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Biodiesel Production from Waste Frying Oil and Its Process Simulation

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The paper explores the effect of the quantity of methanol on biodiesel production and its characteristics from Waste Frying Oil (WFO). Based on the results, it progresses to develop a continuous process simulation that can be scaled-up for commercial applications. Pretreatment of WFO was carried out by acid-esterification, followed by base-catalyzed transesterification. Optimum molar ratio of methanol: oil was found to be 6:1 experimentally which was then used in Aspen HYSYS to develop a continuous process flowchart. The properties of the product from both approaches were found to be comparable and satisfactorily compatible with the ASTM standards for biodiesel fuel.

Keywords: Biodiesel, Waste frying oil, Aspen HYSYS

1. Introduction

Proper utilization of waste frying oil to produce biodiesel is a promising approach to ensure environmental protection and energy security in this era of energy crisis. Due to the depletion of petroleum reserves and the environmental impact of using fossil fuel, it is necessary to look for an alternative source of fuel. Biodiesel, derived from vegetable oil or animal fats, can be a substitute of petroleum based diesel and considered as renewable energy source (Meng et al. 2008; Lapuerta et al. 2008). It is estimated that biodiesel/bio-ethanol could replace approximately 10% of diesel fuel consumption within Europe and 5% of Southeast Asia's total fuel demand (Phan & Phan, 2008). Compared to commercial diesel, biodiesel is environment friendly because of its sulphur free benefit and non-toxicity, lower greenhouse gas emission and higher flash point (Zhang et al. 2003; Gerpen 2005; Zheng et al. 2006; Talebian-Kiakalaieh et al. 2013).

High cost of biodiesel compared to the petroleum based diesel is the major obstacle for commercialization of biodiesel (Meng et al. 2008). In July 2015, the price of biodiesel was $3.55 per gallon whereas for diesel it was $2.93 per gallon in US (Bourbon, E. 2015). The high cost of biodiesel is mainly due to the cost of fresh vegetable oil such as soybean oil. The cost of soybean oil was $751 per metric ton (i.e. $2.61/gal) which is approximately 70%–95% of the total biodiesel production cost (Zhang et al. 2003; Leung & Guo 2006; YCharts 2015). Waste Frying oil (WFO) have the potentiality to be used as the feedstock of biodiesel production as it is 2–3 times cheaper than virgin vegetable oils (Phan & Phan, 2008). The total manufacturing cost of biodiesel can be considerably reduced if WFO is used instead of fresh oil.

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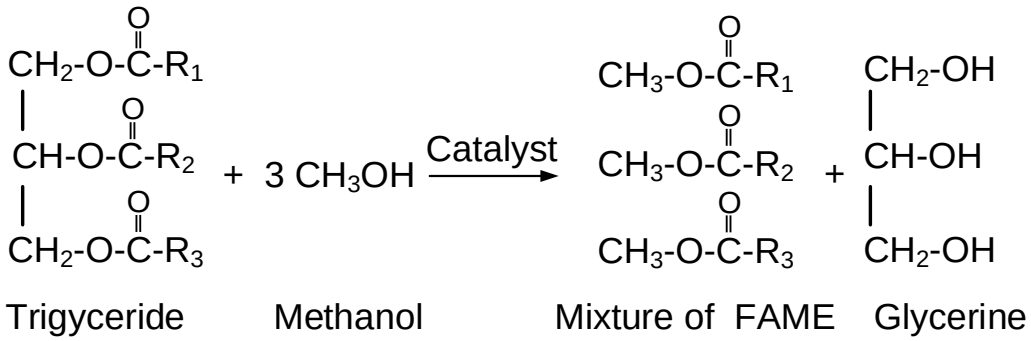
An enormous amount of waste oil is generated from restaurants and food processing industries everywhere in the world. The Energy Information Administration (EIA) in the United States (USA) estimated that around 100 million gallons of waste cooking oil is produced per day in USA and about 9 pounds are generated per person per year. In addition, the estimated amount of waste cooking oil collected in Europe is about 0.49 - 0.7 million gallons/day (Patil et al. 2012). The conversion of this large amount of WFO into fuel can eliminate the environmental impacts caused by the harmful disposal of these waste oils to some extent (Lam et al. 2010). The necessity for finding an appropriate approach for converting the large amount of WFO into biodiesel, not only to reduce the harmful effects on environment but also to meet the present energy crisis, was the drive towards this study.

