palmitic acid, respectively. This result confirms the major presence of ricinoleic acid in castor oil samples, as described in the literature [19,20], between 85% and 95%. Furthermore, in the GC analysis of the methyl esters samples, the final ester content was 80.14% with 66.8% of methyl ricinoleate, confirming its predominance in the mixture.

Thermal cracking experiments

The experiments were carried out in a pilot plant at four temperatures with the residence times ranging from 17 s to 32 s, approximately, under the continuous mode of operation, at steady-state and isothermal conditions, as shown in Table 1. Bio-oil yields from the castor oil, ricinoleic acid and methyl ester decrease from 84%, 81% and 81% to 57%, 48% and 70%, as a function of the temperature increase from 530 °C to

575 °C, respectively. When lower temperatures were used, castor oil presented the highest bio-oil yields, 530 °C (84%) and 545 °C (78%). On the other hand, with higher temperatures, methyl ester showed the highest bio-oil yields, for instance, at 560 °C (72%) and at 575 °C (70%). This fact might be related to the reaction activation energy, once methyl ricinoleate has a value of 172.9 kJ/mol [12], whereas castor oil has a reaction activation energy of 51 kJ/mol [21]. So, a lower reaction activation energy is expected to lead to a higher number of cracking reactions, forming more components with short chains and leading to a higher gas phase yield. In the study of Ganesan *et al.* [20], the catalytic cracking of castor oil was performed at 400 °C using a catalyst (AlMCM-41), and the liquid yield obtained was also around 85%. On the other hand, Nazarudin *et al.* [22–24] performed the catalytic cracking at 450 °C of used cooking oil and methyl esters of cooking oil, giving liquid yields of 35.6% and 38.85%, respectively, showing a lower yield of gas phase for methyl esters.

Table 1. Mass balance and residence time from thermal cracking products.

Run	T (°C)	Feed material	Residence time (s)	Yields (%)	
				Non-condensable gas	Bio-oil
1		Castor oil	28.74±1.07	12.6±1.2	83.9±3.6
2	530	Ricinoleic acid	26.63±3.18	12.8±0.4	81.4±9.7
3		MECO	32.09±4.15	11.5±2.3	81.7±9.9
4		Castor oil	26.73±1.83	15.3±1.4	78.1±6.0
5	545	Ricinoleic acid	23.98±3.70	17.6±0.4	73.1±13.3
6		MECO	30.17±3.51	12.8±1.7	76.9±8.6
7		Castor oil	23.41±1.35	19.9±1.8	68.7±3.9
8	560	Ricinoleic acid	21.52±1.40	20.3±0.6	66.2±4.6
9		MECO	28.26±3.56	20.9±2.6	72.1±9.2
10		Castor oil	20.30±1.91	30.1±5.6	57.3±6.5
11	575	Ricinoleic acid	17.12±4.8	34.6±2.8	48.4±17.9
12		MECO	27.10±2.73	23.8±2.4	70.0±8.0

Results of Table 1 also show that residence time decreases as temperature increases. This behavior was observed for the three materials, but ricinoleic acid had the shortest residence time for all the evaluated temperatures, and the methyl ester had the longest. It is because methyl ester produces fewer gases than ricinoleic acid and castor oil, reducing its velocity inside the reactor.

Figure 2 presents the samples' volumetric percentages of the gases (CO_2, H_2, CH_4, CO, and C_2–C_4). The presence of CO and CO_2 is observed, confirming decarbonylation (CO release) and decarboxylation (CO_2 release) reactions. CO is produced in a higher concentration than CO_2 in the thermal cracking of methyl esters. It can be explained by the fact that thermal cracking promotes the breakdown of triacylglycerol into free fatty acid and glycerol, which decomposes into acrolein, and the decomposition of acrolein generates CO. This behavior was shown to be similar for castor oil and ricinoleic acid, with lower CO contents due to the absence of glycerol and acrolein. For castor oil, the average was 33.65% CO and for ricinoleic acid, 22.6%. The formation of methane (CH_4) and H_2 was also observed, and the difference grouped in larger volumes of C_2–C_4 compounds, characterizing the intensifications of secondary reactions in the thermal cracking.

