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Novel Process Simulation of Biodiesel Production from Crude Castor Oil

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A continuous process flowsheet for biodiesel production from crude castor oil and methanol was developed on Aspen HYSYS™ simulation environment. It consists of an acid-catalysed sub-process for pre-treatment of the crude feedstock and a base-catalysed one for trans-esterification of treated oil. Reactions involved were defined using kinetic parameters obtained from lab-scale experiments for increased realism, and reactor setup was decided based on basic technological and economical assessments. Specifications of other unit operations and flows were obtained from different approximation methods, literature adaptation and trade-off consideration. Input and output quality controls were achieved via simple adjustments with tight tolerances. The use of crude feedstock reduced the cost of raw material while expanding the scale of the process, which managed to produce 8000 tons of biodiesel having purity of over 99 % a year. Specifically, the process could remove up to 90.83 % amount of free fatty acids in the crude oil and convert up to 93.82 % of oil to biodiesel.

1. Introduction

Petroleum, coal and natural gas amount to an 86.0 % share for non-renewable fossil fuels in primary energy consumption in the world (Canan et al., 2018). Transportation and industrial sectors are major contributors to this inclination, accounting for 92 % of the overall fossil fuel consumption, mostly diesel fuel (Bisheswar and Gopinath, 2019). Given that state of indispensability of fossil fuels, the large amount of CO_2 emission they emit and their irreproducibility have increasingly become a critical energy and environmental issue. In order to save the deteriorating environment, the need for green and renewable energy sources has been more urgent than ever, and biodiesel seems to be a promising alternative to conventional diesel fuel to meet the greenhouse gas reduction target (Rajendra et al., 2018). In addition to its cheaper investment cost, its renewability is achieved easily by chemically combining any natural oil or fat with an alcohol, such as methanol and ethanol.

Modern types of biodiesel feedstocks include oils of jatropha, karanja, mahua, linseed, cottonseed, neem, camelina and beauty leaf tree/polanga plants, many of which have been processed successfully on an industrial scale around the world. Within the scope of this study, the case of castor oil as a potential feedstock for biodiesel manufacturing will be examined and reported in details. The reason is that economy-wise, the cost of cultivation of castor plant can be 50 % of the cost of cultivation of rapeseed and 25 % of the cost of cultivation of jatropha (Safaa et al., 2018). Additionally, the castor oil-based biodiesel is superior for cold winters, because of its exceptionally low cloud and pour points (Carmen, 2005).

Mono alkyl esters that are produced from fatty acid esters of straight vegetable oil, animal oil/fats, tallow and waste cooking oil, etc. are called biodiesel (Digambar et al., 2019). The process used to convert these oils to biodiesel is called trans-esterification, which refers to a catalytic process involving triglycerides, the main component of feedstock oil, and an alcohol (usually methanol or ethanol) to yield fatty acid alkyl esters, as known as biodiesel, and glycerol. When triglycerides react with the alcohol, the three fatty acid chains are released from the glycerol skeleton and combine with the alcohol to yield fatty acid alkyl esters. Methanol is preferred over ethanol because of its kinetic (Sridharan and Mathai, 1974), technological and economic advantages and glycerol is produced as a by-product.

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The purpose of this study is to design a practical process and to provide preliminary analysis of the process' parameters on a computer model. There have been numerous attempts to design and generate computer models of a workable biodiesel plant, such as biodiesel plant utilizing waste cooking oil by Zhang et al. (2003) and biodiesel process design using virgin castor oil by Santana et al. (2010), but very few have managed to accurately describe important phenomena occurring in the process, most notably the detailed design and economic evaluation of a castor-oil-based biodiesel process by Dimian et al. (2019). With access to up-to-date research data banks and industry-applicable studies, this work aims to contribute to the global commercialization of biodiesel, forever replacing the need for fossil fuels. Aspen HYSYS™ V10 will be chosen to simulate the castor oil-based biodiesel production process due to its user-friendliness.

