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Thermal Self-Sufficient Operation of Hydrogen Production from Used Vegetable Oil

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This work aims to investigate the hydrogen production from used palm oil and used soybean oil through autothermal reforming (ATR). Thermodynamics analysis of this process was performed by using Aspen plus V9 simulation software. The gas compositions at equilibrium were calculated by using the Gibbs free energy minimization method. The hydrogen production process was composed of ATR reactor, high-temperature water gas shift (HT-WGS), low-temperature water gas shift (LT-WGS) and absorber. Considering the optimal conditions of each unit operation, it was found that the maximum hydrogen production can be provided when ATR reactor was operated at temperature of 580 °C, atmospheric pressure, steam to carbon (S/C) molar ratio of 10 and oxygen to carbon (O/C) molar ratio of 0.1. HT-WGS and LT-WGS reactors should be operated at temperature of 300 °C and 200 °C. For the absorber, the optimal conditions were at 40 atm with 6 kmol/h of MDEA solution at 35 °C. Under these operating conditions, hydrogen can be generated as 2.56 kmol/h or 99.7 mol%. Then, the hydrogen production under thermal self-sufficient operation was studied. The simulation result indicated that the ATR reactor should be operated at temperature of 580 °C and atmospheric pressure with S/C molar ratio of 4.5 and O/C molar ratio of 0.47 to achieve thermal self-sufficient operation. When the ATR reactor was operated under these operating conditions whereas the operating conditions of HT-WGS, LT-WGS and absorber were constant, it was found that hydrogen with molar flow rate of 1.71 kmol/h (99.7 mol%) can be provided.

1. Introduction

Energy is necessary for any activities in life of human, industry, agriculture and even within our bodies. In 2019, about 70 % of the world energy consumed is fossil fuels, which are non-renewable energy are reported in International Energy Agency (IEA). Since the amount of fossil fuels has been reduced and the air pollution always occurs during the combustion process, the use of alternative fuel has been received much attention. Hydrogen is the one of interesting non-polluted fuels, which is used in a variety of purposes. For transportation, hydrogen can be used as a fuel in fuel cell or internal combustion engine. Hydrogen combines with oxygen where ignites to produce only water and heat. For chemical industry, hydrogen is mainly used to produce ammonia and methanol, and used as a fuel for many chemical plants. In addition, various useful of hydrogen is a result of increasing consumption approximately 6% per year (Kalamaras and Efstathiou, 2013).

In general, hydrogen can be produced from various resources, such as natural gas, coal and biomass. Among these, biomass has been received much interest due to its cheap and availability. Biomass can be converted into renewable energy and value-added products. A lot of primary fuels, including hydrogen can be produced from biomass. One of biomass that humans used in daily life is vegetable oils. Global edible vegetable oil demand increased by about 48% from 1995 to 2011 and keep slightly growing (Parcell et al., 2018). The palm oil and soybean oil are two most types of the highest consumed vegetable oils in the world (38.3% and 28.5%,

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respectively). Therefore, the used palm oil and used soybean oils are considered as resource for hydrogen production in this work.

Hydrogen can be produced from three main thermochemical technologies: (1) steam reforming (SR), (2) partial oxidation (POX) and (3) autothermal reforming (ATR). Currently, about half hydrogen of the world is produced by SR process because the highest yield of hydrogen can be produced by this process. However, large amount of heat is required since SR is the endothermic reaction (Chen et al., 2020). While POX process is exothermic reaction, the heat requirement can be eliminated. But, the use of pure oxygen will increase the operation cost. Thus, air is commonly used in the POX reaction and this causes low concentration hydrogen due to the dilution by nitrogen (Siang et al., 2020). ATR process is the combination of SR and POX. The process can produce higher yield of hydrogen than POX process and require less energy than SR process (Castro et al., 2010). Therefore, ATR process is a sustainable process that is appropriate with sustainable energy.