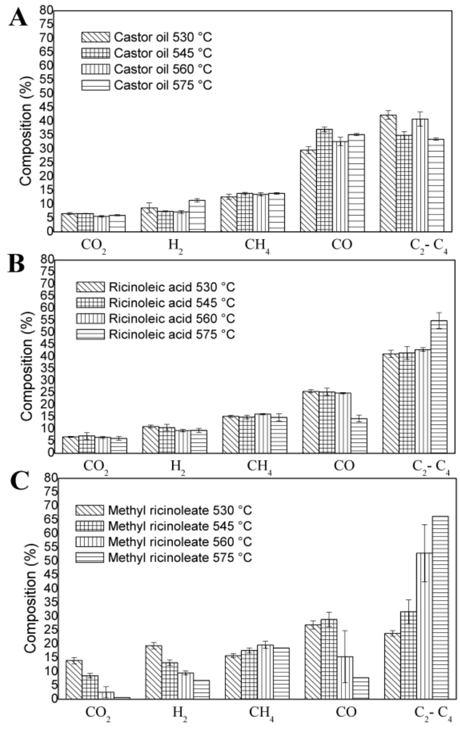
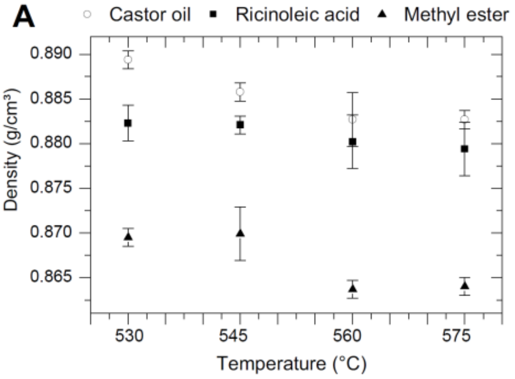


Figure 2. Composition of the non-condensable gases generated for (a) castor oil, (b) ricinoleic acid, and (c) methyl ricinoleate.

The variation in the density of the liquid products (Figure 3A) was obtained using a pycnometer. It was observed that there was a slight reduction in density as a function of temperature in all experiments. This density drop is due to reactions that divide the larger chains into smaller chains, creating products with smaller molar masses.



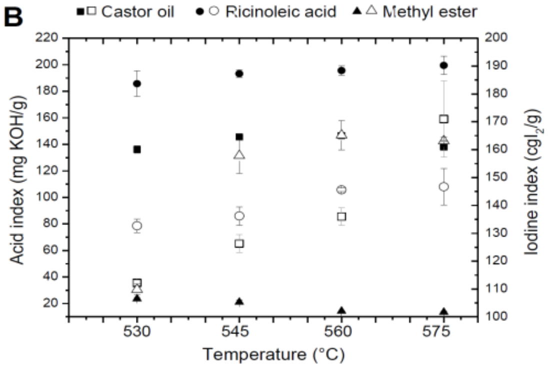


Figure 3. Values of (a) density, (b) acid index (■, ● and ▲), and iodine index (□, ○ and Δ) for castor oil bio-oils, ricinoleic acid, and MECO after thermal cracking at 530, 545, 560 and 575 °C.