Although several studies have been made on production of biodiesel from waste frying oil (WFO) and optimization of reaction conditions in laboratory scale, this research is unique as it also includes the implementation of the experimentally found process conditions into continuous steady state process simulation using Aspen HYSYS for commercial production. Aspen HYSYS is a current software to simulate any proposed chemical process and to assess the commercial feasibilities of the process. It can provide reliable information on process operation because of its inclusive thermodynamic packages along with vast component libraries and advanced calculation techniques. The process flow sheet serves as a model, representing the real process. As the simulation is based on the optimum conditions verified experimentally, it can be readily scaled up to achieve the most profitable industrial production. The significance of this study lies in the harmonised combination of the experimental study and Aspen technology.

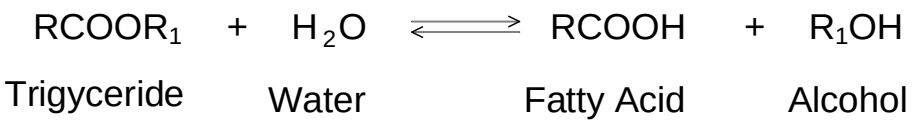
Section 1 presents a simple “Introduction” to the paper. Section 2 focuses on a detailed “Literature Review”. Section 3 describes the “Methodology” employed followed by the “Results and Discussions” in Section 4. Section 5 finally presents a brief “Conclusion”.

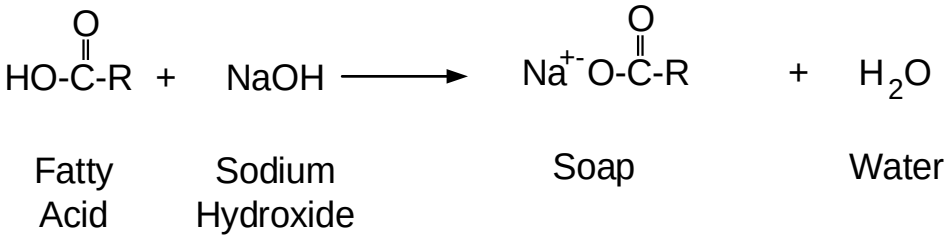
2. Literature Review

The process for biodiesel production is known as transesterification which involves chemical reaction between oil (triglycerides) and short chain alcohol such as methanol and ethanol in presence of a suitable catalyst to yield fatty acid alkyl esters i.e. biodiesel and glycerin as by-product (Predojević, 2008). Methanol is mostly used for the transesterification due to its low cost and advantageous physical and chemical properties (Demirbas 2009). Moreover, catalyst can be dissolved faster in methanol than other alcohols to react easily with triglycerides (Talebian-Kiakalaieh et al. 2013). According to stoichiometry, three moles of methanol reacts with one mole triglyceride to produce fatty acid methyl ester (FAME) as shown in the following reaction.

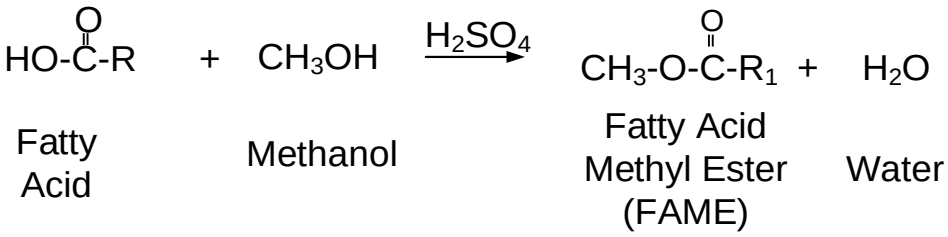


Transesterification reactions are basically of three types: alkali-catalyzed, acid-catalyzed or enzyme-catalyzed. The third one is expensive and relatively slow than the first two (Marchetti et al. 2007). Sodium or Potassium hydroxide (KOH) are the commonly used alkali catalysts due to rapid reaction rate and high yields. By alkali catalyzed process, biodiesel production from WFO is challenging due to the presence of undesirable components such as free fatty acids (FFAs) and water. The FFA content is directly related to the acid number of WFO and is a serious issue when feedstock with high FFA are used for manufacturing. Water can be originated from the oils and formed during the saponification reaction and can hydrolyze the triglycerides to diglycerides resulting in the formation of FFA (Komintarachat & Chuepeng, 2010). WFO typically contain 2–7% FFAs and upon addition of an alkali catalyst to it, the FFAs react with the catalyst to form soap and water. The reactions are given below:





