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Design and simulation of an integrated process for biodiesel production from waste cooking oil using supercritical methanolysis

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ABSTRACT

Non-catalytic transesterification has been recognised as an effective technique for biodiesel production. It has many advantages over conventional catalytic transesterification, where it eliminates the difficulties of catalysts preparation and separation. It also produces high biodiesel yield in shorter reaction time. However, it requires harsh operating conditions at high reaction temperature and pressure, in addition to using large excess of methanol. In an attempt to mitigate these problems, a process design/integration for biodiesel production has been performed. The process has been subjected to both mass and energy integration to minimise fresh methanol requirements and to minimise heating and cooling energies, respectively. A new graphical Pinch Analysis method has been used to evaluate the energy performance of a literature design for the current process. It has been subsequently used to develop an optimum heat exchanger network (HEN) for the process by matching of process streams. Also, the design made by using an automated commercial simulation (Aspen Energy Analyzer) has been evaluated using the same graphical method. The produced HEN design from graphical method has achieved the optimum results with respect to energy targets.

1. Introduction

Diesel fuel is the most consumed fuel over other petroleum products where it is used extensively in transportation sector and energy generation [1]. Consequently, biofuels with similar properties to diesel fuel are considered the future of energy resources as they could be implemented directly to the existing diesel engines with minor or without modifications [2]. Biodiesel has been considered as the most promising substitute for petroleum diesel fuel. It is a biomass-derived fuel from vegetable oils, animal fats and recently from micro-algae. Biodiesel is defined as mono alkyl esters of long chain fatty acids derived by alcoholysis of triglycerides from different feedstocks [3]. Biodiesel is characterised by its biodegradability, low emissions of particulates, carbon monoxide and hydrocarbons, absence of sulphur emission and high cetane number [4]. The similar properties of biodiesel to petroleum diesel besides being a sustainable green fuel have promoted biodiesel as a significant alternative fuel for petroleum diesel.

Transesterification reaction has been considered the most commonly used method for biodiesel synthesis. The reaction is usually catalysed using different techniques including alkaline, acidic and biological catalysts [5]. Recently, non-catalytic transesterification has been reported using supercritical alcohols [6]. Origin and quality of the feedstock are responsible for selecting the processing technique. Presently, edible oils are considered the main feedstock for biodiesel. However, the raising competition with food industry resulted in food insecurity has boosted the research towards non-edible and waste oils (second generation feedstock). The second generation feedstock is considerably cheaper than edible oil, which contributes in lowering the overall cost of the produced biodiesel [7].

Waste cooking oil (WCO) has been recognised as a potential feedstock for biodiesel as it is relatively cheaper than fresh edible oils and it contributes in waste utilisation [8]. However, the high free fatty acids (FFA) and water content are the main drawbacks of using WCO as a feedstock. Alkaline homogenous catalysed technique, using either sodium hydroxide (NaOH) or potassium hydroxide (KOH), is considered the most commonly used technique

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for biodiesel synthesis. The high FFA content in WCO leads to saponification reaction while using alkaline homogenous catalysts, which results in lowering biodiesel yield and preventing product separation. Using heterogeneous catalyst prevents saponification side reaction. However, it is very sensitive even at low water content in addition to high cost of catalyst preparation as it requires extremely harsh conditions (700–900 °C). Two-steps transesterification is considered as an acceptable technique for producing biodiesel from WCO. A pre-treatment esterification of FFA step using acidic catalysts is followed by transesterification step using alkaline homogenous catalysts. Nevertheless, the lengthy process leads to increase in biodiesel cost [9].

Non-catalytic transesterification has been considered as an ideal technique for biodiesel production from WCO as it prevents all the above-mentioned problems. It tolerates both esterification of FFA and transesterification of triglycerides in a single step reaction. However, it requires high reaction temperature and pressure, where the alcohol should be at the supercritical state [10]. Several supercritical technologies have been used for non-catalytic production of biodiesel using methanol, ethanol, 1-propanol, dimethyl carbonate (DMC), methyl *tert*-butyl ether (MTBE) and methyl acetate [11,12].