The acidity indexes in Figure 3B for the bio-oils increased in relation to the index of each corresponding feed material. The acidity of the bio-oil of castor oil presents a slight increase at 545 °C and then stabilizes. The increase in the acidity index for the bio-oil of castor oil and the bio-oil of ricinoleic acid is because the increase in temperature promotes a higher formation of short-chain carboxylic acids in the secondary reactions. For the ricinoleic acid bio-oil, there was a change as a function of the increase in temperature, with a slight increase from 185.7 mg KOH/g (530 °C) to 199.5 mg KOH/g (580 °C). The decrease in the acidity index of methyl ricinoleate in higher temperatures is related to the higher formation of esters, promoting a reduction in the values starting at 530 °C with 23.6 (mg KOH/g) and ending with 13.5 (mg KOH/g) at 575 °C. For the castor oil bio-oil, the iodine index gradually increases with the temperature, going up from 110 cg I_2/g to 171.0 cg I_2/g with a cracking temperature of 575 °C. It shows that for this temperature, an increase occurs in the breaking reactions forming more unsaturated compounds for the castor oil bio-oil. For the bio-oil of ricinoleic acid, the increase was also gradual for all temperatures, with a higher value of 146.7 cg I_2/g. For the bio-oil of methyl ricinoleate, its greatest variation was from 109.8 at 530 °C to 165.2 cg I_2/g at 560 °C, showing a higher intensity of cracking reactions at higher temperatures.

Green chemical production

All the results of the chromatograms are compared through software (GCM Solution) with its data and compound library (NIST). This software presents a probability of the compounds' identity based on the chromatographic column's retention times and their mass spectra. In the castor bean bio-oil chromatogram (Figure 4A), the volumetric percentage of heptaldehyde and undecylenic acid was determined, with a retention time of 7.97 min for heptaldehyde and 34.8 min for undecylenic acid, respectively. These are the components of higher concentration and targets of this investigation. However, the other compounds had smaller peaks, which make up the total volumetric percentage. Figure 4B and Figure 4C show the chromatograms of the bio-oils obtained at 530 °C of ricinoleic acid and methyl ricinoleate, respectively. The first shows the presence of heptaldehyde, methyl undecenoate, and undecylenic acid from the unconverted triglyceride portion in the esterification. The percentages were obtained by comparison with the methyl undecenoate, heptaldehyde, and undecylenic acid standards.

The final values of the yields of the green chemical produced are given in Table 2. For castor oil, the best yield of the heptaldehyde and undecylenic acid mass yields occurred at 530 °C with 19.03% and 16.5%, respectively. The yield values for ricinoleic acid were 530 °C for both heptaldehyde and ricinoleic acid, with results of 15.2% and 17.8%, respectively.

Methyl ricinoleate obtained its best mass percentage result for heptaldehyde at 530 °C and methyl undecenoate at 560 °C with 20.7% and 23.8%, respectively. Based on these results, the best result for producing heptaldehyde was 20.7% of mass yield at 530 °C, with the methyl ricinoleate material. The best result for the production of undecylenic acid occurred with the thermal cracking of ricinoleic acid, with its mass yield occurring at 530 °C, with a value of 17.8%. For the production of methyl undecenoate, the best temperature was 560 °C, with a mass value of 23.8.

The yield of desirable products was calculated considering the bio-oil yield. The response surface plots are presented in Figure 5 and Figure 6, with

