Process Design for Pentadecane Production from Methyl Palmitate

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Abstract

Methyl palmitate (C16:0) is the major saturated fatty acid methyl ester (FAME) of palm oil-based biodiesel. The high composition of saturated FAMEs leads to poor cold flow properties and high cloud point. However, methyl palmitate can be used as raw materials for production of higher-value chemicals used by many different industries such as food, beverage, cosmetics, pharmaceutical and lubricant industry. In this work, the production of pentadecane was selected because it has a wide range of applications such as a chemical intermediate to produce other products, a component of gasoline and diesel fuels and a solvent. According to the research by Yan et al. (2017), pentadecane production uses a catalytic deoxygenation (DO) process of methyl palmitate over molybdenum oxide doping nickel phyllosilicate (Mo-Ni@PSi) bifunctional catalyst. The results showed that 3% Mo-Ni@PSi(B) exhibited the highest catalytic activity with 70.0% yield of pentadecane at 220 °C and 1.0 MPa H_2. Thus, the purpose of this work was to perform the process design based on the above research. This process was divided into four systems: reactor feed preparation system, reaction system, phase separation system and separation system. Mass balance and energy balance were calculated for each stream of the process. A preliminary design that may be obtained in this work can provide beneficial alternatives for the biodiesel industry in the near future.

Keywords: Methyl palmitate, Pentadecane, Hydrodeoxygenation, Process design

1. Introduction

Nowadays, everyone is concerned about the environmental impacts of using fossil fuels. Therefore, vegetable oils, animal fats and waste cooking oils are good alternatives to substitute the non-renewable energy. In many countries, palm oil is used as raw material for biodiesel production because palm oil-based biodiesel has similar properties to the petrol-diesel (Zahan & Kano, 2018). However, palm oil-based biodiesel is mainly rich in methyl palmitate (47.2%) and methyl oleate (40.8%).

Methyl palmitate is a saturated FAME which causes poor cold flow properties in biodiesel. Consequently, there are many methods to improve cold flow properties (Dunn, 2011) such as blending with petrodiesel, using chemical additives and reducing total saturated fatty acid methyl ester concentration by fractionation process. Methyl palmitate which is fractionated from biodiesel can be used as raw materials to produce other valuable chemicals.

Pentadecane promises a chemical that can be utilized as a chemical intermediate, a solvent, a perfuming agent in cosmetics and phase change material (PCM) for cooling applications. The deoxygenation (DO) reaction of methyl palmitate and hydrogen to produce pentadecane is presented in figure 1. This reaction consists of three pathways: (i) Palmitic acid is produced via hydrogenolysis and then converted to hexadecanal through hydrogenation. Finally, pentadecane is generate by decabonylation (DCO). (ii) Hexadecanal is converted to hexadecanol by hydrogenation and then transform into hexadecane via hydrodeoxygenation (HDO). (iii) Pentadecane could directly generate from palmitic acid by decarboxylation (DCO_2). In addition, alkanes could convert to light alkanes and iso-alkanes via cracking and isomerization reaction, respectively.

This work presented a preliminary design and simulation of pentadecane production process from methyl palmitate. Initially, we identified and arranged the sequence of the unit operation in the process and then specified the operating condition of each equipment. In addition, Mass balance and energy balance were calculated for each stream of the process.