2. Methods and materials

To fulfill a simulation case, several preparation steps to input crucial process parameters are needed.

2.1 Chemical components involved

There are 2 main categories of chemical components available in HYSYS™: pure and hypothetical. Pure components are those whose physic-chemical parameters are already embedded in HYSYS™ database and require no further adjustment, while hypothetical components are those not available in the HYSYS™ database. The result of this study is the yield of fatty acid methyl esters (FAME) mixture having purity high enough to be classified as biodiesel. The feed stream enters the process at ambient condition, whose composition is derived from that of the Malaysian castor oil study by Jumat et al. (2010) with some modifications for simulation purposes, as presented in Table 1.

Table 1: List of chemical components simulated

Component	Pure	Hypothetical	Source	Component's mass fraction (%) in stream
Feed stream				
Triricinolein		X	Sara et al. (2018)	96.4000
Ricinoleic acid		X	Ram et al. (2017)	2.8628
Oleic acid	X		HYSYS Databank	0.2652
Linoleic acid	X		HYSYS Databank	0.2720
H_2O	X		HYSYS Databank	0.2000
Product stream				
Methyl ricinoleate		X	Santana et al. (2010)	99.61
Methyl oleate	X		HYSYS Databank	0.28
Methyl linoleate	X		HYSYS Databank	0.10
Others				
NaOH	X		HYSYS Databank	
HCl	X		HYSYS Databank	
NaCl	X		HYSYS Databank	
H_2SO_4	X		HYSYS Databank	
Glycerol	X		HYSYS Databank	
Methanol	X		HYSYS Databank	

2.2 Thermodynamic models

The Peng-Robinson-Stryjek-Vera (PRSV) package and the Non-random two-liquid (NRTL) package were chosen to accurately describe separation processes and to derive the chemical-physical properties of the non-ideal liquid phases involved in the bio-oil extraction process (Piemonte et al., 2014).

2.3 Reactions and their kinetic parameters

In general, there should be 3 sets of reactions to accompany 3 sections – pretreatment, trans-esterification and product purification and waste treatment, whose details are reported in Table 2.

- The first set consists of 3 kinetic reactions, which are 3 esterification reactions of 3 main types of free fatty acids (FFA) that are often encountered in crude castor oil with methanol: ricinoleic, oleic and linoleic acid.
- The second set consists of only 1 reaction – the trans-esterification of triricinolein to methyl ricinoleate in basic environment.
- The final set of reaction has only 1 reaction and occurs in the catalyst removal step. NaOH catalyst's presence in the final product is unacceptable and must be removed, using a strong acid such as HCl,

before the end of the process. The neutralization reaction is a complete conversion one since it is irreversible and happens quickly to completion.

Table 2: Kinetic parameters of main reactions

Reaction	Activation energy (kJ/mole)	Frequency factor	Target conversion	Source
Acid-catalyzed esterification of FFA	8.184	16.62	90.83 %	Bisheswar et al. (2018)
Base-catalyzed trans-esterification of triglycerides	21.95	6.02	97.82 %	Omar et al. (2018)
Base catalyst neutralization	N/A	N/A	100 %	User-defined

3. Process design

The whole biodiesel process relies on 3 main sections: pretreatment – acid-catalyzed esterification, production – base-catalyzed trans-esterification, product purification and waste treatment. Specifically configured and optimized conventional equipment is prioritized to maximize technical feasibility and economic efficiency.

3.1 Choosing the best reactor setup

To decide which setup is the most satisfactory in terms of optimization of reactor's size and cost for a given conversion, a study by Rachid (2014) on choosing the right kind of reactor (CSTR vs. PFR) was proposed for either minimization of volume or minimization of total cost as reference. Three possible scenarios (CSTR, PFR and combined) for reactor setup were applied for both the pre-treatment and the trans-esterification sections.

3.2 Equipment sizing

For different types of unit operations, appropriate methods to acquire their basic dimensions and configuration are required.

