Recycling of Waste Cooking Oils (WCO) to Biodiesel Production

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Abstract—**A process for biodiesel production by using a waste cooking oils is studied depending on a Libyan market data. The considered process contains two units: first unit is free fatty acids pretreatment followed by alkali-catalyzed trancesterification process as a second unit. Simulation models of these processes are developed using the chemical process simulator ASPEN Hysys®. Results show the gained production feedback of biodiesel reaches 97% wt. with a purity of 99.95% wt. Thereby making it a competitive alternative to petrodiesel fuel in the future Libyan market.**

Keywords—Biodiesel; Triolein; Hysys; Libya; Waste cooking oils; Vegetable oils.

I. INTRODUCTION

Biodiesel, as an alternative fuel, has many merits. It is derived from a renewable, domestic resource, thereby relieving reliance on petroleum fuel imports [1]. It is biodegradable and non-toxic. Compared to petroleum-based diesel, biodiesel has a more favorable combustion emission profile, such as low emissions of carbon monoxide, particulate matter and unburned hydrocarbons. Carbon dioxide produced by combustion of biodiesel can be recycled by photosynthesis, thereby minimizing the impact of biodiesel combustion on the greenhouse effect [2, 3]. Biodiesel has a relatively high flash point (150 ^{o}C), which makes it less volatile and safer to transport or handle than petroleum diesel [4]. It provides lubricating properties that can reduce engine wear and extend engine life [5]. Biodiesel represents a largely closed carbon dioxide cycle (approximately 78%), as it is derived from renewable biomass sources. Compared to petroleum diesel, biodiesel has lower emission of pollutants, it is biodegradable and enhances the engine lubricity [6] and contributes to sustainability [6, 7]. Biodiesel has a higher cetane number than diesel fuel, no aromatics, no sulfur, and contains 10–11% oxygen by weight [8]. In brief, these merits of biodiesel make it a good alternative to petroleum based fuel and have led to its use in many countries, especially in environmentally sensitive areas [1].

The most common way to produce biodiesel is by transesterification, which refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters (i.e., biodiesel) and glycerol. In which the diversity and the extent of vegetable oils has created a potential for biodiesel production in different countries regarding various climate conditions [9]. Triacylglycerols (triglycerides), as the main component of vegetable oil, consist of three long chain fatty acids esterified to a glycerol backbone. When triacylglycerols react with an alcohol (e.g., methanol), the three fatty acid chains are released from the glycerol skeleton and combine with the alcohol to yield fatty acid alkyl esters (e.g., fatty acid methyl esters or FAME) [1]. Transesterification reactions can be alkali-catalyzed, acid-catalyzed or enzyme-catalyzed. The first two types have received the greatest attention but due to despite its insensitivity to free fatty acids in the feedstock, acid-catalyzed transesterification has been largely ignored mainly because of its relatively slower reaction rate. In this method, the resulting biodiesel has high cetane number, low emission of pollutants, and high combustion efficiency and besides, this method leads to conserve oxygen atoms in biodiesel molecule [10]; so, transesterification by alkali-catalyzed is the dominant process and focus of this article. As for the enzyme-catalyzed system, it requires a much longer reaction time than the other two systems [11, 12]. To date it has only been carried out on the laboratory scale and therefore will not be further discussed herein. Huge quantities of Waste Cooking Oils (WCO) and animal fats are available throughout the world, especially in the developed countries. So, producing biodiesel from waste edible oils is a promising alternative, since this type of oils can be provided in lower cost compared with fresh oils [10]. Management of such oils and fats pose a significant challenge because of their disposal problems and possible contamination of the water and land resources [13]. Even though some of this waste cooking oil is used for soap production, a major part of it is discharged into the environment. Furthermore, using waste edible oils helps to protect the environment because these oils are discharged into the environment without any processing [14]. From the other side, due to the exposure to high temperature, waste edible oils possess high levels of free fatty acids from which one stage biodiesel production causes a reduction in product level and two-stage biodiesel production applying such methods as pre-esterification causes an increase in production total cost [15].

