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Biodiesel Production using Heterogeneous Catalyst in CSTR: Sensitivity Analysis and Optimization

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Abstract. Biodiesel as a renewable fuel has emerged as a potential replacement for petroleum-based diesels. Heterogeneous catalyst has become the focus of researches in biodiesel production with the intention to overcome problems associated with homogeneous catalyzed processes. The simulation of heterogeneous catalyzed biodiesel production has not been thoroughly studied. Hence, a simulation of carbon-based solid acid catalyzed biodiesel production from waste oil with high FFA content (50 weight%) was developed in the present work to study the feasibility and potential of the simulated process. The simulated process produces biodiesel through simultaneous transesterification and esterification with the consideration of reaction kinetics. The developed simulation is feasible and capable to produce 2.81kmol/hr of FAME meeting the international standard (EN 14214). Yields of 68.61% and 97.19% are achieved for transesterification and esterification respectively. Sensitivity analyses of FFA composition in waste oil, methanol to oil ratio, reactor pressure and temperature towards FAME yield from both reactions were carried out. Optimization of reactor temperature was done to maximize FAME products.

1. Introduction

Biodiesel has emerged as one of the potential alternative fuels to replace petroleum-based fuels as its properties are similar to that of petroleum-based diesel [1]. Biodiesel has an edge over petroleum-based fuels in view of its sustainability as it is biodegradable, non toxic and biodiesel produces less pollutants after it is burned. There are no modifications required to the current automobile engine in order for the engine to run on biodiesel blend. Biodiesel produced from waste cooking oil can be used in engines without modification for up to 30% blend [2]. Biodiesel consists of a mixture of fatty acid methyl esters (FAMEs) which can be produced through transesterification of vegetables fats or animal oils with methanol. The reaction can be represented as shown in Figure 1. Biodiesel production through transesterification is usually carried out by homogeneous alkaline catalyst like NaOH and KOH. Although ethanol can be used for biodiesel production, the use of methanol in biodiesel production is more common and preferable due to the cheaper price and the large available feedstock of methanol. Esterification, required when FFA content is more, on the other hand is usually catalysed by a homogeneous acid catalyst like sulfuric acid [1,3]. Other approaches for biodiesel production are: use of heterogeneous catalyst, supercritical methanol and enzymes in the reactions [4]. These methods are still under research and development, and have become the focus of research in recent years. Many

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studies have considered heterogeneous catalyst in order to get rid of the problems faced in homogeneous catalyst. Heterogeneous catalysts ease the separation process as heterogeneous catalyst removal is easier than homogeneous catalyst removal. Heterogeneous catalyzed biodiesel production required less process unit compared to the homogeneously catalyzed process [3]. Thus, the process equipment cost is generally lower compared to homogeneously catalyzed process. Thus, in this study, the heterogeneously catalyzed biodiesel production process is simulated. Later, sensitivity analysis and optimization are carried out to determine the effect of operating parameters and find optimal parameters.