- Reactor sizing: experience-based approximation and ASME-codes-based calculations were used to obtain overall dimensions of the reactors
- Distillation column configuration: "Shortcut Column" utility available in Aspen HYSYS™ was used to estimate essential column's data from any given input.
- Other unit operations: either trial-and-error practice or literature adaptation.

3.3 Quality control and optimization

During process design, the need to vary input parameters for adjustment of equipment and flow data is irreplaceable, resulting in uncontrollable deviation in supposedly fixed process specifications. To remedy this issue, some adjustment operations were introduced to maintain stable output specifications.

4. Results and discussion

Sections of the complete process are presented as follows. The pretreatment section is illustrated in Figure 1.

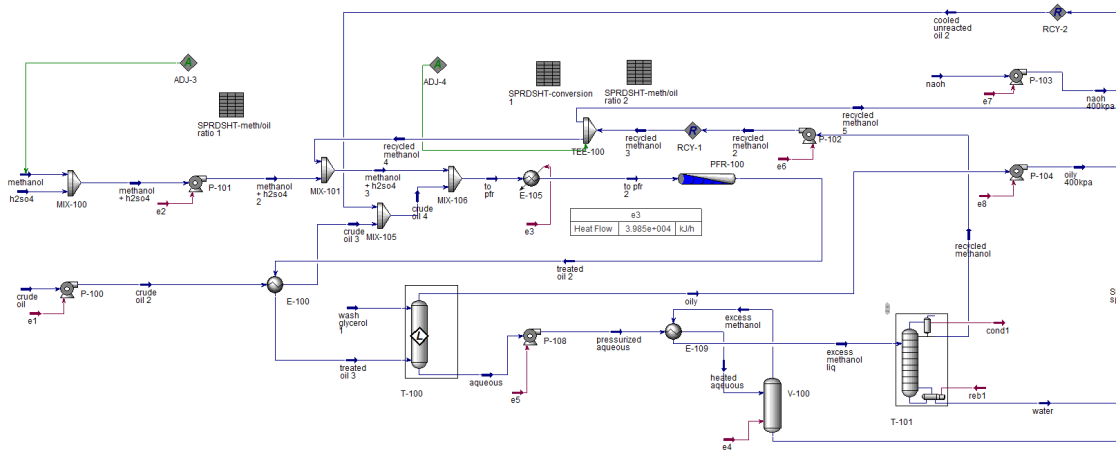

Figure 1: The acid-catalyzed pre-treatment section

In this section, input quality control was achieved by connecting inlet material streams with adjustment operations (ADJ-3 and ADJ-4) to maintain optimal methanol-to-oil ratios of 20:1 (Bisheswar et al., 2018) and 5.4:1 (Omar et al., 2018) for the pretreatment section and the trans-esterification section, shown as Figure 2.