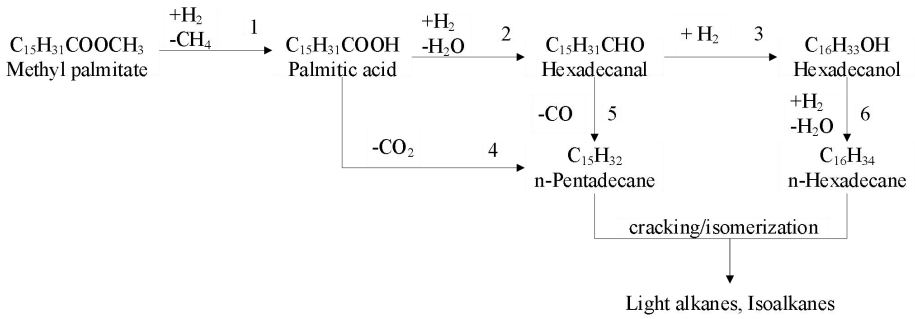

Fig.1 Reaction pathways in deoxygenation

2. Material and methods

2.1 Process overview

Pentadecane production process is divided into four systems: reactor feed preparation system, reaction system, phase separation system and separation system. Block Flow diagram (BFD) is illustrated in figure 2 and the detailed of each system are described below.

2.1.1 Reactor Feed Preparation System

This process is designed to operate continuously 8,000 hrs over a year with methyl palmitate feed rate of 100,000 ton/yr. Methyl palmitate and hexane (used as an inert solvent) are fed to a mixing tank (M-101) and flowed through a pump (P-101) to increase the pressure as required in the reactor. Meanwhile, the hydrogen gas stream is passed through a pressure reducing valve (V-101). The gas feed stream, liquid feed

stream and recycle stream are mixed and then heated in a heater (E-101) before sent to the reactor system.

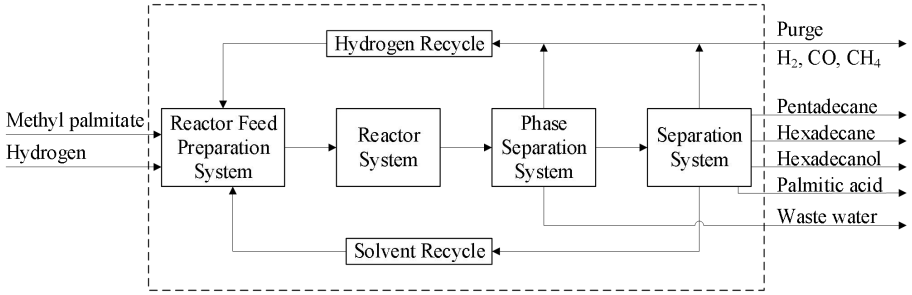

Fig. 2 Block Flow Diagram (BFD)

2.1.2 Reactor System

According to the research by Yan et al. (2017), the reactor is operated at 220 °C and 10 bar using 3% Mo-Ni@PSi(B) as a catalyst. 10 wt% Methyl palmitate in hexane with excess hydrogen (95:1 H_2/MP mole ratio) is fed into the reactor. Yan et al. reported that no CO_2 was detected in the gas product; therefore, the reaction pathways involved under this condition are decarbonylation and hydrodeoxygenation. The experiment results provide 100% conversion of methyl palmitate with 70.0% yield of pentadecane and 28.3% yield of hexadecane. Considering reactor operation, the temperature change is calculated by equation (1). The reactor should be operated adiabatically since the adiabatic temperature rise is less than 10 to 15% of the inlet temperature.

$$\text{Temperature Change:} \quad \Delta T = \frac{Q_R}{\sum F_i C p_i} \qquad (1)$$

$$\text{Reactor Heat Load:} \quad Q_R = \text{Heat of Reaction x Reactant Reacted}$$

Where ΔT is temperature change (K or °C), Q_R is reactor heat load (kJ/hr), F_i is mole flow rate of the reactor outlet stream (kmol/hr) and Cp_i is heat capacity (kJ/kmol-K)

2.1.3 Phase Separation System

The reaction product stream is cooled in a cooler (E-301) and then delivered to flash unit operation (F-301, F-302) to separate the gas phase from the liquid phase. After that, the gaseous stream consisting mainly of unreacted hydrogen is split into two streams: purge and recycle stream. Purge stream is removed from the process in order to avoid an accumulation of byproducts (CO and CH_4), whereas the remaining stream is recycled to the reactor feed preparation system. The two liquid streams from flash drums are mixed in a mixing tank (T-301) and followed by a decanter (F-303) to remove water.