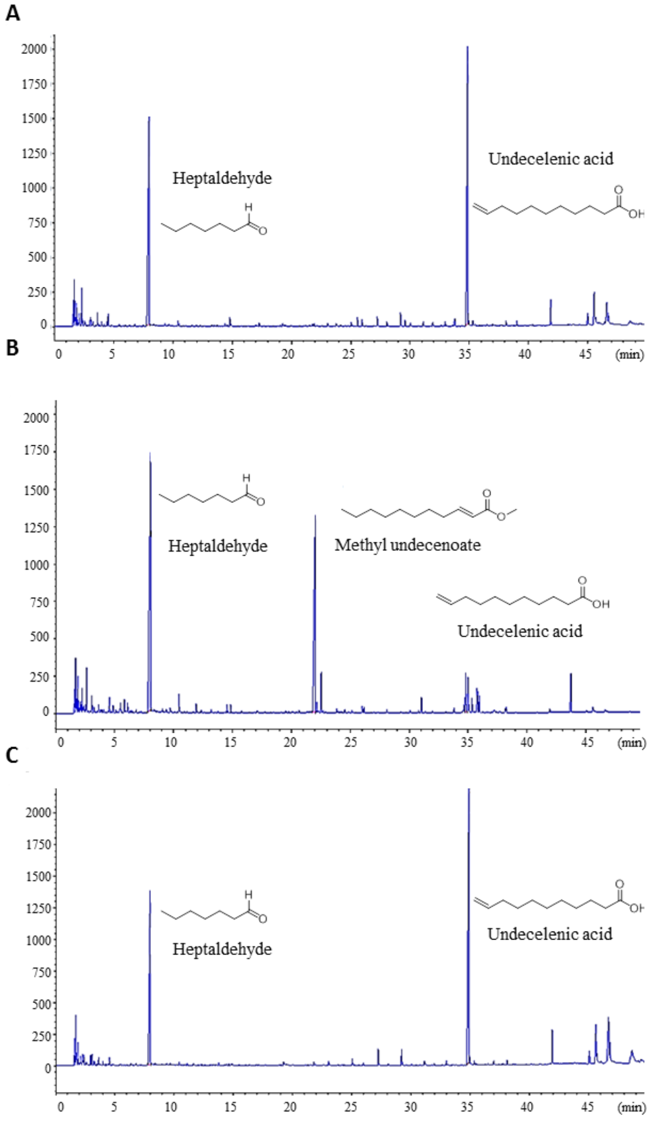


Figure 4. Chromatogram of bio-oil from thermal cracking with 25% of water at 530 °C of (a) castor oil, (b) MECO, and (c) ricinoleic acid.

Table 2. Mass yields of the green chemicals produced - heptaldehyde, undecylenic acid, and methyl undecenoate.

T (°C)	Feed material	Heptaldehyde (%)	Undecylenic acid (%)	Methyl undecenoate (%)
529.7±0.8	Castor oil	9.3±1.4	16.5±1.6	ND*
544.7±0.6		7.9±1.6	15.6±1.6	ND
559.6±1.1		5.1±1.0	13.1±0.8	ND
574.2±0.9		2.3±1.4	10.1±1.4	ND
528.9±2.2	Ricinoleic acid	5.2±1.8	17.8±2.7	ND
544.8±4.5		3.8±2.2	15.7±2.8	ND
557.2±4.4		2.5±0.7	14.4±0.3	ND
580.2±8.3		.5±3.2	9.2±3.4	ND
529.7±0.8	Methyl ester	0.7±3.7	0.8±0.3	20.9±6.1
544.7±0.6		9.7±2.2	1.0±0.3	22.4±3.9
559.6±1.1		8.8±2.1	0.9±0.2	23.8±4.5
574.2±0.9		7.0±2.3	0.8±0.1	23.4±3.5

products yield surface plots as a function of residence time and temperature. Response surfaces were obtained using experimental data, and this analysis provides a possibility of scientific visualization of the entire experimental set in a single color map. The contour plots depict that heptaldehyde behavior was similar for all three materials (Figure 4). The highest yield was achieved at the maximum values of residence time and lower temperatures. Undecylenic acid (Figure 6b) from castor oil and ricinoleic acid also presented this behavior. However, the best conditions for the undecylenic acid from MECO were intermediate temperature and residence time conditions.

If considering that 1 mol of methyl undecenoate generates 1 mol of undecylenic acid, it was possible to relate the methyl undecenoate yield with its acid and thus to compare the results with a base calculation of 1000 g of crude oil with 1000 g of castor oil yield ± 873 g of methyl ricinoleate. With these comparisons, it is clear that the cracking of methyl ricinoleate presented the highest value for producing heptaldehyde when considering the deviation. It was also the one that produced the most undecylenic acid. However, these results show that the yields of desirable products remain lower than expected for commercial-scale production using only the thermal cracking process. In fact, this suggests the use of a catalyst for increasing the selectivity of the cracking in heptaldehyde and undecylenic acid for future investigations.