Since the gas product obtained from reforming process always contain carbon monoxide and carbon dioxide, the separation of carbon dioxide to provide the higher hydrogen content is necessary. Among the variety of carbon dioxide separation processes (absorption, adsorption, membrane and cryogenic process), the absorption process is a good choice to purify hydrogen product and separate carbon dioxide because of simple process, easy regeneration and excellent properties of attracting gases (Patcharavorachot et al., 2014). In order to produce the highest purity of hydrogen, the absorption process is suggested to subsequent implement after the reforming process.

This work aims to propose the hydrogen production process that mainly consists of ATR reactor and absorption process. Used palm oil (UPO) and used soybean oil (USO) are considered as feedstock for hydrogen production. The hydrogen production is investigated through Aspen plus V9 simulation software. The optimal conditions of ATR reactor and other units are identified to provide the maximum hydrogen production. In addition, the hydrogen production under thermal self-sufficient operation is further determined.

2. Process description of hydrogen production

Figure 1 presents a schematic of hydrogen production from used vegetable oil through ATR process. UPO and USO without the contaminants are considered as feedstock. The composition of each used vegetable oil that is used in the simulation is shown in Table 1. From Figure 1, the used vegetable oil and reforming agent (steam and oxygen) are firstly fed into the mixer. Then, the gas mixture is delivered to ATR reactor. There are many possible chemical reactions carried out in ATR reactor as shown in Eq(1) to Eq(8).

Steam Reforming: $C_nH_mO_k + (n\text{-}k)H_2O \leftrightarrow nCO + (n+m/2\text{-}k)H_2$ (1)

Partial Oxidation: $C_nH_mO_k + (n\text{-}k/2)O_2 \leftrightarrow nCO + (m/2)H_2$ (2)

Water Gas Shift: $CO + H_2O \leftrightarrow CO_2 + H_2$ (3)

Methanation of CO: $3H_2 + CO \leftrightarrow CH_4 + H_2O$ (4)

Methanation of CO_2: $4H_2 + CO_2 \leftrightarrow CH_4 + 2H2O$ (5)

Methane dry reforming: $CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$ (6)

Oxidation of CO: $CO + 0.5O_2 \leftrightarrow CO_2$ (7)

Oxidation of H_2: $H_2 + 0.5O_2 \leftrightarrow H_2O$ (8)

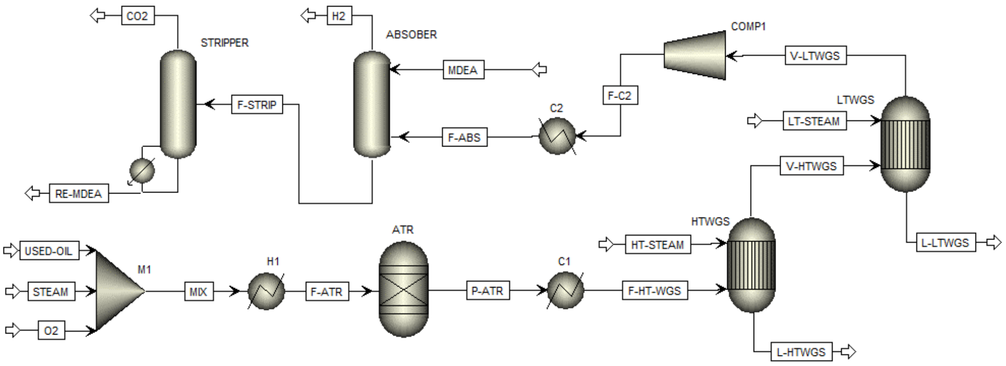

Figure 1: Schematic of hydrogen production designed in Aspen Plus V9

Table 1: The composition of used vegetable oil

Fatty acids			Fatty acid composition (%)	
Name	Molecular formula	Carbon: Double bond	UPO	USO
Palmitic	$C_{16}H_{32}O_2$	16:0	38.35	12.40
Stearic	$C_{18}H_{36}O_2$	18:0	4.33	4.53
Oleic	$C_{18}H_{34}O_2$	18:1	43.67	24.30
Linoleic	$C_{18}H_{32}O_2$	18:2	11.39	51.97
Linolenic	$C_{18}H_{30}O_2$	18:3	0.29	5.48
Other carbon	-	-	1.97	1.32