For WFO with up to about 5% FFA content, the reaction can still be catalyzed with an alkali catalyst. However, additional catalyst must be added to compensate for the catalyst lost to soap. The formed soap should be removed to meet the standard such as European Union standards for alternative diesel fuel which restricted minimum biodiesel purity to 96.5%. Removal of soap and purification of biodiesel can be done by washing with hot distilled water, citric, 5% phosphoric acid and with silica gel (Predojevic´ 2008). When the FFA level is above 5%, an acid catalyst, typically sulfuric acid, is more suitable for esterification of FFAs to methyl esters, as shown in the following reaction:



Acid catalyzed process is non-practical for biodiesel production commercially because of its slow reaction rate, high molar ratio of alcohol to oil condition, requirement of high temperature and problem related to separation of the catalyst. For WFO with a high free fatty acids content (acid value higher than 2mg KOH/g), a dual step transesterification process is recommended to improve the bio-diesel yield (Jacobson et al. 2008). In the first step, FFA is converted to methyl ester in presence of methanol and an acid catalyst. After this pre-treatment, transesterification process is carried out in which triglyceride portion of the oil reacts with methanol and base catalyst to form biodiesel (Bautista et al. 2009; Felizardo et al. 2006).

3. Methodology

a. Laboratory Experiment

Waste frying oil collected from different restaurants in Dhaka, Bangladesh were mixed. This mixture of WFO was filtered to remove any suspended food particles and organic residues, and heated to about 100°C for water removal. 200 mL of the WFO was weighed, and heated to 55°C in a 1L glass conical flask. Methanol was pre-mixed with 2mL of 95% sulphuric acid, and transferred to the reactor containing the hot oil. The reactor was equipped with a reflux condenser using cold tap water to condense and return to flask any vaporizing methanol and a magnetic bar to stir the reactor contents at 700 rpm. This pre-treatment reaction was allowed to proceed for 2 hours. Then methanol dissolved in sodium hydroxide was added to the reaction mixture. The reactor temperature was maintained at $55 \pm 2^{o}C$ throughout the experiment. The pre-treatment was done using an invariant methanol:oil molar ratio of 12, and for the transesterification this ratio was varied. After one hour of transesterification, the reactor contents were transferred to a separating funnel and allowed to settle. The glycerine was separated from the biodiesel and the biodiesel layer was washed with warm water several times. The obtained biodiesel were heated to remove any water. The WFO and the clear biodiesel samples were analysed for different fuel properties.

b. Aspen HYSYS Simulation

Process simulation for the production of biodiesel from waste frying oil was carried out in Aspen HYSYS 2006 at steady state mode. Non-random two-liquid (NRTL) thermodynamic package model was used due to the presence of highly polar glycerol and methanol. The chemical components methanol, glycerol, sulphuric acid, and sodium hydroxide are available in the HYSYS component library, but waste frying oil had to be defined as a hypothetical component. Since oleic acid is the major fatty acid in vegetable oil, biodiesel was represented by methyl oleate and WFO by hypothetical component triolein ($C_{57}H_{104}O_6$) (Zhang et al. 2003). The molecular weight, normal boiling point, density, critical temperature and pressure, heat of formation and combustion of triolein were defined from NIST (National Institute of Standards and

Technology) Chemistry Webbook, and others were estimated by HYSYS. Molar ratio of methanol: oil of 6:1 was used for the transesterification reaction, as this ratio gave maximum yield from the experiment. A continuous transesterification and biodiesel production process flow sheet was developed.