West et al. [13] have designed and simulated four biodiesel production processes using different techniques including homogenous alkaline catalysed, homogenous acidic catalysed, heterogeneous alkaline catalysed and non-catalytic supercritical processes. They have also performed an economic comparative analysis between the designed processes for the cost of production 8000 tonne/y of biodiesel from WCO. They have concluded supercritical process as the second most profitable process next to heterogeneous catalysed process. Lee et al. [10] have simulated production process for biodiesel using both fresh and used cooking oils. They have reported that the cost of the feedstock attributes with about 64–84% of the produced biodiesel cost. They have also reported that using supercritical methanol is the most economically favourable process over alkaline catalysed processes. Manuale et al. [14] have simulated an energy-integrated biodiesel production process using supercritical methanol. They have proposed that using the enthalpy content of the reactor product stream to separate most of the unreacted methanol in a flash drum decreased the process required heating energy.

Pinch technology is recognised as one of the most effective methods used to assess the efficiency of energy utilisation for production processes. The idea was proposed in 1978 by Umeda et al. [15] which has been developed for further aspects by Linnhoff and Hindmarch [16]. The principle has been subsequently extended into several areas including mass Pinch, hydrogen Pinch and water Pinch. Smith [17] has discussed the principles for Pinch Analysis which have been implemented in mass and energy integration applications and extensively applied in heat recovery. The applications of such principles are very critical for providing energy and mass targets that should ideally be achieved in a process [18]. El-Halwagi [19] has introduced systematic and graphical procedures based on Pinch Analysis to design both mass and heat exchanger networks in complicated process industries.

Process integration for energy or materials savings can be achieved through two approaches, one which is based on insights derived from Pinch Analysis and the other is based on mathematical programming methodologies. The first approach normally comprises of two stages, first determining the energy (or mass) targets known as targeting, and then designing the heat and/or mass exchanger network to achieve these targets [20]. The mathematical programming-based approach relies on building superstructure for all alternatives and then using simultaneous optimisation and integration to explore all interconnection within the proposed superstructure. This is followed by screening of all the alternative to find the optimal combination [21,22]. The recent handbook of Klemes [23] is a good source for such literature.

Gadalla [24] has reported a novel graphical technique for HEN designs based on Pinch technology. The graphical method has been defined by plotting process hot streams *versus* process cold streams. Each process heat exchanger has been represented by a straight line where its slope is the function of the ratio between heat flows and capacities. In addition, each line is proportional to the flow of the heat transferred across the exchanger. This method could easily analyse any proposed HEN to identify inappropriate exchangers whether across the Pinch, network Pinch and improper placements. In addition, he reported that the developed method could be implemented in designing optimum HENs using numerical process streams matching technique. Gadalla [25] has also extended the same conceptual novel graphical method for mass integration applications and mass exchanger networks (MEN) designs.

In this study, a comprehensive integrated design for biodiesel production process using supercritical methanol has been simulated. The reactor has been designed based on previous experimentally reported kinetic parameters. Energy and mass integration principles have been applied to reduce the process required external energy and fresh resources, respectively. Graphical Pinch method has been applied to design and develop a new optimum HEN responsible for reduction of heating and cooling required energies. In addition, it has been used to evaluate previously reported designs.

2. Materials and methods

The transesterification/esterification reactions for WCO were carried out using supercritical methanol. The details about the experimental design and procedures are presented elsewhere [26]. Aspen HYSYS simulation programme version 8.8 was used for simulating the biodiesel process (Aspen Technology Inc., USA). The procedures for process simulation based on HYSYS simulator consist of several steps including selection of chemical components for the process, appropriate thermodynamic models, required process units and operating conditions. The actual existing pressure drop in different equipment was neglected in the present study.

The assumptions associated with the present simulation are as follows:

1. The transesterification reaction steps were represented by only overall step where triglycerides (TG) are converted to fatty acid methyl esters (FAME).
2. Glycerol methanol side reaction was ignored.
3. Heat exchangers were selected as counter flow type and were simulated by a means of a shortcut module.

2.1. Chemical components

Most of the required information for chemical components used in the process design were included in HYSYS data bank library. Triolein ($C_{57}H_{104}O_6$) and Trilinolein ($C_{57}H_{98}O_6$) were used to represent the triglycerides exists in the WCO as they were reported as the major compositions (~86%) based on the chromatographic analysis reported elsewhere [26]. Oleic and linoleic acids have been used to represent the FFAs exist in the WCO. Methyl oleate ($C_{19}H_{36}O_2$) and methyl linoleate ($C_{19}H_{34}O_2$) were considered as the desirable product of the reaction. Conferring to the WCO's total acid number (TAN) of 0.8 mg KOH/g oil, the FFAs weight percentage were equivalent to 1.6%. Trilinolein component was not available in