In the EU countries, the total waste cooking oil production was approximately 700,000-1,000,000 t/y [16]. The UK produces over 200,000 tons of waste cooking oil per year [17]. While in Canada could be

approximately 135,000 t/y [13]. In Libya, The Box of Prices Balance (followed by a State is responsible for determining the amount of basic foods requirements and the prices of consumer) estimated that some 5,000 liter of waste cooking oil is produced per day in Libya, where the average per capita waste cooking oil was reported to be 15,000 liter of yellow oil (corn and sun flower) oil consumed per day [18]. Hence, the total waste cooking oil produced in Libya could be approximately 1,650 t/y. As large amounts of waste cooking oils are illegally dumped into rivers and landfills, causing environmental pollution [19], the use of waste cooking oil to produce biodiesel as petrodiesel substitute offers significant advantages because of the reduction in environmental pollution. The use of waste cooking oil as a biodiesel source has a potential to reduce CO_2, particulate matter and other greenhouse gases as the carbon contained in biomass-derived fuel is largely biogenic and renewable [13].

Waste cooking oil, which is otherwise wasted, is one of the most economical choices to produce biodiesel. Since one of the major concerns on biodiesel production is the price of feedstock, utilization of waste cooking oil significantly enhances the economic viability of biodiesel production. In which concerns biodiesel production the transesterification reaction is very sensitive to the feedstock purity that directly affect the reaction performance. Contrarily to refined vegetable oils, waste oils and animal fats usually have a lot of impurities, such as FFA and water that negatively affect the reaction yield, reducing the reaction rate by several orders of magnitude, even in small amounts [8]. For this reason some pre-treatment operations are conducted, such as the esterification of FFA to biodiesel [20].

II. MATERIALS AND METHODS

A. Plant Capacity

The determination of plant capacity was based on the reported availability of waste cooking oil in the Libya. Box of prices balance (followed a Libyan State, it is responsible for determining the amount of basic foods required and the prices for consumers) analyzed data on oil consumption in Libya. Concludes that on average, 15,000 litre/day of yellow grease (Corn Oil, Sun flower oil) were consumed in Libya [18]. Depending on this fact, assume that about one third of this quantity are produced as a waste cooking oil may be collect from restaurants, hotels, and households. So, the biodiesel plant capacity is approximately 1,600 t/y (about 202 kg/h) for a 330 day as operation time.

B. Process Simulation

In this study, mass and energy balances for each unit are done, depending on the input information and operating unit models were set up. The process steady-state simulation was executed by the ASPEN Hysys® simulator v7.3. A Wilson-ideal thermodynamic package model was used to predict the activity coefficients in the process simulations. The procedures for process simulation mainly involve defining chemical components, selecting a thermodynamic model, determining plant capacity, choosing proper operating units and setting up input conditions (flow rate, temperature, pressure, and other conditions).

Information on most components, such as methanol, glycerol, sulfuric acid, sodium hydroxide and water is available in the ASPEN Hysys component library. Regarding the WCO feedstock in this study the triglycerides are represented by Triolein ($C_{57}H_{104}O_6$) with (90% wt.), the FFA present in the waste vegetable oil are represented by oleic acid ($C_{18}H_{34}O_2$), (10% wt.), and FAME are represented by oleic acid methyl ester ($C_{19}H_{36}O_2$). Accordingly, methyl oleate ($C_{19}H_{36}O_2$) was taken as the resulting biodiesel product and its properties were available in the Aspen Hysys v7.3 component library. For those components not available in the library, such as triolein, sodium hydroxide and sulfuric acid, they were defined using "the Hypo Manager" tool in ASPEN Hysys v7.3. Detailed procedures for defining each component were presented by Zhang [21] and Morrais, et al. [22].

C. Process Design

A continuous process was designed and simulated through two units. The first unit of process is prêtreatment of waste coke oil followed by the alkali-catalyzed as the second unit of process for biodiesel production.