4. Results and Discussion

Experimental Results

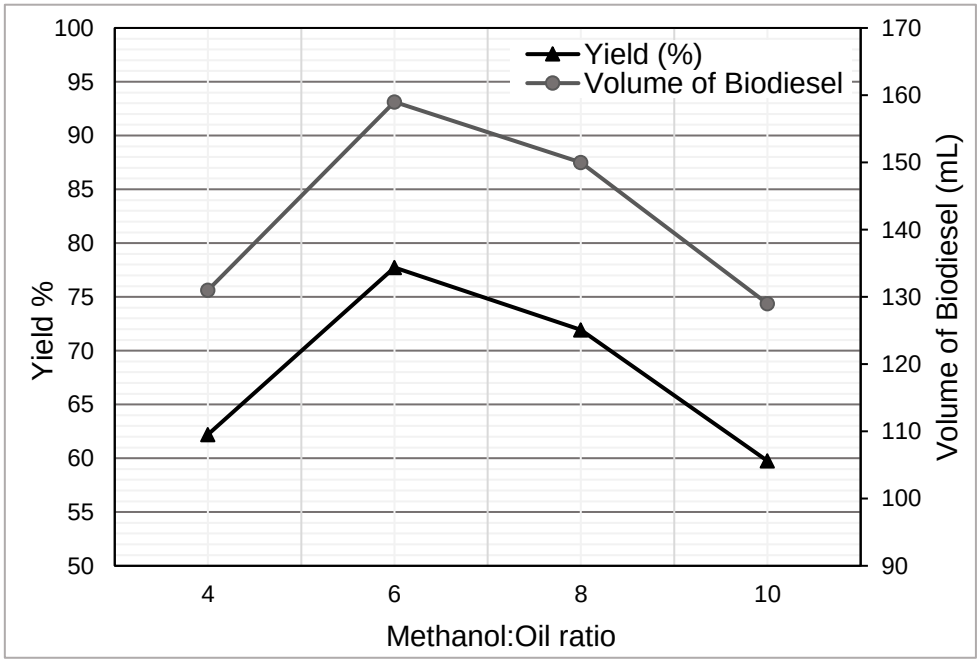
Experimental Biodiesel Yield

The influence of the variable methanol:oil ratio on the yield of biodiesel was studied for the ratios 4, 6, 8, and 10. The stoichiometric ratio of methanol to triglyceride in the transesterification reaction is 3:1. So, 4:1 was taken as the starting value.

$$\text{Mass Yield (\%)} = \frac{\text{mass of biodiesel}}{\text{mass of waste frying oil}} \times 100$$

Figure 1 illustrates the variation of percentage mass yield and volume of biodiesel production with different methanol:oil ratio. It was found that at 6:1 molar ratio maximum yield of 77.7% was obtained. At this ratio maximum volume of 159 mL biodiesel was obtained.

Figure 1: Yield and Volume of Biodiesel at Different Methanol: Oil Ratio



Characterization of waste frying oil and Biodiesel

Physical Properties of Biodiesel:

