NON-CATALYTIC PRODUCTION OF BIODIESEL USING SUPERCRITICAL METHANOL: A BRIEF REVIEW

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ABSTRACT

This paper aims to review the potential and challenges of non-catalytic transesterification as a sustainable route for biodiesel synthesis. Recently, biodiesel production using supercritical technology has undergone rapid developments as it provides numerous advantages over conventional catalytic technologies, including elimination of catalyst preparation and product separation and purification processes, higher biodiesel yield, shorter reaction time, applicability to a wide variety of feedstocks without any pre-treatment requirements. Nevertheless, there are many concerns regarding the massive energy obligation to conduct the reaction at the supercritical conditions of methanol, which requires high temperature and pressure. Accordingly, the challenges facing the supercritical technology to be considered as a sustainable process have been elaborated through this review. Different production techniques using supercritical technology have been addressed. Several reaction variables affecting the supercritical reaction and their optimisation methodologies have been discussed in this review. Moreover, some constructive recommendations have been proposed thoroughly to overcome the limitations of this technology. Biodiesel production using supercritical technology could be considered as a sustainable route in the near future.

Keywords: Biodiesel, Supercritical methanol, Non-catalytic transesterification.

1 INTRODUCTION

World's energy consumption has extensively increased following an exponential growth due to the huge industrial developments and increasing world's population. The world's total primary energy consumption (TPEC) had a huge jump during the last decades reaching 150,000 TW.h in 2015. In addition, 57% growth in TPEC is predicted by the year 2050 [1]. The observed and predicted growth in energy consumption will eventually result in higher greenhouse gases emissions which is directly affecting the global warming and causing other environmental concerns [2].

There are numerous reasons to search for alternative fuels, e.g. limitation of petroleum resources, increasing demand for fuels, environmental impact of fossil fuels and instability of crude oil prices. Various applications of fossil fuels including transportation sector, industrial applications, power generation and domestic heat applications have led to steep rise of crude oil from $20/barrel to $140/barrel in the period between 2000 to 2015, where recently the price dropped back to nearly $60/barrel [3]. Accordingly, during the last decades, researches have focused on finding applicable renewable replacement to reduce the dependence on fossil fuels in energy production [4].

Biodiesel is considered as the most promising substitute for petroleum diesel fuel. It is defined as mono alkyl esters of long chain fatty acids derived from vegetable oils and animal fats [5]. It has many advantages over petroleum diesel fuel including biodegradability, sustainability, zero sulphur emissions, greener exhaust emission with less smoke, CO, hydrocarbons and particulates and better performance of engine lubricity [6].

Numerous methods have been reported for biodiesel production, e.g. microemulsion, pyrolysis and transesterification. Among all the mentioned methods, transesterification is considered the most commonly used method for biodiesel production. It includes alcoholysis reaction of triglycerides to fatty acid alkyl esters (FAAE) [7]. Non-catalytic biodiesel production has been reported with various advantages over catalysed methods including shorter reaction time and higher biodiesel yield. It could be applied on a wide

range of feedstock without any pre-treatment restrictions. It also eases product separation and purification processes [8].
This paper aims to provide a brief review on the latest progress in supercritical biodiesel production. The factors affecting the production process including temperature, pressure, residence time and methanol to oil (M:O) molar ratio have been discussed. Finally, challenges for scaling-up supercritical process and recommendations for future considerations have been proposed.

2 PRODUCTION PROCESSES

2.1 Catalysed Processes

Catalyst selection depends on various properties of the feedstock including free fatty acids (FFA) and water contents.

Alkaline Catalysed Processes

Alkaline homogenously catalysed process is considered as the conventional process for biodiesel production. These catalysts, i.e. sodium hydroxide (NaOH), potassium hydroxide (KOH) and sodium methoxide (CH_3OH), have high reaction activity where biodiesel is produced in high quality within reasonable reaction time. In addition, these catalysts are considerably cheap and readily available. However, using alkaline homogenous catalysts has many drawbacks including the sensitivity of the presence of high FFA and water in the feedstocks. At high FFA content, saponification reaction occurs in parallel to transesterification reaction, which reduce biodiesel yield and complicate product separation. In addition, the catalyst removing process through washing include consumption of large amount of water and producing wastewater with appropriate treatment requirements. Aboelazayem et al. [9] have investigated biodiesel production through methanolysis of castor oil using KOH. They have optimised the process resulting in 97.82% biodiesel yield at optimum conditions of 0.73% KOH concentration, 64^{o}C temperature, 2.5 h reaction time, 5.4:1 M:O molar ratio and 320 rpm for mixing rate.
On the other hand, using heterogeneous catalyst in transesterification reaction reduces the wastewater effluent of the process. Moreover, it simplifies the separation and purification steps of the reaction products. In addition, most of the heterogeneous catalysts have high possibilities for regeneration to be reused in different reaction where it attributes to decrease the cost of the produced biodiesel [10]. However, the main disadvantage of using heterogeneous catalyst technique is the diffusion limitations in the three-phase (oil–alcohol–catalyst) reaction mixture which lower the reaction rate. Moreover, catalyst preparation includes several costly steps including crushing, washing, drying and calcinating at very high temperatures [11]. El-Gendy et al. [10] have investigated calcium oxide (CaO) prepared from snails shells as heterogenous catalyst for biodiesel production from waste frying oil. They have reported 96.7% biodiesel yield at optimal conditions of 6:1 M:O molar ratio, 3 wt% of catalyst concentration, 1 h reaction time at 200 rpm.

