HEPTALDEHYDE AND UNDECYLENIC ACID FROM *RICINUS COMMUNIS*: KINETICS AND PROCESS DESIGN

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Ricinus communis is a non-food plant, one of the main products of the plant are the seeds from which castor oil is extracted. Castor oil pyrolysis produces heptaldehyde and undecylenic acid. A kinetic model of this reaction is not reported in the literature. The simulation and economic evaluation of this process are not possible without an appropriate kinetic and thermodynamic model. A pseudo-first-order kinetic model for the pyrolysis reaction was obtained in a semicontinuous reactor. Kinetic parameters were obtained at 2.67 kPa, the frequency factor of 19.2 s^{-1}, and the activation energy of 54013.3 kJ/kmol. A conceptual design for the process was proposed. The process was simulated in Microsoft Excel® using add-ins developed for the authors. The main equipment was sized. Capital costs, operating costs and financial profitability were estimated. In accordance with an internal rate of return of 44%, the project proved attractive for the investors. Finally, the results indicated that the castor oil pyrolysis is feasible, thus the *Ricinus communis* crop could be valorized into high value-added products.

Keywords: heptaldehyde, undecylenic acid, *Ricinus communis*, kinetics, pyrolysis

INTRODUCTION

The castor oil plant (*Ricinus communis*), a member of the spurge family (Euphorbiaceae), is native to tropical Asia and Africa.[1] Today, it is grown on a commercial scale around the world in temperate zones. Leader countries in castor oil production are estimated to be: India, China, Brazil, Thailand, Ethiopia and Russia, while leading importers are Germany, Netherlands, France, United Kingdom, United States, Brazil, China, Japan and Thailand.[2] Like other vegetable oils, castor oil can be extracted by a variety of processes or a combination of them, such as presses and solvent extraction. The mechanical isolation method is preferable in comparison with the solvent extraction method. However, a disadvantage of this method is the low yield, therefore solvent extraction is often applied for the remaining oil.[3] Castor oil can have different physical and chemical properties. However, regardless of its origin country or season in which it is grown, its chemical composition remains relatively constant.[4] Castor oil is a triacylglycerol composed of various fatty acids and glycerol. Fatty acids are composed of more than 89% ricinoleic acid and small amounts of saturated and unsaturated fatty acids.[5] The hydroxyl group, ester bond and double bond in castor oil provide reaction sites for obtaining useful industrial products. Today, castor oil is used for applications such as functional liquids and process oils, raw materials for fuels and oleochemicals, reactive components for paints, coatings and inks, polymers, foams etc.[4–6] Meanwhile, the hydroxyl group may be alkoxylated and can be removed by dehydration to increase the unsaturation of the molecule.[7] The hydroxyl position is so reactive that the molecule can be split at this point by pyrolysis at high temperature. Triacylglycerols pyrolysis is not as well established as that related to other sources, such as lignocellulosic biomass. There are few studies investigating the triacylglycerols pyrolysis, these studies can be divided into two categories. One focuses on the pyrolysis of model triacylglycerols for food science research, while the other is devoted to the pyrolysis of vegetable oils and fats for fuel and chemicals applications.[8]

Mainly, heptaldehyde (C7), undecylenic acid (C11) and a low proportion of non-condensable products are obtained from the castor oil pyrolysis. Heptaldehyde and undecylenic acid are imported by Colombia, these are employed in

sectors, such as the pharmaceutical, cosmetics and toiletries industries. Pyrolysis is carried out in a semicontinuous reactor, the products are removed and condensed. Pyrolysis is not possible in a batch reactor because the products must be removed for the reaction to proceed. Castor oil conversion under these conditions must not exceed 46%, a resinous substance is formed, which can not be pyrolysed under working conditions.

Considering that castor oil also has a great demand due to a large number of industrial applications, in Colombia, as well as in countries such as Spain, France, Germany, Costa Rica, Ecuador and Brazil, the objective of this work has been to determine the kinetics of castor oil pyrolysis, at vacuum pressures, and temperatures of no more than 400 °C, in a semicontinuous reactor. The weight loss of castor oil is quantified from the mass of the products generated. With a kinetic model for the pyrolysis reaction and an appropriate thermodynamic model, it is possible to design the process and optimize its conditions. Finally, in the perspective of using castor oil as precursor of C7 and C11, the *Ricinus communis* plant may become a good source crop to be exploited for high value-added products in Colombia.