- State: Liquid
- Colour: Brown

- Clarity: Clear
- Solubility: Immiscible in water

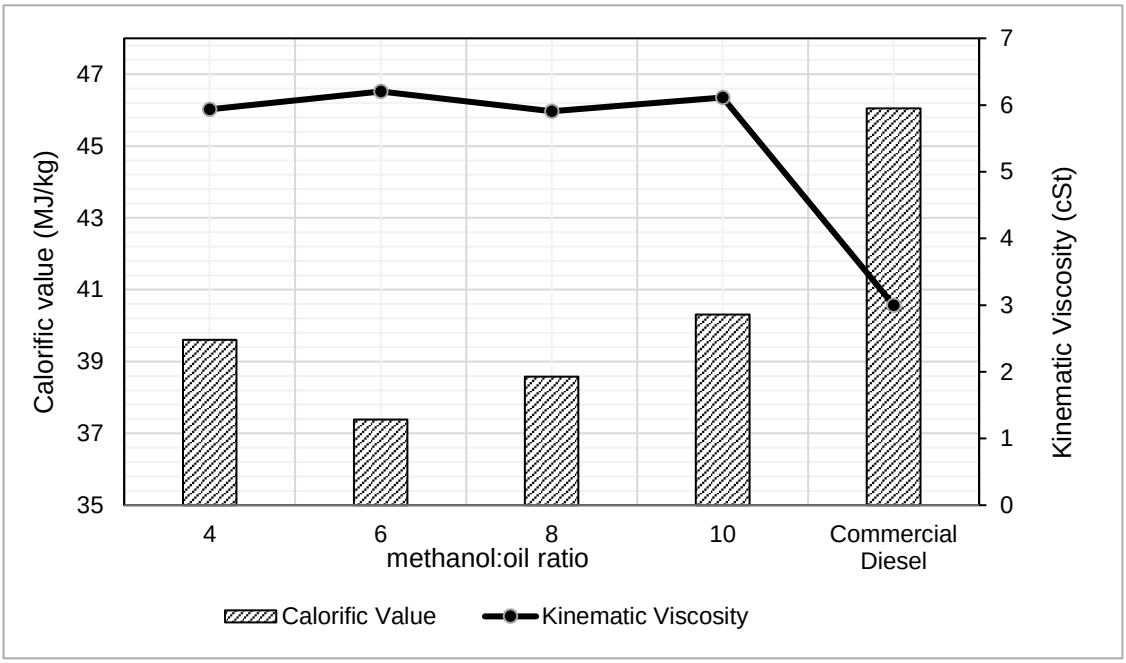
Fuel density and viscosity are very important properties for fuels, as it affects engine performance and combustion. Density is also a strong indication of presence of impurities, as any contaminant will largely influence it. For complete combustion inside engine, small fuel drop is required. Lower viscosity ensures more efficient fuel atomization inside engine combustion chamber, thus lessening the chance of harmful incomplete combustion products formation. Calorific Value is important for biodiesel not only to comprehend its consumption for a certain purpose but also to compare it with other mineral diesels on the basis of energy content. Water content of the fuel needs to be within a certain limit, otherwise corrosion of the engine might occur. These properties are summarized in Table 1.

Table 1: Properties of Biodiesel and Waste Frying Oil

Property	ASTM Method	Biodiesel				WFO
		Methanol: Oil Ratio				
		4:1	6:1	8:1	1:10	
Specific gravity	ASTM D 1298-67	0.88	0.88	0.88	0.88	0.92
API gravity	ASTM D 1298-67	31.5	31.0	31.0	31.0	23.5
Kinematic Viscosity at 40℃ (cSt)	ASTM D 88-94	5.94	6.20	5.91	6.12	41.98
Calorific Value (MJ/kg)	ASTM D 2015-96	39.61	37.38	38.58	40.30	39.18
Water and Sediment (v/v %)	ASTM D 1796-97	0.0	0.0	0.0	0.0	0.0

The specific and API gravity of the biodiesel produced from different methanol amount were similar, and it can be concluded that amount of methanol does not have any influence on them.

Figure 2: Comparison of Calorific Value and Kinematic Viscosity of the Biodiesel Produced from Different Methanol: Oil Ratio and Commercial Diesel



From Figure 2, the kinematic viscosity and calorific value data were analysed, and it was seen that the molar ratio 6:1 produces biodiesel with the least calorific value, and highest viscosity. Thus, although 6:1 gives maximum yield, the properties of the biodiesel thus produced are less in favour than other samples. However, it satisfied the requirements of related International Standard. The vast difference of the calorific value and viscosity of the biodiesel and of commercial diesel signifies the necessity of blending it with commercial diesel and engine modification requirements for higher blends.

Simulation Results

Process-flow diagram (PFD)

WFO was heated to 55^{o}C in heater E-100 and warm WFO was reacted with methanol and sulphuric acid in *Pre-treatment Vessel*. The unreacted methanol was separated in the *Methanol Separator* to ensure that in *Transesterification Vessel* the WFO reacts with the freshly prepared sodium methoxide only. The product from transesterification vessel was settled in the *Separating Vessel*, which represents the initial separation of the lower layer in the separating funnel in laboratory experiment. Glycerol along with most of the other unconverted reactants are removed in the lower layer. The trace amounts of methanol, sulphuric acid, sodium hydroxide present with the methyl oleate in the upper layer were removed in *Water Washing*. This represents the several washes in the separating funnel. This column with 10 theoretical stages produced the raw biodiesel, which was purified by removal of excess water as water vapour in *Final Purification* unit. The purpose of this step was to obtain a biodiesel product obeying the ASTM specifications. The hot biodiesel was then cooled. The entire process flow diagram (PFD) is shown in Figure 3 and the stream specifications from the material and energy balances performed in Aspen HYSYS is summarized in Table 2.