Acidic Catalysed Processes

Acidic catalysed technique has lower susceptibility to the presence of FFA in the feedstock as it acts to convert both FFAs and triglycerides (TG) to FAME in both esterification and transesterification reactions, respectively. Nevertheless, using acid catalysed technique showed slower reaction rate with longer reaction time in comparison with alkaline catalysed technique [12]. The most commonly used acids in biodiesel production process are hydrochloric, sulphuric and phosphoric acids [13].

Two-steps Catalysed Processes

Two-steps technique has been developed to combine both benefits of alkaline and acidic processes. The two-steps technique includes esterification of FFAs to FAMEs using acidic catalyst as a pre-treatment step to reduce the FFA content to 1% followed by transesterification reaction using alkaline catalyst to convert TG to FAME. Soap formation has been eliminated in this process as FFA of the feedstock has converted to FAME during the esterification step using acidic catalysts. However, the main disadvantage of using two-steps technique is the higher production cost as compared to conventional, one-step process [16-18].

Comparative analysis between both one-step and two-steps techniques of biodiesel production has been studied to evaluate the process from both productivity of FAMEs and economical points of view. It has been reported that higher FAMEs yield has been achieved using two-steps technique (about 90%), while one-step alkaline transesterification reaction reported 55% yield of FAMEs [17]. Deng et al [18], have reported similar evaluations using jatropha oil with 10% FFAs where they observed 96.4% yield of FAMEs using two-steps technique while only 50% FAMEs yield was obtained using one-step alkaline transesterification reaction.

Enzymatic Catalysed Processes

Lipases enzymes are used to catalyse both esterification and transesterification reactions of FFAs and TGs, respectively. The main advantages of using enzymatic technique are the capability of operating both esterification and transesterification reactions simultaneously, minimisation of waste water and using feedstocks with high FFA content. However, the high price of the enzyme and the lengthy process are considered the main drawback of using enzymatic technique for biodiesel production [21-24].

2.2 Non-catalysed Processes

In an attempt to overcome the previously mentioned problems of the catalysed techniques, non-catalytic technique has been developed as a promising technique for biodiesel production where alcohol and oil are mixed in the absence of catalyst at the supercritical conditions of alcohol. The main reason of using catalyst in both esterification and transesterification reactions is the low solubility of the alcohol in the oil phase. However, it has been observed that alcohols have very high solubility in oil at their supercritical state. Using non-catalytic reaction has several advantages, e.g. shorter reaction time, elimination of wastewater effluent, exclusion of catalyst preparation cost, elimination of soap formation and simplification of the product separation. However, the drawbacks of using this technique are mainly due to the requirement of large excess of alcohol and high cost of apparatus that maintain harsh reaction conditions [1,23,49].

3 SUPERCRITICAL METHANOLYSIS PROGRESS

Saka and Kusdiana [25] have firstly introduced biodiesel production using supercritical methanol. They have used rapeseed oil as a feedstock where the reaction was conducted in a batch reactor at 350-400^{o}C and 45-65 MPa. They have reported that supercritical reaction could overcome many problems associated with the conventional catalysed processes in addition to its shorter reaction time with simple product separation step. Kusdiana and Saka [26] have examined the effect of water content of supercritical methanolysis. They have reported that water content does not have any significant effect on biodiesel formation. Moreover, they have observed that adding water within certain amount enhance biodiesel formation. Garcia et al. [27] have investigated the conversion of raw Jatropha oil to biodiesel using supercritical methanol. They have optimised the reaction conditions to maximise biodiesel yield. They have reported 99.5% biodiesel yield at optimum conditions of 325^{o}C in 90 min. Aboelazayem et al. [28] have used supercritical methanol for biodiesel production from waste cooking oil. They have developed a quadratic model representing biodiesel yield function in different reaction parameters including M:O molar ratio, temperature, pressure and reaction time. They have reported 91% biodiesel yield at optimum conditions of 37:1, 253.5^{o}C, 198.5 bar and 14.8 min for M:O molar ratio, temperature, pressure and residence time, respectively.