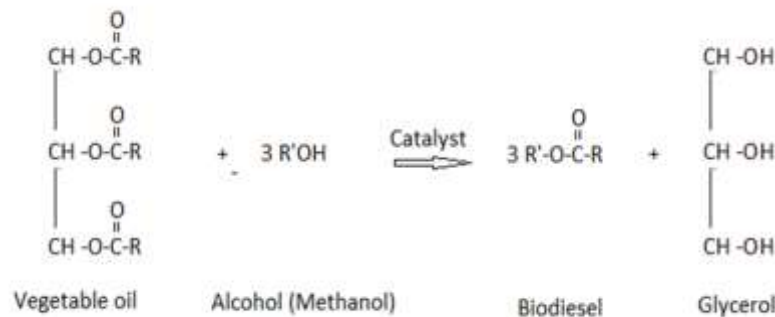


Figure 1. Transesterification chemical equation

2. Biodiesel production using heterogeneous catalyst

The process is developed based on the works of West et al [5]. The same production capacity (800 metric tonnes per annum) is assumed in this process. However, instead of a packed bed reactor, a CSTR is used for the simultaneous reactions of esterification of FFA and transesterification of triglycerides. The reactions and the composition of waste oil are based on the reactions reported by Shu et al [6]. Shu et al [6] used a carbon based solid acid catalyst from petroleum asphalt for the simultaneous reactions. The temperature used for the reaction is chosen as 200°C which is the mean temperature of the temperature range in the study of Shu et al [6]. High pressure is commonly used for the heterogeneous biodiesel production. This pressure is chosen as this is higher than the methanol vapour pressure at the reaction temperature [7]. Thus, 40 bar is used for the present study. Figure 2 shows the schematic diagram of the process flow for the production of biodiesel from waste oil.

The fresh methanol (METH stream) is mixed with recycled methanol (REC-MET stream) in a mixer (MIX2) to form the mixed methanol stream (M-METH stream), which consist mainly of methanol with trace amount of other recycled impurities from the recycle stream. Waste oil (WCO stream) with flow rate of 985 kg/hr is considered as a mixture of triolein and oleic acid (FFA). The compositions of FFA and the triglyceride (TG) is 50 wt% each. The waste oil (WCO stream) is mixed with the mixed methanol stream and fed to the reactor. The feed stream is pumped into the CSTR by a pump (P1) at high pressure. The solid catalyst is continuously fed into the CSTR with a rate of 4.9 kg /hr. It is equivalent to 0.005 mass ratio of the catalyst to waste oil. The methanol to waste oil molar ratio is fixed at 10.4 for waste oil with 50 wt% of FFA. The residence time in the CSTR is fixed at 2 hours since the reaction reaching its steady state at around 100 to 120 minutes [6].

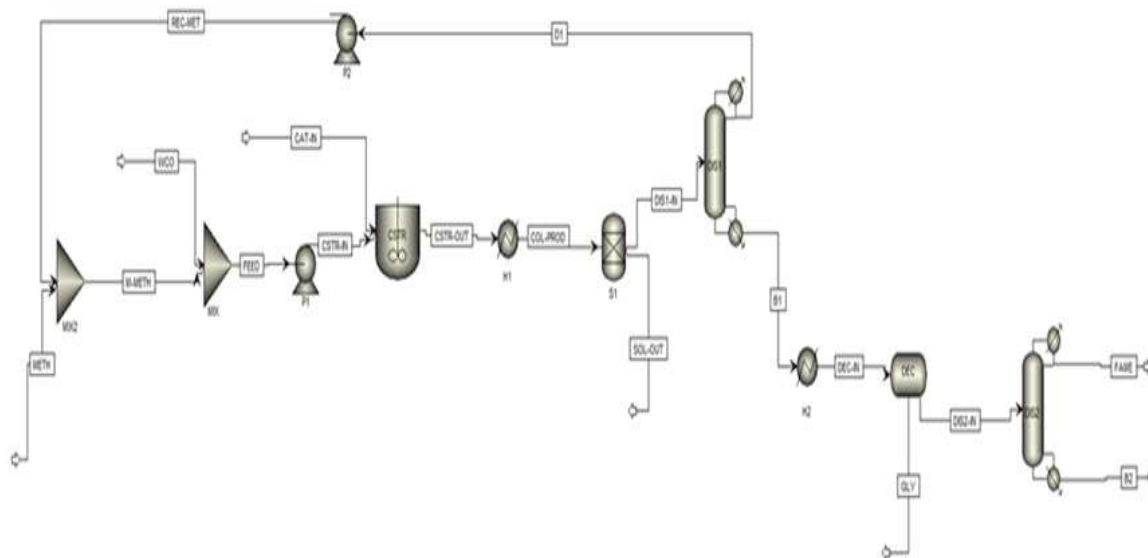


Figure 2. Heterogeneously catalyzed biodiesel production process.