Figure 3: Process Flow Diagram (PFD) of Biodiesel Production Along with Purification from Waste Frying Oil (WFO) Generated in Aspen HYSYS

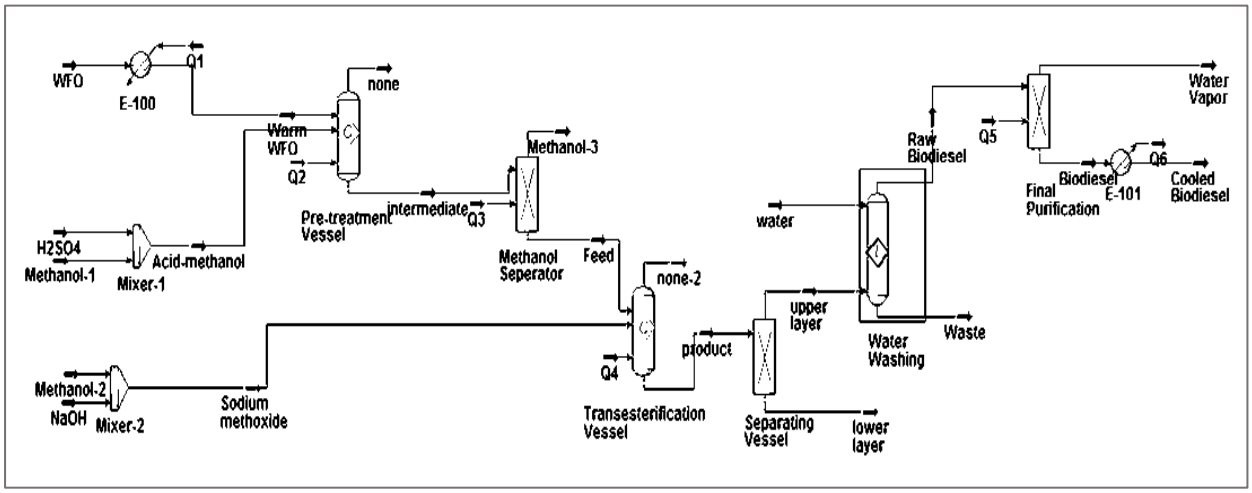


Table 2: Material Streams and Their Compositions Extracted from HYSYS Workbook

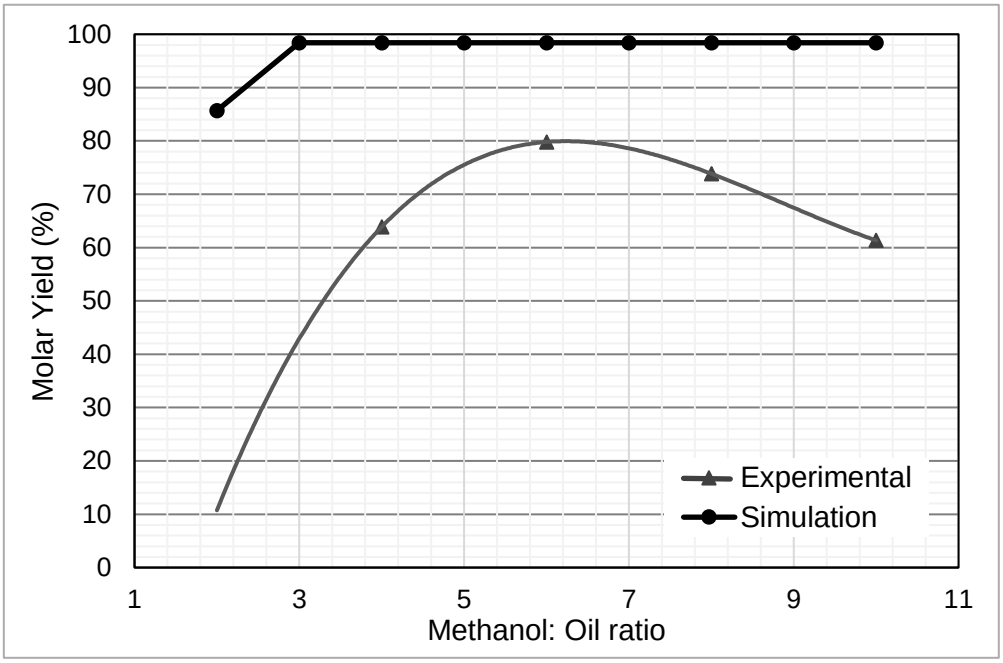
Stream Specification	Material Streams							
	WFO	Warm WFO	H_2SO_4	Methanol-1	NaOH	Methanol-2	Intermediate	Feed
Molar Flow (gmole/h)	0.215	0.215	4×10^{-5}	0.429	0.119	1.287	0.681	0.381
Liquid Volume flow (mL/h)	200	200	2	17.28	-	52.09	220.8	208.7
Temperature (°C)	25	55	25	25	25	25	55	55
Composition								
M-Oleate	1.000	1.000	0.000	0.000	0.000	0.000	0.189	0.338
Methanol	0.000	0.000	0.000	1.000	0.000	1.000	0.441	0.000
H2SO4	0.000	0.000	1.000	0.000	0.000	0.000	0.055	0.099
Glycerol	0.000	0.000	0.000	0.000	0.000	0.000	0.063	0.112
NaOH	0.000	0.000	0.000	0.000	1.000	0.000	0.000	0.000
H2O	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Triolein	0.000	0.000	0.000	0.000	0.000	0.000	0.252	0.451
Stream Specification	Material Streams							
	Product	Lower Layer	Upper Layer	Water	Raw Biodiesel	Waste	Water vapor	Biodiesel
Molar Flow (gmole/h)	1.787	1.112	0.675	15	3.9515	11.724	3.318	0.634