Recent studies have been performed to investigate the significance of using supercritical methanolysis in converting feedstocks with high FFA content into biodiesel. Aboelazayem et al. [16] have studied the conversion of high acid value waste cooking oil using supercritical methanol. They have reported high biodiesel yield without any pre-treatment processes. The optimum conditions resulted in 98.8% biodiesel yield at M:O molar ratio, temperature, pressure and residence time of 25:1, 256^{o}C, 110 bar and 20 min, respectively. They have reported that M:O molar ratio is the most significant parameter affecting biodiesel yield followed by reaction temperature. Ong et al. [29] have studied the conversion of leather tanning waste with high FFA content using supercritical methanol. They have performed experiments at 12 MPa and M:O molar ratio of 40:1 between temperature ranges of 250-325^{o}C. Aboelazayem et al. [30] have investigated the

esterification kinetics of FFA to FAME in high acid value waste cooking oil using supercritical methanol. They have optimised reaction conditions resulting in 97.7% conversion of the total FFA existed in the feedstock at M:O molar ratio, temperature, pressure and residence time of 35:1, 260^{o}C, 110 bar and 16 min, respectively. They have reported that the reaction kinetics is following pseudo first order reaction with reaction rate constant, activation energy and frequency factor of 0.00103 s^{-1}, 34.5 kJ/mol and 1.26 s^{-1}, respectively. In addition, they have simulated a reactor using the experimentally determined kinetic data at the optimum conditions.

4 CHELLENGES AND RECOMMENDATIONS

4.1 Challenges

The main challenges facing supercritical methanolysis from scaling up to industrial scale could be summarised into two points, e.g. excessive energy consumption and huge excess of methanol. Many studies have been reported in lowering the reaction conditions by introducing co-solvents including; propane [31], *n*-hexane [31], and carbon dioxide (CO_2) [24]. These co-solvents act to enhance the solubility of methanol in oils, where it acts in lowering reaction conditions. In addition, it has been reported that using spiral reactor would improve the process energy efficiency. This reactor has been reported by Farobie et al. [32] where it composed of a parallel tube heat exchanger and a high temperature transesterification reactor. They reported that the reactor is superior to conventional reactors in terms of heat recovery.
Process integration techniques have been also reported in very limited studies. Debora et al. [33] have designed an energy integrated process for biodiesel production from low cost chicken oil using supercritical methanol. They have studied to recover the excessive energy consumed through the reaction. Aboelazayem et al. [34] have designed an energy integrated process for biodiesel production from waste cooking oil. They have simulated a continuous reactor based on experimental kinetic data. They have designed a heat exchanger network (HEN) for the process to maximise energy integration through the process.
The excessive use of methanol has been observed by all studies where the minimum reported ratio was 25:1 [16], which represent about 8 times higher than the stoichiometric requirements. Moreover, excessive methanol recovery also needs high energy.
In addition to the previously mentioned challenges, other limitations should be addressed for scaling-up this process to industrial scale. As the reaction operates at high temperature and pressure, the safety issue is still a debate. In addition to the impurities that should be recovered to produce high quality biodiesel. Economically, supercritical technology requires high capital costs of special designed equipment, high temperature furnace and high-pressure pump. Moreover, operational costs would be relatively high to maintain the required reaction conditions.

4.2 Recommendations

Although supercritical methanolysis has proved to be an efficient technique for biodiesel production with various advantages, its feasibility in industrial scale is still a debate. Hence, techno-economic analysis should be studied extensively for supercritical processes. In addition, biodiesel production in supercritical DMC, methyl acetate and methyl tert-butyl ether (MTBE) where some value-added by-products would be considered apart from glycerol. Simultaneous mass and energy integration should be considered while designing supercritical processes. Finally, work integration should be addressed in this process as it is operated under high-pressure.

5 CONCLUSIONS

Biodiesel production using supercritical methanolysis has been reviewed in this paper. Progress and latest developments of biodiesel production using supercritical methanol has been discussed. Supercritical transesterification has many advantages over catalysed processes, e.g. shorter reaction times, higher biodiesel yields, elimination of catalysts preparation and separation cost and applicability to handle variety of feedstocks. However, many limitations have been addressed for scaling-up this technology for industrial

scale. Techno-economic studies have been recommended for future work in addition to replacing alcohols with different supercritical compounds that would produce value-added by-products other than glycerol.

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