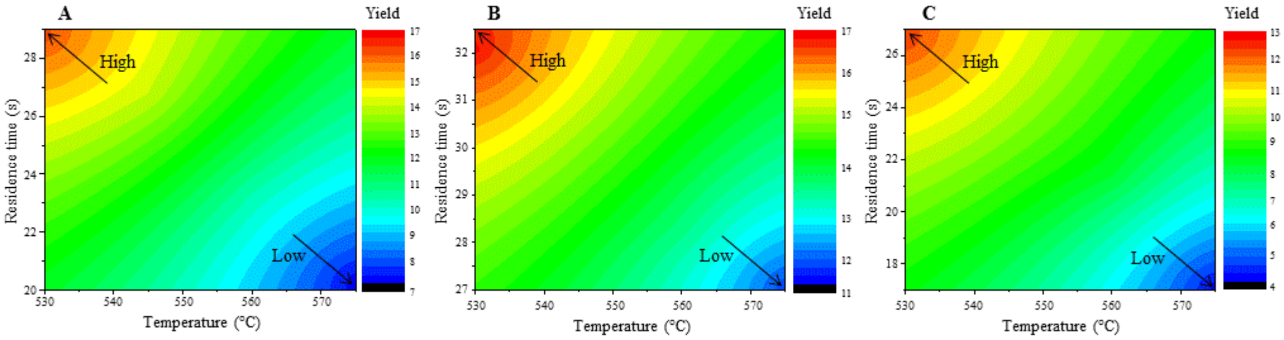


Figure 5. Response surface of heptaldehyde yield from (a) castor oil, (b) MECO, and (c) ricinoleic acid.

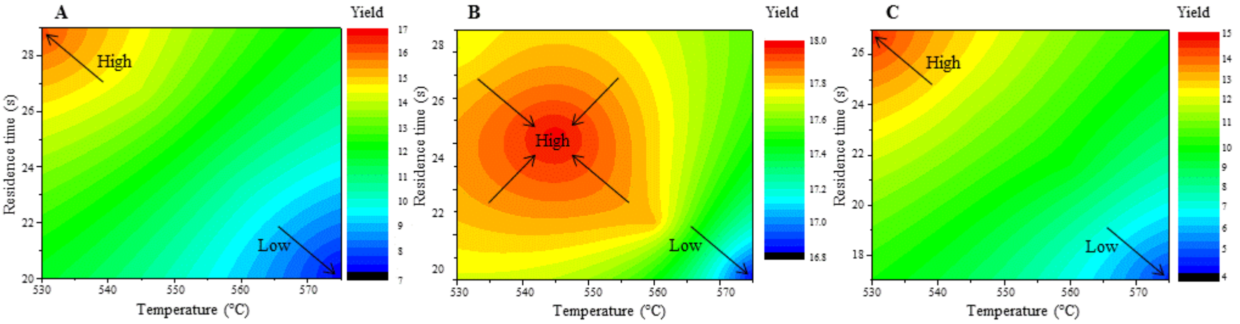


Figure 6. Response surface yield: (a) undecylenic acid yield from castor oil, (b) undecylenic acid and methyl undecenoate from MECO, and (c) undecylenic acid yield from ricinoleic acid.

CONCLUSION

Among the conditions proposed in this work, the best condition for the production of heptaldehyde and undecylenic acid occurred with the thermal cracking of methyl ricinoleate at 530 °C and 560 °C, respectively. While the best mass yield value for heptaldehyde was 20.7%, and the best mass yield value for undecylenic acid (as ester) was 23.8%.

Compared to the yields of castor oil and ricinoleic acid, the production of heptaldehyde was favorable for using castor oil and more favorable for ricinoleic acid in the production of undecylenic acid. It was possible to see the presence of the formation of glycerol and acrolein by its decomposition through the difference in the generated volume of carbon monoxide, which was higher for castor oil. The thermal cracking of methyl ricinoleate presents a smaller volume of secondary reactions in relation to castor oil and ricinoleic acid, yet this fact needs further evaluation. On the other hand, the use of catalysts to make the process more attractive for commercial production appears like a good opportunity for future work.