3. Biodiesel process simulation

The process was simulated using Aspen Plus V8.6, as shown in Figure 2. All the components involved except for the catalyst are chosen from the components data banks available in Aspen. These components are water, methanol, glycerol, oleic acid (FFA), methyl-oleate (FAME), triolein, diolein, and monoolein. The catalyst, however, is input as a nonconventional solid in Aspen simulation as the molecular weight of the catalyst used (i.e. carbon-based solid acid catalyst from petroleum asphalt) is unknown. Since non-conventional solid is involved, the stream class for the simulation is chosen as MIXNCPSD. The base method for the simulation is chosen as NRTL for all unit operations as in West et al [3] except for decanter. NRTL is chosen because the components involved in the mixture are highly non-ideal due to the presence of high polar compound like methanol [3]. UNIF-DMD method is used for decanter in order to achieve the desired phase split [1,8]

4. Result and discussions

The details of all unit operation are shown in Table 1, while the details of the feeds and products stream are shown in Table 2. Table 3 shows the yields of both esterification and transesterification reactions. The yield of esterification is much higher than that of the transesterification. Shu et al [6] reported that triglyceride molecule with large alkyl chain is harder to activate compared to FFA. Their study on biodiesel production from high free fatty acid waste oil shows that esterification has higher activity compared to transesterification for all carbohydrate-based solid acid catalyst used in their study. The low yield of transesterification is due to the relatively low selectivity of FAME. On the other hand, the yield of FAME from esterification is higher. Therefore, large amount of FAME is produced, which drives the equilibrium of the transesterification reactions towards the reactant side, causing a low yield in the transesterification of oil [6]. In order to achieve higher yield, sensitivity analysis and optimization of the process towards several significant reaction variables is also carried out.

4.1. Sensitivity analysis

The flow rate of FFA in WCO stream is varied from 300 kg/h to 492 kg/h, which is equivalent to 38 wt% to 50wt% of FFA in the WCO feed. The decrease in FFA composition causes a slight drop in the yield of both transesterification and esterification (see Figure 3). The changes in both yields are about one percent for a 10% decrease in FFA composition. The increase in FFA composition drives the equilibrium of esterification towards the products side, which causes the slight increase in the

esterification yield. The rate of transesterification is much slower compared to the rate of esterification due to higher activation energy and the complexity of transesterification. Therefore, high FFA is favorable for simultaneous esterification and transesterification. The same trend is reported in the study carried out by Li et al. [9]. FAME yield (Y_T) from transesterification is given by;

$$Y_T = \frac{\% \text{ conversion of TG}}{100} \times \frac{\% \text{ selectivity for FAME}}{100} \times 100\%$$

Table 1. Operation details of all unit operations

Process	Operating Details		
Reaction	Reactor type	CSTR	
	Reaction Involve	Transesterification & Esterification	
	Reaction Type	Second order kinetic	
	Catalyst	Carbon based solid acid catalyst	
	T, P	200 °C, 40 bar	
	Methanol to oil ratio	10.4	
	Residence Time (hr)	2	
	Methanol Recovery	Reflux ratio	1.1
		Number of Stages	14
		Feed Stage Position	5
Distillate to Feed ratio		0.8	
Distillate purity (%)		99.71	
Catalyst Separation	Top/Bottom Stage Temperature	64.3/126.7	
	Separator Type	Solid-Liquid Separator	
Glycerol & Water Separation	Solid Split Fraction	1	
	Mechanisms	Gravity Separation	
Biodiesel Purification	Reflux ratio	1.2	
	Number of Stages	19	
	Feed Stage Position	10	
	Distillate to Feed ratio	0.79	
	Distillate purity (%)	99.1	

Table 2. Feed and product stream details

	Feed Stream			Product Stream				
	METH	WCO	CAT-IN	FAME	B2	GLY	SOL-OUT	
Phase	Liquid	Liquid	Solid	Phase	Liquid	Liquid	Liquid	Solid
Temperature (°C)	25	25	25	Temperature (°C)	60.98	248.72	23.58	25
Pressure (bar)	1.013	1.013	1.013	Pressure (bar)	1.013	1.013	1.013	1.013
Molar Flow (kmol/hr)	2.96	2.30	-	Molar Flow (kmol/hr)	2.81	0.75	1.70	-
Mass Flow (kg/h)	94.78	985.09	4.90	Mass Flow (kg/h)	775.65	265.36	38.90	4.90