The gas product obtained from ATR reactor are mainly composed of H_2, CO, CO_2 and H_2O. In order to decrease CO, two water gas-shift (WGS) reactors are required. Although gas product from WGS reactor contains high H_2 and less CO, it always consists of high amount of CO_2. Therefore, the absorption process is further applied in hydrogen production process. In this work, 40 wt% of methyl-diethanolamine (MDEA) is used to capture CO_2. In general, the absorption process consists of two columns that include absorber and stripper. The gas product stream from LTWGS reactor is fed into the absorber simultaneously with MDEA solution. The purified H_2 can be provided whereas the used MDAE solution is regenerated in the stripper. The unit models and their specifications used in the simulation are listed in Table 2.

Table 2: Specification of each unit operation used in the simulation

Code	Unit Model	Range of Operation
M1	Mixer	-
H1	Heater	580 °C, 1 atm
ATR	RGibbs reactor	500-800 °C, 1-5 atm
C1	Heater	300 °C, 1 atm
HTWGS	REquil reactor	300-450 °C, 1 atm
LTWGS	REquil reactor	200-250 °C, 1 atm
COMP1	Compr	40 atm
C2	Heater	50 °C, 40 atm
ABSORBER	RadFrac	10-40 atm
STRIPPER	RadFrac	1.1 atm

3. Methodology

In this work, thermodynamic calculation of hydrogen production process from used vegetable oil is performed through Aspen Plus V9 simulation software. The UNIF-LBY is selected as thermodynamic method because it can be used for simulation of triglycerides. When the composition of used vegetable oils (Table 1) are specified corresponding with steam to carbon (S/C) molar ratio and oxygen to carbon (O/C) molar ratio and the operating conditions of all units (Table 2) are given, the equilibrium compositions from ATR process can be calculated by the minimization of the Gibbs free energy. In this work, the effect of important parameters in each unit on hydrogen production are studied to determine the optimal conditions of the ATR reactor, HT-WGS and LT-WGS reactors and absorber that provide the maximum amount and the highest purity of hydrogen product. Then, the optimal operating conditions of ATR reactor is further determined under the thermal self-sufficient condition.

4. Model validation

In order to ensure that the proposed model as described in Section 2 can provide the predictable results, the simulated results are compared with the experimental results of Gornay et al. (2019), as shown in Figure 2a. It is found that the model prediction shows a good agreement with the experimental data when the reformer was operated at 650 °C and 1 atm. In the experiment, the waste cooking oil consisting of 47 wt% of oleic acid, 15 wt% of linoleic acid, 35 wt% of stearic and 3 wt% of palmitic acids is reformed through SR process with S/C molar ratio of 1.

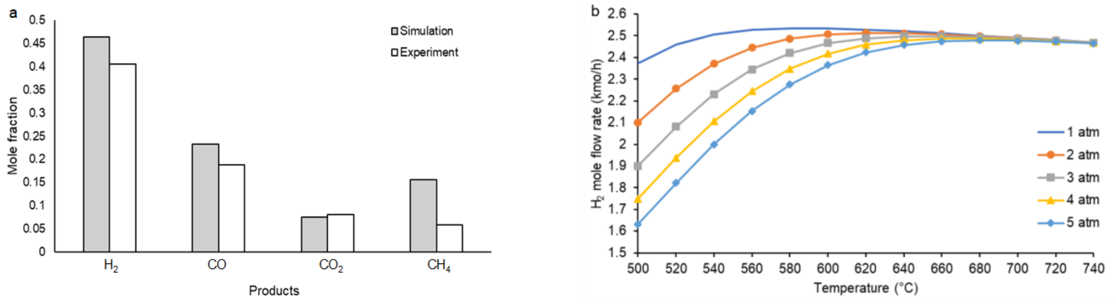

Figure 2: (a) Comparison of each product between the simulation result and experimental result of Gornay et al. (2019) and (b) effect of pressure and temperature in ATR reactor on hydrogen production at S/C ratio = 10 and O/C ratio = 0.1