Liquid Volume flow (mL/h)	269.2	50.31	218.9	270.8	274.1	215.6	-	214.2
Temperature (°C)	55	76.61	45.77	50	50	48.17	59.9	100
Composition								
M-Oleate	0.354	0.000	0.938	0.000	0.160	0.000	0.000	0.9999
Methanol	0.427	0.652	0.057	0.000	0.000	0.003	0.000	0.0000
H2SO4	0.032	0.051	0.000	0.000	0.000	0.000	0.000	0.0000
Glycerol	0.118	0.190	0.000	0.000	0.000	0.000	0.000	0.0000
NaOH	0.067	0.107	0.000	0.000	0.000	0.000	0.000	0.0000
H2O	0.000	0.000	0.000	1.000	0.840	0.997	1.000	0.0000
Triolein	0.002	0.000	0.005	0.000	0.000	0.000	0.000	0.0001

Analysis of Experimental and Simulation Results

Yield comparison

Data for the simulation curve was generated in the Case Studies of databook of HYSYS. For doing so, molar flow of biodiesel was taken as the dependant and that of WFO as the independent variable and nested state input for 9 states was used. The curve for experimental data was extrapolated backwards to make a general prediction as shown in Figure 4. In the Simulation curve, maximum yield of 98.4% was achieved at 3:1, which is the stoichiometric ratio.

Figure 4: Comparison of Yield of Biodiesel from Experimental and HYSYS Simulation