2.1.4 Separation System

A liquid mixture stream is passed through a pressure reducing valve (V-401) and sent to a distillation column (D-401) with a partial condenser. The vapor distillate stream which consists of light gas (H_2, CO and CH_4) is removed from the process while liquid distillate stream is recycled to reactor feed separation system. The liquid bottom stream is further delivered to a series of distillation columns. Finally, we obtained four

final products: pentadecane, hexadecane, hexadecanol and palmitic acid with purity of 98% or more.

3. Process Design

Pentadecane production from methyl palmitate was performed using Aspen Plus V9 software. NRTL and PENG-ROB are used as a thermodynamic model for the separation system and the remaining system, respectively. Moreover, Henry parameters are required because we have supercritical gases (H_2, CO and CH_4) in this simulation. The process flow diagrams of each system are shown below. A summary of the operating conditions of each unit is presented in Table 1 and the inlet and outlet stream tables are given in Table 2 and Table 3.

Table 1 Operating conditions for the pentadecane production process

Operating parameter	**Value**			
Reactor	**R-201**			
Inlet and outlet temperature (°C)	220, 233			
Pressure (bar)	10			
Flash	**F-301**	**F-302**		
Temperature (°C)	50	20		
Pressure (bar)	10	10		
Distillation column	**C-401**	**C-402**	**C-403**	**C-404**
Reflux ratio	1	1	4.61	5.62
Number of stages	4	45	102	76
Feed Stage	3	26	57	39
Condenser pressure (bar)	1.5	1.5	1.5	1.5
Reboiler pressure (bar)	2.0	2.0	2.0	2.0
Distillate rate (kmol/hr)	1,240.75	45.23	31.14	0.38

Table 2 Inlet stream table for the pentadecane production process

Stream	**H_2 (FEED)**	**METHPALM**	**MAKEUP**
T (°C)	35	35	35
P (bar)	137.09	1.01	1.01
Mass Flow (kg/hr)	1,113	12,500	1,526
Mass Fraction			
Hydrogen	1.000	0	0
Methyl palmitate	0	1.000	0
Hexane	0	0	1.000

Table 3 Outlet stream table for the pentadecane production process

Stream	N-PEN	N-HEX	HEXA-NOL	PALMACID	WASTE
T (°C)	234.84	320.44	345,28	384.05	48.05
P (bar)	1.5	2.0	1.5	2.0	10.0
Mass Flow (kg/hr)	6,683.7	2,962.44	91.45	96.56	1,307.11
Mass Fraction					
Hexane	0.0147	0	0	0	0.0002
Pentadecane	0.9853	0.0002	0	0	0.7742
Hexadecane	0	0.9998	0	0	0.2193
Hexadecanal	0	0	0.0003	0	0
Hexadecanol	0	0	0.9995	0.0002	0.0030
Palmmitic acid	0	0	0.0001	0.9998	0.0032