5. Results and discussion

5.1 Effect of operating condition on maximum hydrogen production

In this section, the effect of operating condition of each unit is examined based on the use of UPO which is fed into the process as 0.058081 kmol/h. This is equal to 1 kmol/h of carbon while steam and oxygen are fed into the system as 10 and 0.1 kmol/h which are corresponded with S/C molar ratio of 10 and O/C molar ratio of 0.1. Firstly, the effect of pressure and temperature in ATR reactor on hydrogen production is studied as shown in Figure 2b. The simulation results show that the H_2 amount decreases when the ATR reactor pressure increases from 1 to 5 atm. This is because the chemical reactions are considered at equilibrium. Higher pressure operation will shift reaction toward the reactant side and thus, H_2 production is decreased. Therefore, the ATR reactor should be operated in atmospheric pressure. Moreover, the simulation results indicate that at the constant ATR reactor pressure, H_2 product increases when temperature is increased from 500 to 580 °C and then, it is slowly decreased at temperature above 580 °C. This is since both endothermic reaction and exothermic reactions occurred in the ATR reactor. In the first period, the endothermic reaction is carried out more than exothermic reaction. This is caused higher H_2 production since the endothermic reaction is prefer at high temperature. However, when ATR temperature is more than 580 °C, the exothermic reaction which is favourable at low temperature leads to lower H_2 production. From the simulation, it is found that the maximum H_2 product of 2.53 kmol/h can be obtained at 580 °C and atmospheric pressure.

Figure 3a demonstrates the effect of S/C molar ratio on each gas product. The simulation result shows that increasing S/C molar ratio can produce more H_2. Because the addition of steam as a reactant of the SR reaction can promote the reaction shifted toward the product side. As a result, higher H_2 amount can be obtained. Addition of steam also shifts the WGS reaction toward and this causes a decrease in CO and an increase in CO_2. While the amount of CH_4 decreases with increasing steam feed because the reverse methanation reaction can be occurred.

Figure 3b presents the effect of O/C molar ratio on hydrogen production at the temperature of 580 °C, pressure of 1 atm and S/C molar ratio of 10. It is found that H_2 amount is continuously decreased when the amount of O_2 increases. This is since the excess O_2 will promote the hydrogen oxidation reaction, H_2 will react with O_2 and thus, H_2 amount is reduced whereas more steam can be produced. Besides the hydrogen oxidation reaction, the oxidation of CO reaction is more pronounced when O_2 is higher. This leads to the increment of CO_2.

Under the optimal operating condition of ATR reactor at the temperature of 580 °C and pressure of 1 atm with S/C molar ratio of 10 and O/C ratio of 0.1, it can provide the gas product (P-ATR stream) consisting of 22.2 %H_2, 0.75 %CO, 7.58 %CO_2 and 69.47 %H_2O. In order to decrease CO amount, the gas product exited from ATR reactor is supplied to the HT-WGS followed by LT-WGS reactor. From the investigation on the optimal operating temperature of both reactors, it is found that HT-WGS and LT-WGS reactors should be operated at 300 and 200 °C, respectively. The gas exited from LT-WGS (V-LTWGS stream) is composed of 22 %H_2, 8 %CO_2 and 70 %H_2O.

The improvement of H_2 purity can be performed by feeding the product stream from LT-WGS into the absorber to remove CO_2. Figure 4a shows the H_2 mole fraction as functions of absorber pressure and amount of MDEA solution. It is found that the H_2 mole fraction is higher when the absorber is operated at higher pressure. Because high pressure operation increases the overall volumetric mass transfer coefficient, which can improve the efficiency of CO_2 separation (Halim et al., 2015).