1) Pretreatment Unit:

A pretreatment unit of WCO including three steps; esterification of FFA, methanol recovery, and glycerol washing. The pretreatment unit is shown in Fig.1. A WCO stream flow rate of 202.0 kg/h is fed to an esterification reactor (CRV-100) where the FFA are converted to methyl esters. It is 10% wt. of oleic acid content in the waste cooking oil [23]. It is used a fresh methanol stream flow rate of 2.304 kg/h mixed together with a stream of recycled methanol and the sulfuric acid catalyst as reactants to perform the esterification. The esterification reaction is performed at a temperature of 70 ^{o}C, a pressure of 400 kPa, a methanol to oil molar ratio of 6:1 and with 5% (wt./wt.) of sulfuric acid catalyst in methanol [1, 24, 25]. All the free fatty acids were converted to methyl esters [1]. The esterification products are sent to a methanol recovery (T-100) to recovering most of the methanol in this stream for reuse in CRV-100, by reducing the capacity of the products after releasing to 200 kPa. In T-100, five theoretical stages and a reflux ratio of 2 were used.
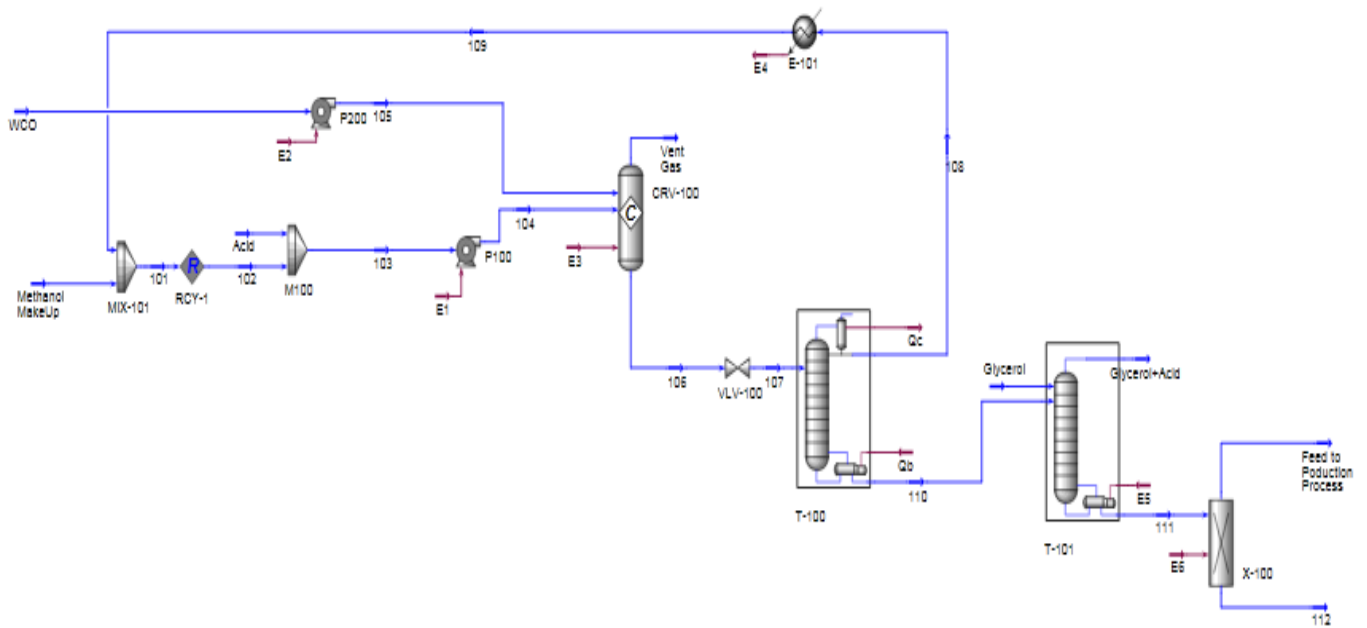
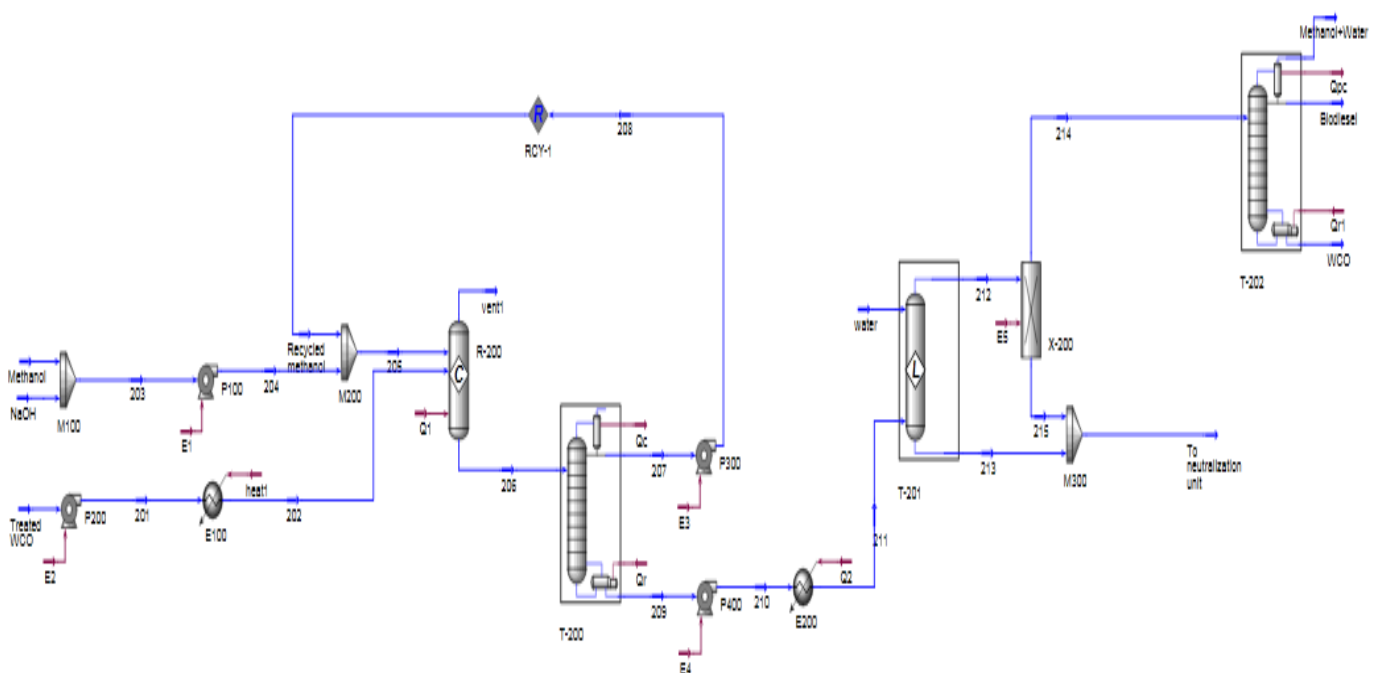Fig.1 Pretreatment process of Waste Cooking Oils (WCO)