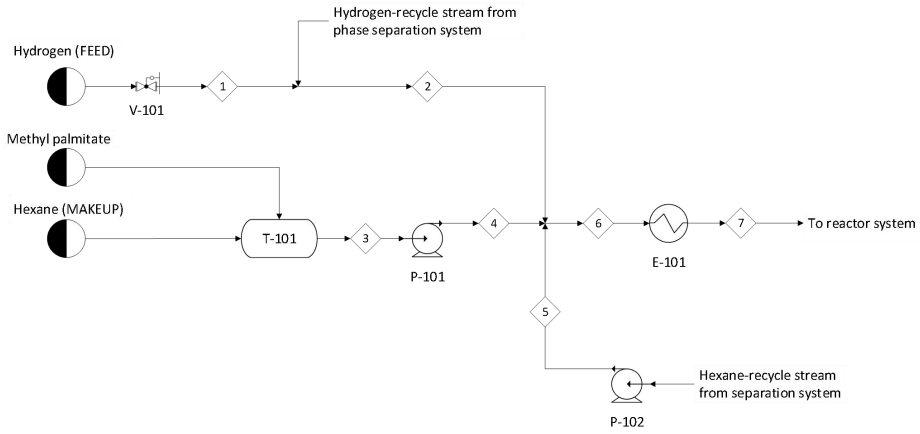

Fig.3 Process flow diagram of the reactor feed preparation system

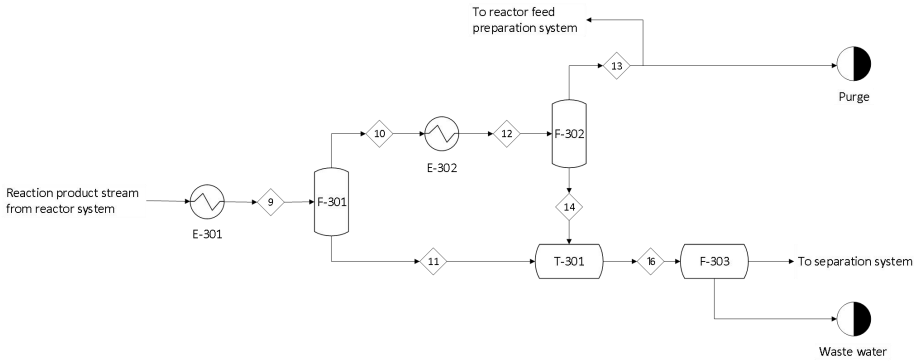

Fig.4 Process flow diagram of the phase separation system

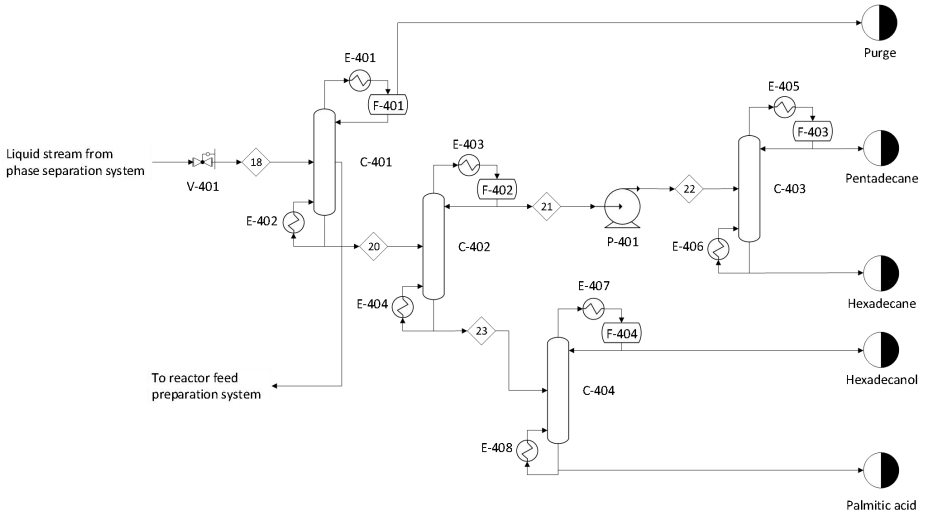

Fig.5 Process flow diagram of the phase separation system

4. Conclusions

This work presented preliminary process design of pentadecane production from methyl palmitate in which condition of methyl palmitate at first was to be set at 100,000 ton/yr. Based on Yan et al. (2017) report, deoxygenation of methyl palmitate was carried out via decarbonylation and hydrodeoxygenation. The optimal operating condition was at 220 °C, 1.0 MPa over 3%Mo-Ni@Psi(B). The obtained stream result from Aspen Plus showed that 52,682 ton/yr of pentadecane (which equal to 52.68% of methyl palmitate) with 98.5 % purity of pentadecane was produced from this process. The by-products of both pathways contained 23,694 ton/yr of hexadecane, 731 ton/yr of hexadecanol and 772 ton/yr of palmitic acid. Economic analysis should further perform to examine the profitability of this process.

5. References

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