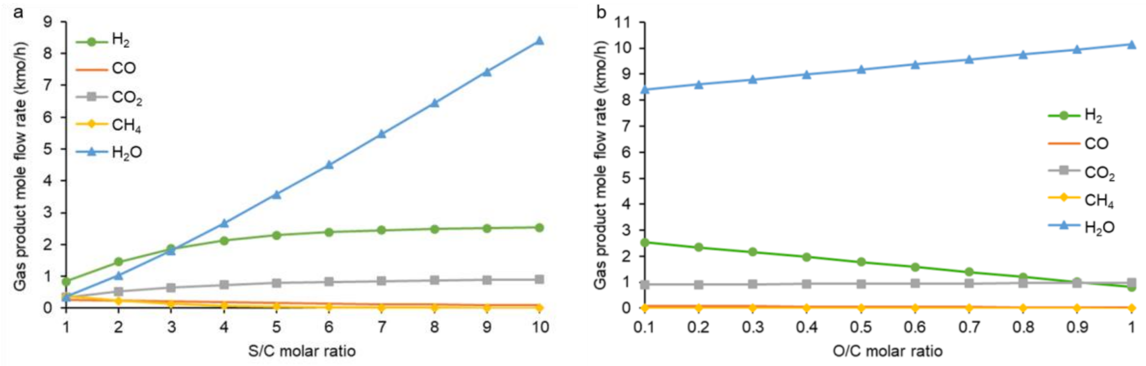

Figure 3: Effect of (a) S/C molar ratio and (b) O/C molar ratio on each gas product at temperature = 580 °C, pressure = 1 atm, at O/C molar ratio = 0.1 and S/C molar ratio = 10

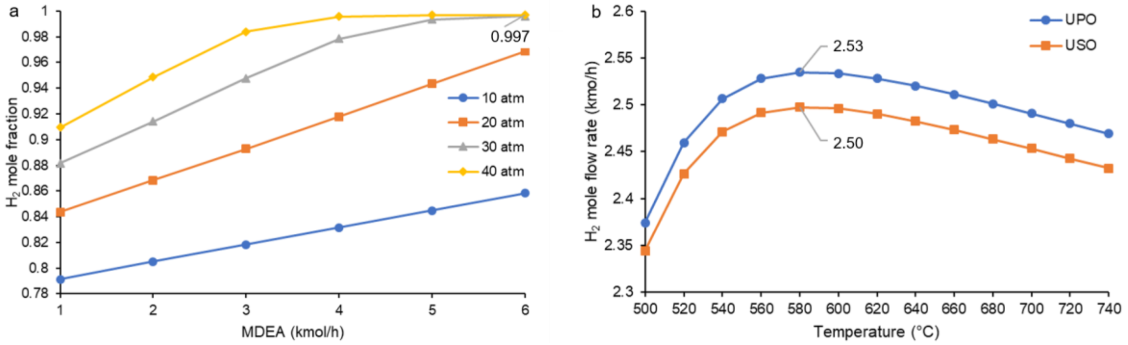

Figure 4: Hydrogen production as functions of (a) absorber pressure and amount of MDEA solution at the MDEA temperature feed = 35 °C and (b) ATR reactor temperature and used vegetable oil types at S/C molar ratio = 10, O/C molar ratio = 0.1 and pressure = 1 atm

Considering amount of MDEA solution, Figure 4a also reveals that increasing MDEA solution can increase the purity of H_2. At absorber pressure of 40 atm, the purity of H_2 product increases sharply and reaches to the maximum value as 99.7 % at 6 kmol/h of MDEA. Addition of MDEA solution causes the reaction of MDEA shift toward and thus, more amount of CO_2 is captured. It should be noted that the use of high MDEA amount may spend more time for circulation and require higher energy consumption in the stripper.

Figure 4b presents the comparison of H_2 mole fraction obtained from UPO and USO as a function of ATR reactor temperature. It is found that the maximum H_2 product can be provided as 2.53 and 2.50 kmol/h when UPO and USO are used, respectively. The simulation result indicates that the H_2 production from UPO is higher than that from USO. This is mainly caused by the different components of fatty acids. From Table 1, the average component in terms of %C, %H and %O in UPO is 32.93, 63.23 and 3.83 whereas that in USO is 33.93, 62.25 and 3.82, respectively. Higher H content in the UPO is a result of higher H_2 product than USO.