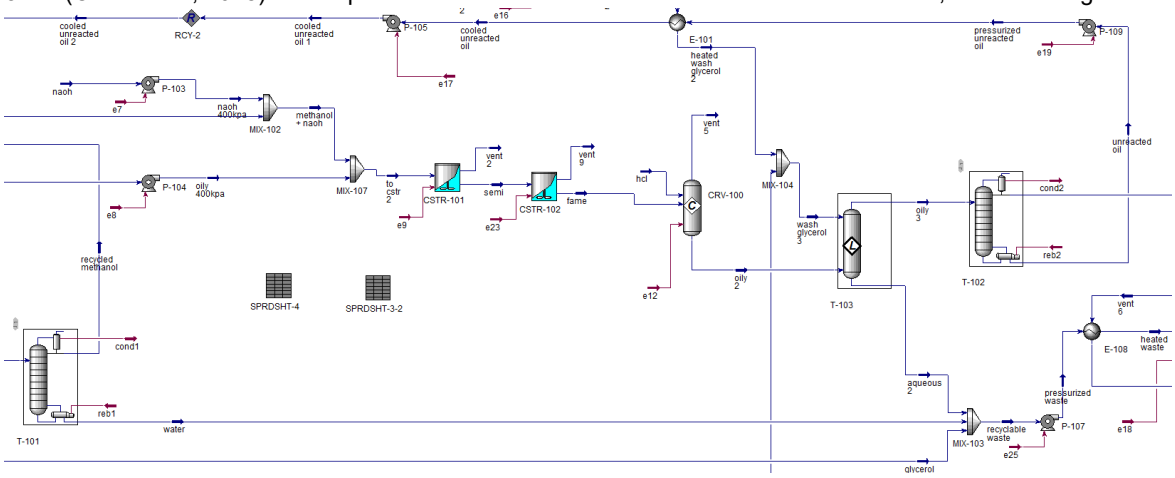

Figure 2: The base-catalyzed trans-esterification section

Combining minimization of equipment size with economic trade-off (Rachid, 2014), a single PFR for the pretreatment section and a series of two CSTRs for the trans-esterification section were selected in the final design.

The purification and waste treatment section in Figure 3 finalizes the process as a standard design. After this section, the product biodiesel stream would come out along with by-products such as glycerol and methanol.

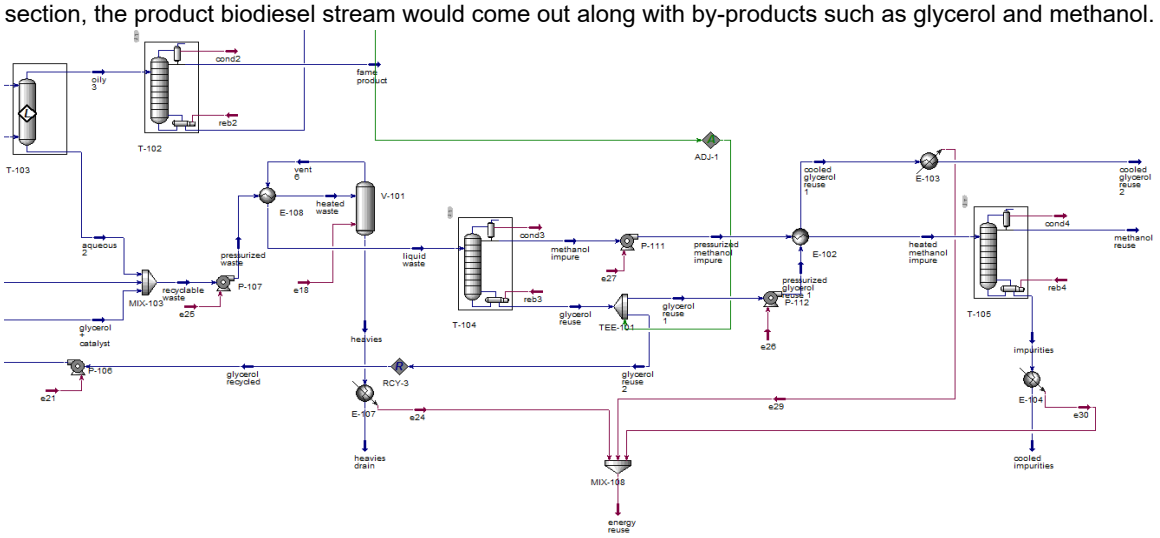

Figure 3: The product purification combined with waste treatment section

The aim of this section is to purify the semi-finished product stream to obtain the final product one whose purity and physico-chemical properties adhere to international fuel standards. Reactants and solvents are recovered as much as possible for economic purpose.