ACKNOWLEDGEMENT

The authors are grateful to the University of Blumenau (FURB) and the Chemical Engineering Department of FURB. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior e Brasil (CAPES) Finance Code 001.

REFERENCES

[1] H. Mutlu, M.A.R. MeierEur. J. Lipid Sci. Technol. 112 (2010) 10–30. http://dx.doi.org/10.1002/ejlt.200900138.

[2] X. Mao, Q. Xie, Y. Duan, S. Yu, Y. Nie, Appl. Therm. Eng. 194 (2021) 117093. http://dx.doi.org/10.3390/ma15041565.

[3] E.B. Mubofu, Sustain. Chem. Process. 4 (2016). https://doi.org/10.1186/s40508-016-0055-8.

[4] M. Van der Steen, C.V. Stevens, ChemSusChem. 2, (2009) 692–713. https://doi.org/10.1002/cssc.200900075.

[5] W.J. Kh'ng, W.A. Ibrahim, Z. Hassan, I. Izirwan, Energy Reports. 8, (2022) 11–18. https://doi.org/10.1016/j.egyr.2022.10.111.

[6] S. Singh, S. Sharma, S.J Sarma, S.K. Brar, Environ. Prog. Sustain. Energy. 42 (2022) E14008. https://doi.org/10.1002/ep.14008.

[7] FAOSTAT Statistical Database (2019), Food and Agriculture Organization of the United Nations, http://www.fao.org/faostat/en/#compare [accessed 7 December 2021.

[8] V. Botton, R. Torres De Souza, V.R. Wiggers, D.R. Scharf, E.L. Simionatto, L. Ender, H.F. Meier, J. Anal. Appl. Pyrolysis 121 (2016) 387–393. http://dx.doi.org/10.1016/j.jaap.2016.09.002.

[9] G. Das, R.K. Trivedi, JAOCS 66 (1989) 938–941. https://doi.org/10.1007/BF02682613.

[10] C. Tang, Z. Yuan, Catalytic cracking method for preparing 10-undecenoic acid and heptaldehyde - PCT CN103819330 (2014).

[11] G. Wetroff, L. Thillay, G. Divachetf, J. Khaladji, Pyrolysis of Ricinoleates - PCT US2807633 (1957).

[12] H. Guobin, L. Zuyu, Y. Suling, Y. Rufeng, JAOCS 73 (1996) 1109–1112. https://doi.org/10.1007/BF02523370.

[13] G. Menshhein, V. Costa, L.M. Chiarello, D.R. Scharf, E.L. Simionato, V. Botton, H.F. Meier, V.R. Wiggers, L. Ender, Renew. Energy 142 (2019) 561–568. https://doi.org/10.1016/j.renene.2019.04.136.

[14] G. Menshhein, V. Costa, L.M. Chiarello, D.R. Scharf, E.L. Simionato, V. Botton, H.F. Meier, V.R. Wiggers, L. Ender, Data Br. 25 (2019) 104325. https://doi.org/10.1016/j.dib.2019.104325.

[15] K. Ramezani, S. Rowshanzamir, M.H. Eikani, Energy 35 (2010) 4142–4148. https://doi.org/10.1016/j.energy.2010.06.034.

[16] V. Botton, D.R. Riva, E.L. Simionatto, V.R. Wiggers, L. Ender, H.F. Meier, A.A.C. Barros, Quim. Nova 35 (2012) 677–682. https://doi.org/10.1590/S0100-40422012000400004.

[17] H.F. Meier, V.R. Wiggers, G.R. Zonta, D.R. Scharf, E.L. Simionatto, L. Ender, Fuel 144 (2015) 50–59. https://doi.org/10.1016/j.fuel.2014.12.020.