EXPERIMENTAL

Castor oil characterization

The castor oil employed was of commercial origin. Its physico-chemical characterization included: appearance (visual description), specific gravity (at 25 °C) according to ASTM D-891-95, moisture according to ASTM D-5556-95, saponification index according to ASTM D-1962-85, acid number (acid value) according to ASTM D-465-05, solubility according to ASTM D-960, refraction index (at 25 °C) according to ASTM D-1218-12 using a digital refractometer (Abbe), and apparent viscosity (at 25 °C) by a flow test using a DHR-2 rheometer (TA Instruments).

Castor oil pyrolysis in a semicontinuous reactor

Castor oil samples (about 100 g) were pyrolysed at variable temperature, no more than 400 °C, at pressures between 2.67-10.67 kPa, in a glass flask of 500 mL with three necks. The first neck had a thermocouple with its indicator. The second neck had a Claisen glass multipurpose adapter, which prevented the boiling liquid from passing to the condenser. The vapors generated passed to a rectum condenser, whereby reaction products were condensed. The third neck remained closed. The products were separated by fractional distillation, and the fractions collected were analyzed by FTIR. This method to separate and identify compounds is as good as chromatography when azeotropes are not formed.

Rate data analysis

In the semicontinuous system in which pyrolysis occurred, the weight loss of castor oil was quantified from the mass of products generated over time. These data were used to determine the rate law. The detailed procedure is as follows: from the mass variation of the product over time, dN_{CO}/dt (CO, castor oil) and the reaction volume in time were determined. Using previous data and Equation 1 (molar balance of castor oil), the experimental reaction rate was determined. The castor oil concentration was determined in the reactor, and a pseudo-first-order kinetic model was proposed, Equation 2:

$$r_{\text{exp}} = \frac{-dN_{CO}/dt}{V} \quad (1)$$

$$r_{\text{mod}} = A\exp\left(\frac{-E}{RT}\right)C_{CO} \quad (2)$$

In Equation 1: r_{exp}, experimental reaction rate; V, reaction volume. In Equation 2: r_{mod}, model reaction rate; A, frequency factor; E, activation energy; R, gas constant; T, absolute temperature; C_{CO}, castor oil concentration in the reactor.

Separation and identification of main pyrolysis products

Heptaldehyde and undecylenic acid were collected in the glass flask (250 mL) of one neck. To this flask, a fractional distillation column was attached. Temperature was continuously recorded to associate to the distillates obtained. The products obtained at different temperatures were collected and analyzed by FTIR and compared with the analytical standards of the products expected. The products were analyzed by Fourier Transform with attenuated total reflectance (FTIR-ATR) at 20 °C using an infrared spectrophotometer of the 6700 series Nicolet equipped with ATR type IIA, diamond crystal, wavelength range of 4000-400 cm^{-1}, and a spectral resolution of 4 cm^{-1}. The spectrum was averaged over sixty four sweeps.

Cost estimation and financial evaluation of castor oil pyrolysis

A cost estimate offers information to propound a cash flow model, which serves as basis for the financial evaluation. Capital costs were estimated according to the Guthrie Method.[9] Operating costs were estimated considering that each cost is directly proportional to one or to the sum of some of the following costs: fixed capital investment, raw material costs, waste treatment costs, utilities costs, and labor costs.[10] For the evaluation and for profitability calculation, an operating time horizon of 10 years and a pre-operating period of 2 years were considered. Finally, from the cash flow, the net present value

(NPV) and the internal rate of return (IRR) were calculated.

RESULTS AND DISCUSSION

Castor oil characterization

Table 1 presents the physico-chemical characterization results of castor oil, reference values and the relative errors.

Castor oil pyrolysis in a semicontinuous reactor and rate data analysis

Pyrolysis was carried out at variable temperatures and pressures between 2.67-10.67 kPa. A pseudo-first order kinetic model was chosen to fit the experimental data (at 2.67 kPa) by a nonlinear regression using the objective function of Equation 3. The fitting parameters were the frequency factor (19.2 s^{-1}) and the activation energy (54,013.3 kJ/kmol).

$$O.F. = \sum_{i=1}^{N} (r_{i,\exp} - r_{i,\mathrm{mod}})^2 \qquad (3)$$

Separation and identification of main pyrolysis products

The heptaldehyde and undecylenic acid obtained in the laboratory were identified by FTIR-ATR. These products were compared with their analytical standard. A better coincidence (97.0%) was obtained for heptaldehyde than for the acid (87.4%), so it is possible that the acid should be distilled again to increase its purity.