Composition (mass fraction)				Composition (mass fraction)				
Methanol	1.00	0	-	Water	0.0036	0.0000	0.7124	-
Triolein	0	0.5	-	Methanol	0.0025	0.0000	0.0490	-
Oleic Acid	0	0.5	-	Glycerol	0.0001	0.0000	0.2386	-
				Oleic acid	0.0000	0.0521	0.0000	-
				Methyl-oleate	0.9912	0.2755	0.0000	-
				Triolein	0.0025	0.1081	0.0000	-
				Mono-olein	0.0000	0.5638	0.0000	-
				Dirolein	0.0000	0.0005	0.0000	-

Table 3. FAME yield of transesterification and esterification

Reaction	Parameter	
Transesterification	Conversion of Triolein (%)	93.78
	Selectivity of FAME (%)	73.16
	Yield (%)	68.61
Esterification	Conversion of FFA (%)	97.19
	Yield (%)	97.19

Table 4. Comparison of Optimization results against base case

Variables	Optimization Results	Base case
FAME stream flow rate (kmol/hr)	2.8132	2.8129
Manipulated:		
Reactor Temperature (°C)	223.1	200
Constraints		
FAME purity (wt%)	99.0	99.1
Methanol purity at the top of DIS1 (wt%)	99.7	99.7
Temperature of DIS1 (°C)	125.1	126.7
Temperature of DIS2 (°C)	249.6	248.7

From Figure 4, it is seen that the increase in temperature leads to a decrease in FAME yield from transesterification. From the kinetic of the reactions, higher temperature favors the formation of monoglycerides [6]. This also explains why the monoglyceride in the simulated process has a much higher composition compared to diglyceride and glycerol. On the other hand, an increasing trend in FAME yield is found with increasing temperature in esterification reactor.

4.2 Optimization.

Table 4 shows that the FAME product flow rate is above 2.81 kmol/h for all tested temperature. The biodiesel flow rate is maximized considering CSTR temperature (180°C to 250°C) as a decision variable and FAME purity (>98%), Methanol recovery purity (>98%), Temperature of DIS1 (<150°C) & Temperature of DIS2 (<250°C) as constraints. The optimized results show that a higher temperature of 223.1°C can produce the maximum FAME product (see Table 4). However, the increase of the FAME product flow rate is insignificant. The use of higher temperature is coupled with the increase of pressure and thus it will result in higher operating cost.

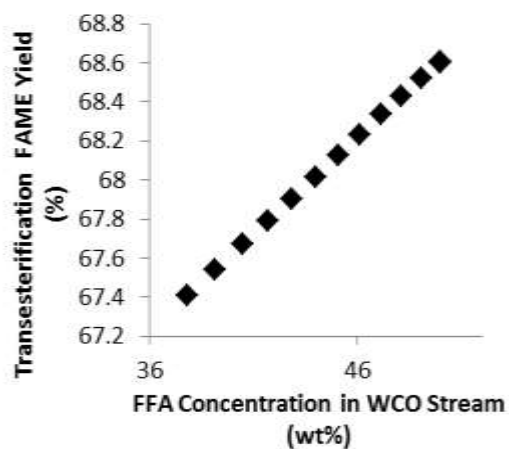


Figure 3a. Sensitivity Analysis by varying FFA concentration in WCO stream in transesterification

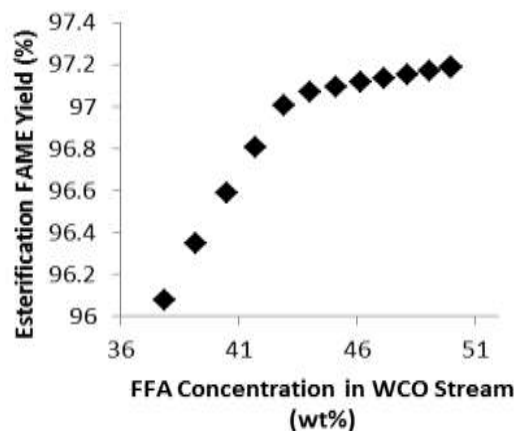


Figure 3b. Sensitivity analysis by varying FFA concentration in esterification.