4.1 Properties of the simulated feed

Comparison between the properties of the simulated feed (triricinolein:ricinoleic acid:oleic acid:linoleic acid:moisture 96.4000:2.8628:0.2652:0.2720:0.2000) and those of the real feedstock obtained from lab-scale analyses by Jumat et al. (2010) (triricinolein:diricinoleoylstearoylglycerol:diricinoleoyloleoylglycerol: diricinoleoyllinoleoylglycerol:diricinoleoylpalmitoylglycerol:ricinoleic acid:linoleic acid:oleic acid:palmitic acid:stearic acid:linolenic acid:moisture 81.0724:7.9048:5.3984:1.1568:0.8676:2.8628:0.2482:0.187:0.0442: 0.0408:0.017:0.2) and Sara et al. (2018) (composition not available), to which the simulated one was referred, is provided in Table 3 to assess the accuracy of this simulation from the beginning.

Table 3: Comparison between the properties of the simulated feed and those of the real one

Property	This study	Reference
Average molecular weight	794.4	937.7 (Jumat et al., 2010)
% free fatty acid	3.4	3.4 (Jumat et al., 2010)
Viscosity (cP)	6.14, at 25°C	287.3, at 15°C (Sara et al., 2018)
Density (kg/m^3)	937	964 (Sara et al., 2018)
Boiling point (°C)	N/A	313 (Sara et al., 2018)

4.2 Optimization of reactor setup

For the same target conversion, different results for reactor sizing were obtained for the three scenarios of each section and were tabulated in Table 4 as follows.

Table 4: Reactor sizes (m^3) of different scenarios for each section

Scenario No.	Name	Pre-treatment section	Trans-esterification section
1	Single CSTR	20.38	0.636
2	Single PFR	6.889	5.867*10^{-2}
3	Two CSTRs in series	12.73	0.224

4.3 Equipment specifications

Using different methods aforementioned, key specifications of the unit operations used were listed in Table 5.

Table 5: Main unit operations' specifications

Name	Function	Specifications	Method	Source
PFR-100	Plug-flow reactor	D = 0.9144 m, L = 9 m	ASME calculations	ASME/ANSI B36.10/19
CSTR-100 CSTR-101	Continuously-stirred tank reactor	D = 0.4 m, H = 0.9 m Total liquid holdup = 0.112 m^3	Approximation methods	User-defined
T-100	Liquid-liquid extractor	3 stages P = 200 kPa	Literature adaptation	Zhang et al. (2003)
T-101	Distillation column	12 stages RR = 2, P = 60 – 100 kPa	Shortcut column	User-defined
T-102	Distillation column	20 stages RR = 1, P = 10 – 20 kPa	Shortcut column	User-defined
T-103	Liquid-liquid extractor	10 stages P = 101.3 kPa	Literature adaptation	Zhang et al. (2003)
T-104	Distillation column	10 stages RR = 1, P = 60 – 101.3 kPa	Shortcut column	User-defined

4.4 Product specifications and comparison

In Table 6, a comparison between this study's results and those of research works, whose reaction conditions were adopted in this study, was made to assess the deviation between simulation and practice.

Table 6: Product specifications and comparison

Criteria	This study	Reference
Pre-treatment efficiency	90.89 % FFA amount removed	90.83 % FFA amount removed (Bisheswar et al., 2018)
Triglycerides conversion	93.86 %	97.82 % (Omar et al., 2018)
Product purity	99.61 % methyl ricinoleate 0.10 % methyl linoleate 0.28 % methyl oleate	N/A
Kinematic viscosity at 40 °C (mm^2/s)	15.41	ASTM (1.9–5.0) EN (3.5–5.0)
Acid value (mg KOH/g)	0.0	ASTM (0.5 max.)
Gross heating value (MJ/kg)	17.82	EN (35 min.)
Density at 18 °C (g/cm^3)	0.922	EN (0.82–0.85)

5. Conclusion

In this work, a process design for the production of biodiesel from crude castor oil as feedstock and its simulation were developed in order to provide a preliminary assessment of its feasibility in terms of commercial application. Both the results published in literature and those from the simulation indicate that a high-purity (≈ 100 % mole) mixture of fatty acid methyl esters can be obtained from crude feedstock containing high FFA content. Further process optimization and detailed heat exchanger network analysis are necessary to improve the process' functionality.

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