Fig.2 Biodiesel production process of treated WCO (Alkali-catalyzed process)

About 96.6% wt. of the total methanol fed to the column was recovered as distillate then recycled (stream 109) to mixing with feed at (25 °C, 101.3 kPa). While the bottom stream (stream 110) was composed of 87.82% wt. triolein, 10.24% wt. oleic acid, 0.61% wt. water and 1.3% wt. sulfuric acid send to glycerol washing column (T-101). In which the producing water, acid catalyst used in CRV-101 and residual methanol must be removed completely before processing to the alkali-catalyzed transesterification unit. By adding 50 kg/h of glycerol at 25 °C and 200 kPa through 3 theoretical stages. All of water, methanol trace, most of

sulfuric acid and glycerol are exist out as distillate of column T-101. While bottom stream send to separator to separate a residual amount of glycerol and acid as bottom (stream 112), while top product of the separator (202.7 kg/h) is mixture of 89.6% wt. and 10.4% wt. of triolein and methyl oleate respectively are processing to the next unit.

Due to the presence of sulfuric acid these streams (stream 112 and distillate of T-101) were not reused and treated as waste. However, neutralizing the sulfuric acid and then recovering the glycerol is a feasible alternative to reduce waste.

TABLE I.   RESULTS OF SIMULATION PROCESSES

Stream	Unit No. 1					Unit No. 2						
	WCO	104	106	Glyc+Acid	112	Methanol	Treat. WCO	205	206	Biodiesel	Meth.+ Wat.	WCO
Temperature (^{o}C)	25.0	25.1	70.0	296.1	300.0	25.0	25.0	26.7	60.0	201.7	201.7	488.2
Pressure, (kPa)	101.3	400.0	400.0	160.0	200.0	101.3	101.3	400.0	400.0	10.0	10.0	20.0
Mass rate, (kg/h)	202.0	55.7	257.7	41.3	12.7	19.7	202.7	41.3	244.0	196.0	0.4	7.3
Mole rate, (kgmole/h)	0.277	1.688	2.0	0.5	0.138	0.62	0.276	1.277	1.553	0.661	0.006	0.008
Mole Fraction:												
Methanol	0	0.975	0.8	0	0	1	0	0.965	0.415	0	0.56	0
Triolein	0.74	0	0.1	0	0	0	0.74	0	0	0	0	0.989
M-Oleate	0	0	0.036	0	0	0	0.26	0	0.43	1	0.12	0.011
Glycerol	0	0	0	0.7	0.932	0	0	0	0.126	0	0	0
NaOH	0	0	0	0	0	0	0	0.035	0.029	0	0	0
H_2O	0	0.009	0.05	0.13	0	0	0	0	0	0	0.32	0
Oleic Acid	0.26	0	0	0	0	0	0	0	0	0	0	0
H_2SO_4	0	0.016	0.014	0.17	0.068	0	0	0	0	0	0	0

2) Alkali-catalyzed Unit:

Alkali-catalyzed unit of treated WCO including three steps as shown in Fig.2: transesterification, methanol recovery, water washing. A treated oil stream producing from the pretreatment unit is fed to the transesterification reactor (R-200), where a 6:1 molar ratio of methanol to oil is used with 1% wt. of sodium hydroxide (based on oil) to perform the reaction [19, 25, 26]. In R-200, 95-98% of the oil converted to FAME at 60 ^{o}C and 400 kPa, and producing glycerol as by-product. The effluent was introduced to methanol recovery column (T-200). In T-200, 5 theoretical stages and a reflux ratio of 2 were used to obtain a good separation between methanol and other components, the separation efficiency of pure methanol reaches 96% wt. in which recycled to mixing with feed. Bottom product (stream 209) was pumped to washing column T-201 after being cooled to 60 ^{o}C. The main purpose of washing column was to separate the FAME from the glycerol, methanol and catalyst, washing done by 8 kg/h of water inlet at 25 ^{o}C, 101.3 kPa and 4 theoretical stages used. In which all of the glycerol remain in the bottom, while the top product of the column sent to a splitter separate all NaOH. In order to obtain the final biodiesel product adhering to FAME distillation (column T-202) with 4 theoretical stages and reflux ratio 0.3 were used. T-202 operated under vacuum (about 10-20 kPa) to keep temperatures low enough to prevent degradation of the FAME [1]. The distillate amount of biodiesel produced was 196 kg/h with a purity 100% wt., while the bottom stream of the column contain 7.272 kg/h with a purity 99.64% wt. of triolein recycled to the WCO treated stream fed to the process.

III.   RESULTS AND DISCUSSION

Table.1 show the operating conditions and results of the simulation for both units described in Fig.(1, 2). About 196 kg/h ($\cong$1,550 t/y) of biodiesel produced with a purity 100% wt. by transesterification of treated waste coke oils with an alcohol in presence of a catalyst is acceptable as an attractive alternative fuel. Whereas, the alkali-catalyzed process of biodiesel production from waste vegetable oils with and without FFA pre-treatment has a lower contribution to the PEIs in all the impact categories as investigated according to U.S. EPA algorithm [22]. Also, the yield of the process reaches about 97% wt. of biodiesel gained as a pure product, so using of waste cooking oil as biodiesel feedstock reduces the cost of biodiesel production, since the feedstock costs constitutes approximately 70-95% of the overall cost of biodiesel production [8, 27]. Hence, the use of biodiesel produced from waste cooking oils and non-edible oils should be compete of petrodeisel due to cheap of feedstock and has a significant advantages because of the reduction in environmental pollution problems [14].

IV.   CONCLUSION

The liquid-phase biodiesel production plant by Esterification/Transesterification of WCO of corn oil containing 10% wt. of mixed free fatty acids was used as feedstock has been studied and simulated. The proposed design methodology based on a thermo-dynamic insight and a driving force technique was employed to design the biodiesel processes. So, the use of waste cooking oil as a low coat feed stock to produce about 1,550 t/y of pure biodiesel proved to be technically feasible, thereby making it a competitive alternative to commercial petrodiesel   production in future.

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