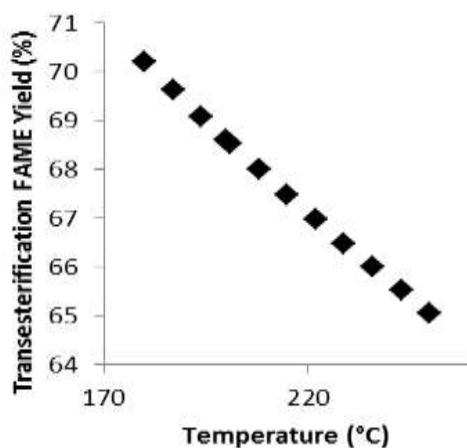


Figure 4a. Sensitivity Analysis by varying reactor temperature in transesterification

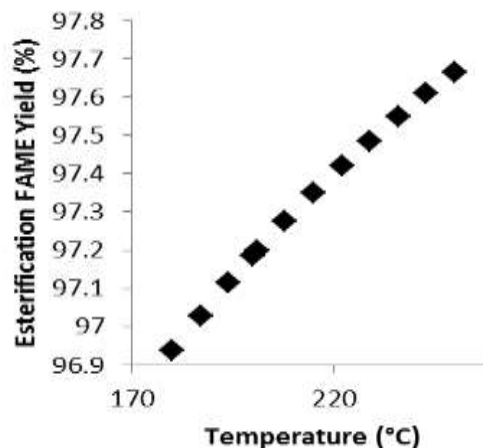


Figure 4b. Sensitivity analysis by varying reactor temperature in esterification.

5. Conclusions

A biodiesel production from the oil having 50% FFA using a heterogeneous catalyst is simulated using Aspen Plus V8.6. The process is relatively simple, and has lesser number of unit operations. Separation of catalyst can be done using a simple solid-liquid phase separator. The kinetics of simultaneous transesterification of triolein and esterification of FFA using a carbon based solid acid catalyst are considered in the simulation. FAME with purity of 99.12wt % at flow rate of 2.81 kmol/hr is produced from this process. The yield of FAME from transesterification and esterification is 68.61% and 97.19% respectively. Thus, the simulated process is feasible in producing FAME meeting the international standard (EN 14214). In addition, optimization and sensitivity analysis studies are carried out.

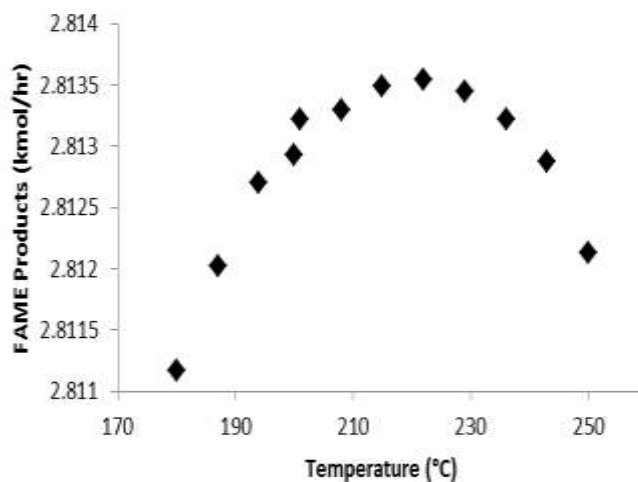


Figure 5. FAME products flow rate at different reactor temperature.

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