5.2 Hydrogen production under thermal self-sufficient operation

Since the ATR reaction is the combination of SR and POX reactions, the feeding steam and oxygen affect not only H_2 production but also energy consumption. In order to find the operating condition that can achieve thermal self-sufficient operation (referred to zero net heat duty of ATR reactor), the effects of S/C and O/C molar ratios on net heat duty of ATR reactor is examined as shown in Figure 5a. It is found that the heat duty of ATR reactor increases with increasing S/C molar ratio and decreasing O/C molar ratio. This is because the SR reaction is an endothermic reaction, heat consumption is higher when S/C molar ratio increases. While the POX reaction as an exothermic reaction can reduce the heat demand. Considering the heat duty corresponding with H_2 production (Figure 5b), it is found that although higher steam feeding (higher S/C molar ratio) can improve H_2 production, it causes more endothermic condition, leading to more energy consumption. In contrast to steam feed, higher O_2 feeding (higher O/C molar ratio) decreases H_2 amount, but it makes the system to be exothermic.

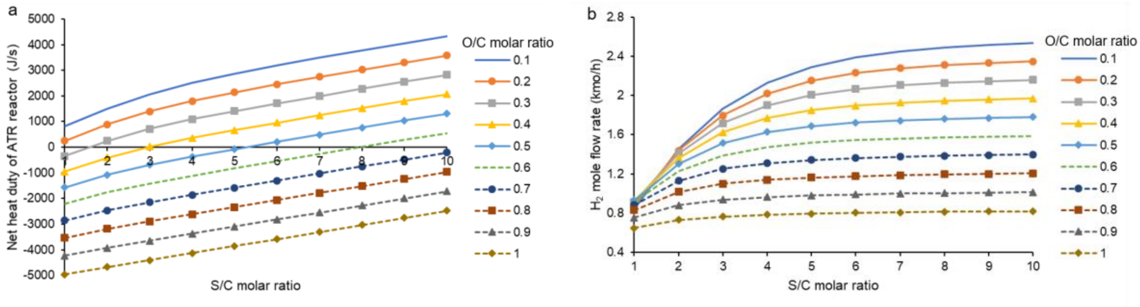

Figure 5: Effect of S/C and O/C molar ratios on (a) net heat duty of ATR reactor and (b) hydrogen production at ATR reactor pressure = 1 atm and ATR reactor temperature = 580 °C

From Figure 5a, it can be seen that the suitable value of S/C and O/C molar ratios under thermal self-sufficient operation is between 4-5 and 0.4-0.5, respectively. In order to find the exact value, the Design-spec option built in Aspen Plus simulator is used. When the net heat duty of ATR reactor is set as zero, it is found that the S/C and O/C molar ratios should be 4.5 and 0.47, respectively. Under the optimal value of S/C and O/C molar ratios, hydrogen can be produced as 1.71 kmol/h.

6. Conclusions

This work presented the investigation of hydrogen production through ATR process from different used vegetable oils. The simulation results showed that the maximum H_2 production of 2.53 kmol/h can be provided when the UPO was used. Hydrogen production can be achieved the highest purity as 99.7 % when ATR reactor was operated at atmospheric reformer pressure, 580 °C, S/C ratio of 10 and O/C ratio of 0.1 while the operations of HT-WGS and LT-WGS were at 300 °C and 200 °C and absorber was operated at 40 atm with MDEA solution of 6 kmol/h. Considering the thermal self-sufficient operation, the use of S/C and O/C molar ratios as 4.5 and 0.47 can provide zero net heat duty of ATR reactor and this operation can generate hydrogen as 1.71 kmol/h (99.7 %). In this work, UPO and USO are considered as feedstock. However, there are various types of used oil in the world market and thus, different types of used oil should be further considered. Moreover, the use of mixed used oil is the interesting issue that should be concerned.

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