Cost estimation and financial evaluation of castor oil pyrolysis

The pyrolysis reaction (Equation 4) to obtain heptaldehyde and undecylenic acid, with species (Equation 5) and energy (Equation 6) balances, allows performing simulations of the reactor. Furthermore, a thermodynamic model was used to determine equilibrium conditions (Equation 7), thermal and volumetric properties. This predictive model is based on a cubic equation of state proposed by Forero and Velásquez,[12] this equation is generalized for all types of substances in terms of critical temperature (Tc), critical pressure (Pc), acentric factor, polar factor, Bures constants and heat formation (ΔH^0_f) (see Table 2). The above critical properties and constants were calculated according to group contribution methods reported in the literature.[13]

$$C_{57}H_{104}O_9 \rightarrow 3.7C_7H_{14}O + 2.3C_{11}H_{20}O_2 + Non-condensable$$

$$\frac{dn_i}{dt} + N_i^{OUT} = V\alpha_i r \qquad with\ i = 1,\ldots,4 \qquad (5)$$

$$\frac{dU}{dt} + N^{OUT}H^{OUT} = \dot{Q}^{IN} \qquad (6)$$

$$\varphi_i^{L} x_i = \varphi_i^{V} y_i \qquad (7)$$

In Equation 5: N, molar flow; t, time; V, reaction volume; α, stoichiometric coefficient; and r, reaction rate. In Equation 6: U, internal energy; H, enthalpy; and $\dot{Q}$, heat flow. In Equation 7: φ, fugacity coeffcients; x and y, molar fractions.

The conceptual design proposed consists of a jacketed CSTR reactor (R-101), where the liquid castor oil is fed, the gaseous products are then cooled and partially condensed in a heat exchanger (E-101). The liquid products are sent to a distillation tower (T-101) for purifying up to ninety-nine percent (99%). The whole process is maintained at low pressure.

Table 1
Physicochemical characterization of castor oil

Analysis	Result	Reference[11]	Relative error
Appearance	Satisfactory	Clear	---
Specific gravity (at 25 °C) (g/cm^3)	0.9661	0.9586	0.0077
Moisture (%)	0.4866	0.54	0.1096
Refraction index (at 25 °C)	1.4784	1.4775	0.0006
Saponification index (mgKOH/g)	182.1508	183.75	0.0088
Acid number (mgKOH/g)	1.8141	1.87	0.0308
Solubility	Satisfactory	Complete without turbidity	---
Apparent viscosity (at 25 °C) (Pa.s)	0.6515	0.65	0.0023

Table 2
Critical properties and some constants necessary for the thermodynamic model

Substance	Tc (°C)	Pc (kPa)	Acentric factor	Polar factor	Bures[1] (kJ/kmolK)	Bures[2] (kJ/kmolK)	Bures[3] (K)	ΔH^0_f (kJ/kmol)
Heptaldehyde	343.7	3160	0.4279	0.0124	171.71	295.32	2127.67	-269400
Undecylenic acid	435.6	2181	0.8364	-0.0137	240.71	441.32	1935.93	-495210
Castor oil*	691.1	336	0.6518	0.1027	1237.11	2292.13	1918.21	-2346100

*Triricinolein

Table 3
Equipment summary

Reactor (R-101)	Heat exchanger (E-101)
CSTR, stainless steel	Double tube, stainless steel
Free volume fraction = 0.3	Total area = 0.81 m^2
Reactor volume = 0.038 m^3	Process stream in inner tube
Reactor length = 0.36 m	Q = 75,008.01 kJ/h
Reactor diameter = 0.36 m	
Q = 22,489.88 kJ/h*	
Distillation tower	
Distillation tower (T-101)	Partial condenser (E-102)
Stainless steel	Double tube, stainless steel
3 ideal trays	Total area = 0.70 m^2
22 sieve trays plus partial condenser and reboiler	Process stream in inner tube
Partial condenser	Q = 14,525.50 kJ/h
Reboiler	
Feed on tray 11	Reboiler (E-103)
0.17 m tray spacing, 0.05 m in weirs	Electric reboiler
Column height = 4.35 m	Q = 21,523.00 kJ/h
Diameter = 0.17 m	

*It was considered that all the heat was delivered to the reactor, and the losses were not taken into account

The objective is to produce approximately 12 kg/day of each product. For reaching this objective, the most important streams in the castor oil pyrolysis are: castor oil (raw material) (1) 21,900.00 kg/year, heptaldehyde (product) (7) 3,771.08 kg/year, undecylenic acid (product) (6) 4,364.89 kg/year, process water (utility) (4, 5, 9, 10) 335,870.35 kg/year, electrical energy (utility) 4,670.00 kWh/year and vapor (residue) 195.39 kg/year (see in Fig. 1 equipment and streams).

The sizing of the reactor, heat exchanger and distillation tower was obtained considering the simulation results and heuristic rules.[10] The simulation fits well to the data obtained experimentally. Table 3 lists the equipment summary.