Characteristics Comparison

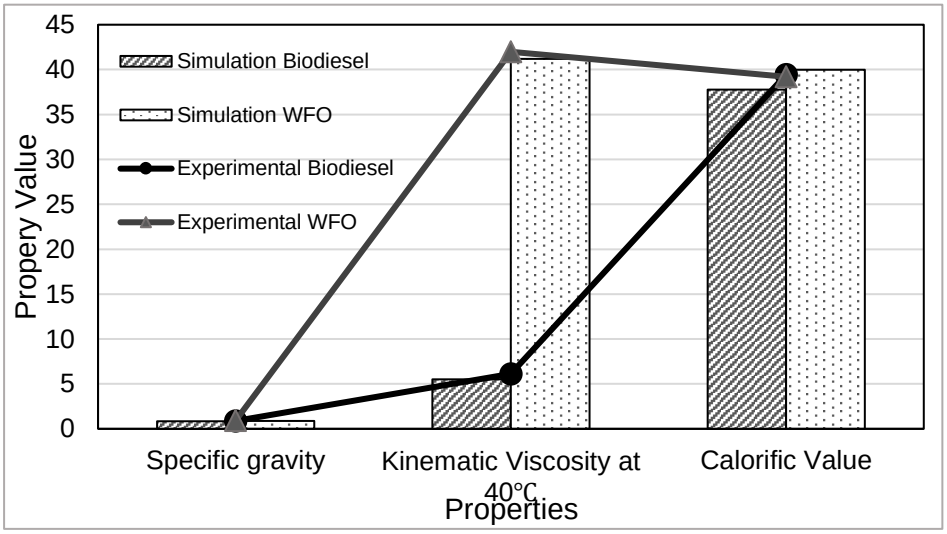
The measure for biodiesel quality is related to the physical and chemical properties set by certain standards and specifications. It is necessary to check if the biodiesel produced met the quality standards. Quality standards are continuously being restructured, based on factors like existing diesel fuel standards, most commonly used diesel engine type, emission regulations, and climatic properties etc., which vary from region to region. The standard ASTM D6751 specifies the quality requirements and the methods of analysis used for biodiesel (B100), including methyl esters (FAME) and ethyl esters (FAEE) for blending with diesel oil. ASTM D6751 specifications for some important properties of B100 were compared with the obtained property. The achieved data from the experiment and the simulation is shown in Table 3. The properties were consistent with the standard values and thus these samples can be used as blends with commercial diesel.

Table 3: Summary of Properties of Waste Frying Oil, Biodiesel and Commercial Diesel

Property	Waste Frying Oil		Biodiesel			Commercial Diesel (Demirbas, 2009)
			Experiment			
	Experiment	HYSYS	Average Values	ASTM D6751 values	HYSYS	
Specific Gravity	0.92	0.89	0.88	-	0.85	0.85
API	23.5	-	31.1	-	-	30-35
Viscosity(cSt)	41.98	41.18	6.10	1.9 -6	5.51	1.9-4.1
Calorific Value(MJ/kg)	39.18	39.98	39.44	35 (min)	37.77	45.62-46.48
Molecular Weight (g/mol)	900	885.4	292.2	N/A	296.5	N/A
Water content (%v/v)	0	0	0	0.05% max	0	N/A

All properties, but kinematic viscosity, of waste frying oil and the biodiesel obtained from it were similar. The difference in properties of the biodiesel from its starting material can be comprehended easily from the graphical illustration in Figure 5. Since the viscosity of the biodiesel samples were found to be much lower than that of the waste frying oil, it burns cleaner. It is the lower kinematic viscosity of the biodiesel that makes it different from the staring material, ensuring that it can be atomized in combustion chambers, and hence can be used in diesel engines.

Figure 5: Comparison of General Properties of WFO and Biodiesel Produced from It.



5. Conclusion

In this study, biodiesel production from waste frying oil (WFO) was demonstrated in laboratory approach and simulation approach. Experimental result identifies one of the major optimum process parameters for base-catalyzed transesterification on biodiesel yield as well as its properties. Simulation of a commercial biodiesel production plant based on laboratory results is a rare study and certainly no previous research has been conducted on this for WFO production in Bangladesh. The HYSYS model for the continuous steady-state process is a remarkable outcome of the study. Further verification of other process conditions can also be conducted experimentally as future work. The simulation results can serve as an efficient tool for scale-up and design of a commercial biodiesel production plant from WFO. The optimum methanol: oil ratio of 6:1 was found to yield maximum biodiesel, and the characteristics of the experimental biodiesel sample and the simulation biodiesel stream well-matched the relevant International Standards for biodiesel quality. However, the viscosity of the biodiesel thus produced was quite high to be directly used in diesel engines. This limitation can be resolved by blending it with commercial diesel and further study on this can be recommended.

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