[18] R.F. Beims, V. Botton, L. Ender, D.R. Scharf, E.L. Simionatto, H.F. Meier, V.R. Wiggers, Fuel 217 (2018) 175–184. https://doi.org/10.1016/j.fuel.2017.12.109.

[19] D.P. Matharasi, G. Ramya, A. Asha, P. Jayaprakash. J. Indian Chem. Soc. 99, (2022) 100757. https://doi.org/10.1016/j.jics.2022.100757.

[20] R. Ganesan, S. Subramaniam, R. Paramasivam, J.S.M. Sabir, J.S. Femilda Josephin, K. Brindhadevi, A. Pugazhendhi, Sci. Total Environ. 757 (2021) 143781. https://doi.org/10.1016/j.scitotenv.2020.143781.

[21] C.A. Canciam, E-xacta 4 (2011) 7–18. http://dx.doi.org/10.18674/exacta.v4i3.667.

[22] I.G. Prabasari, R. Sarip, S. Rahmayani, N. Nazarudin, Makara J. Sci. 23 (2019) 162–168. https://doi.org/10.7454/mss.v23i3.11264.

[23] N. Nazarudin, U. Ulyarti, O. Alfernando, Y.Y. Hans, Reaktor. 22, (2022) 21–27. https://doi.org/10.14710/reaktor.22.1.21-27.

[24] N. Nazarudin, I.G. Prabasari, U. Ulyarti, Susilawati, A. Oktadio, J. Phys. Conf. Ser. 1567 (2020) 022021. https://doi.org/10.1088/1742-6596/1567/2/022021.

VANDERLEI RODRIGUES COSTA[1]
LUANA MARCELE CHIARELLO[1]
VANDERLEIA BOTTON[1]
EDÉSIO LUIZ SIMIONATTO[2]
VINICYUS RODOLFO WIGGERS[1]
HENRY FRANÇA MEIER[1]
LAÉRCIO ENDER[1]

[1]Chemical Engineering Department, University of Blumenau - FURB, Blumenau, SC, Brazil

[2]Chemistry Department, University of Blumenau - FURB, Blumenau, SC, Brazil

NAUČNI RAD

ZELENA HEMIJSKA PROIZVODNJA ZASNOVANA NA TERMIČKOM KREKOVANJU NEJESTIVOG BILJNOG ULJA

Ovaj rad procenjuje proces proizvodnje heptaldehida, undekilenske kiseline i metil undecenoata iz ricinusovog ulja, metil estra ricinusovog ulja i ricinoleinske kiseline. Eksperimenti su izvedeni u kontinualnom poluindustrijskom pirolitičkom reaktoru. Termičkim krekovanjem ricinusovog ulja dobijeni su veoma važni zeleni hemijski proizvodi. Transesterifikacija ricinusovog ulja proizvodi metil ricinoleat, a njegovo termičko krekovanje stvara metil undekenoat i heptaldehid. Ispitivanje pirolize izvršeno je na 530 °C, 545 °C, 560 °C i 575 °C, sa vremenom zadržavanja od 17 s do 32 s i masenim protokom pri 400 g/h mešavine materijala sa 25% destilovane vode. Uočen je uticaj temperature i vrste polazne sirovina na proizvedeno bio-ulje. Bio-ulje je okarakterisano jodnim i kiselinskim brojem i masom, a sastav je određen GC-FID hromatografijom. Najbolji rezultat za maseni prinos undekilenske kiseline postignut je na 530 °C, i to 17,8% od ricinolne kiseline i 16,5% od ricinusovog ulja. Za heptaldehid je, takođe, najveća proizvodnja dobijena na 530 °C, sa vrednošću od 20,7% od metil estra i 15,2% od ricinolne kiseline.

Ključne reči: piroliza triglicerida, ricinusovo ulje, ricinolna kiselina, heptaldehid, undekilenska kiselina, metil undekenoat.