Capital costs, operating costs and financial profitability were estimated. Capital costs were calculated according to the Guthrie Method.[9] The results indicated that all the costs of a plant are directly proportional to the cost of acquiring the equipment. The above method introduces the concept of modular cost of an equipment (C_M), sum of direct and indirect costs of particular equipment. Thus, the total capital cost of a plant (global modular cost, C_{GM}) (see Table 4) can be calculated from the acquisition cost of the equipment and a number of proportionality factors or correction factors.[10] Operating costs as raw material cost (C_{RM}), utilities costs (C_U), waste treatment cost (C_{WT}) and labor cost (C_L) were calculated, as well as the income from the sale of the product (S) (see Table 4). When the capital and operating costs were calculated, it was possible to construct a cash flow model, which would serve as basis for the financial analysis. From these cash flows, some parameters that quantify the profitability such as net present value (NPV) and internal rate of return (IRR) were calculated (see Table 4). Further, in Table 4, the minimum acceptable rate of return (MARR) is indicated. Finally, as NPV $\geq$ 0 implies that IRR $\geq$ MARR, the project proves attractive for investors, it equals or exceeds minimum expectations.

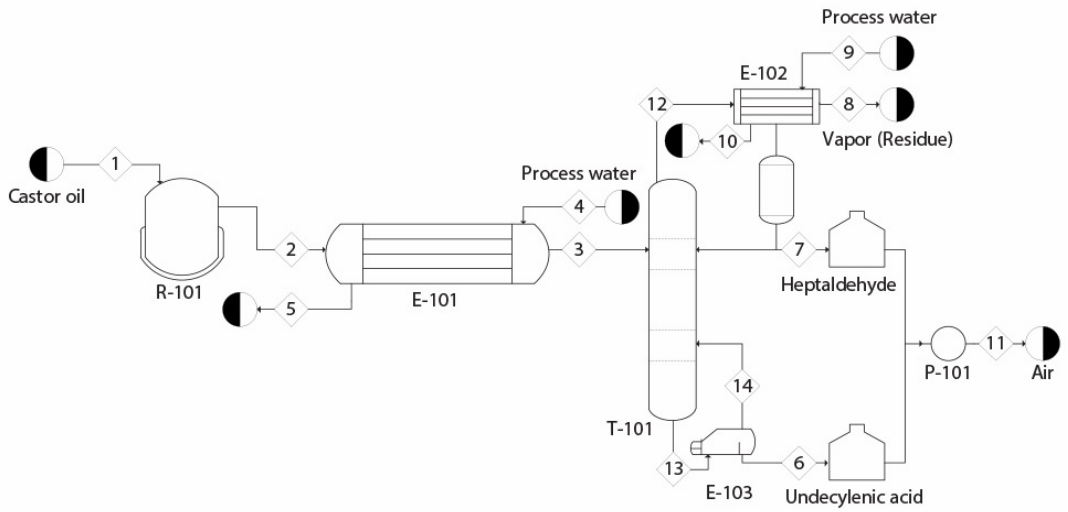

Figure 1: Process flow diagram for heptaldehyde and undecylenic acid production

Table 4
Total capital cost, operating costs and profitability from cash flow

Total capital cost (global modular cost, C_{GM})				
USD$175,736.90				
Operating costs (USD/year)				
(C_{RM})	(C_U)	(C_{WT})	(C_L)	(S)
USD$35,722.19	*USD*$1,074.36	*USD*$7.03	*USD*$39,889.29	*USD*$352,908.97
Profitability from cash flow				
(NPV)		(IRR)		(MARR)
USD$363,496.20		44%		12%

CONCLUSION

The kinetic parameters were obtained at 2.67 kPa. The achievement of the predicted products was verified by distillation and infrared spectroscopy. A conceptual design was put forward and the proposed kinetic and thermodynamic models were successfully used for the process simulation. From the simulation results and heuristic rules, the sizing of equipment was performed. As the net present value was positive, it implied that the internal rate of return was higher than the minimum acceptable rate of return, thus the project proved attractive for investors (generating additional capital), it equals or exceeds minimum expectations. The implementation of this process on an industrial scale would provide an opportunity for communities (Bajo Cauca, Antioquia, Colombia) to give added value to the *Ricinus communis* crop.

ACKNOWLEDGEMENTS: The authors wish to acknowledge the "Technical-social research project on promising oleaginous plants, as castor oil and sacha inchi plants, with a view to agro-industrial development. Partnership agreement No. 4600000480 between the Department of Antioquia-Secretary of Agriculture and Rural Development, EAFIT University and the Pontifical Bolivarian University (UPB). National Science Fund and Technology of the General Royalties System of Colombia" for their financial support.

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