

Intensification of Biodiesel Synthesis in a Cavitation System from *Xanthium Spinosum* Oil

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This article investigates a novel method for increasing the yield of methyl ester through alkali-catalyzed transesterification of *Xanthium Spinosum* in a cavitation reactor. The effects of the oil to methanol molar ratio (1:4 – 1:7), catalyst loading concentration (0.50-1.2 wt. percent), and reaction temperature (50.0 – 65.0 °C) were investigated using an adapted orifice plate with 21 (1 mm diameter) holes and a 2 bar inlet pressure in a 50 L Hydrodynamic Cavitation (HC) reactor assisted by a double diaphragm pump. A maximum conversion of 98.8 wt. percent was achieved in 25 minutes in an HC reactor with a 1:6 molar ratio of oil to methanol, 1.0 wt.% catalyst and a reaction temperature of 60 °C. The optimal reaction time for transesterification was reduced significantly (approximately fivefold) from 90 minutes for the mechanical stirring approach to 25 minutes for the HC approach. The sustainable raw material is capable to produce cleaner production of esters by adopting HC technology.

1. Introduction

Biodiesel contributes to environmental conservation by lowering sulphur oxide emissions, reducing carbon monoxide emissions, and reducing global warming issues, since it is organically degradable, sustainable, non-toxic (Syafiuddin et al., 2020). Approximately 95 % of methyl ester is synthesised from edible sources. In biodiesel production, consumption of edible raw material has resulted in rising prices of edible biodiesel over fossil diesel fuel (Ogunkunle and Ahmed, 2019). This makes it more attractive and promising for a non-edible plant-based oil to be an alternative to the development of biodiesel. The oil having toxic compounds is called as non-edible oil. Clean technical options for both dumping and healthiness issues such as nurturing local animals, reprocessing and recovering, are possible through the use of waste kettle in biodiesel processing. The methanol (short carbon-chain) methanol is the utmost prevalent in the process of esterification and transesterification since it is simple to isolate, lower cost and greater nucleophilicity than long carbon-chain ethanol (Khan et al., 2019). For alkali-catalysts in the transesterification process, the conversion of potassium hydroxide (KOH) in the existence of 1.0 wt.% of catalyst (base) with a 1:3 methanol molar ratio resulted in a conversion rate of 96 wt. % relative to NaOH in the presence of just 77 wt.% conversion rate. The industrial experts also claimed that it was easier to distinguish biodiesel from glycerol when KOH is used as a catalyst (Rezania et al., 2019).

Various intensification equipment has been developed by investigators to eradicate the mass confrontation between the oil and alcohol reactant in a shorter time (Bokhari et al., 2014) and the energy consumption lower than the conventionally available methods. These included supercritical condition, microwave (Bokhari et al., 2015), ultrasound and hydrodynamics. Hydrodynamic Cavitation (HC) can solve the disadvantages of the

traditional system. The transmission of fluid by a narrowing method, e.g. a throttling valve, an orifice plate and a venturi, will create cavitation. The cavities are formed if the pressure from the position falls below the fluid vapour pressure. To diminish mass transfer confrontation throughout the transesterification, the high power of micro level turbulence produced by vacillating voids of extraordinary interfacial areas within an HC device is quite efficient (Bokhari et al., 2017). Although HC has been served extensively in wastewater management, there are rare information in the production of biodiesel (Bokhari et al., 2016). There is only one report published on the effects of operational constraints, including the molar relationship and the concentration of catalysts, but it does not comprise temperature and reaction period in relation to the conversion efficiency with HC during the transesterification process (Chuah et al., 2015). In addition, the final product quality determination has not been stated, even though certain conditions have been checked. With concern to the raw resources, the results of the geometry and the upstream pressure of the centrifugal pump cavitating aperture panel on the conversion of the methyl ester by the waste oil used in a 10 -15 L capacity reactor were analysed (Chuah et al., 2016). The potential yield of *Xanthium spinosum* seed oil (XSO) is entirely satisfactory, and it yields up to 35wt.% oil. The oil has a high content of linoleic and oleic acid, and it is essential to inquire about the conversion of *Xanthium spinosum* oil into methyl ester as it could be a better substitute for petro-diesel. This work reported first time utilisation of XSO for the newly designed cavitation device for methyl ester synthesis. Mechanical stirring was also used in the present work in the identical capability as a reactor to produce biodiesel generated from waste frying triglyceride to compare the conversion, reaction time and production performance with HC. Such non-edible oil was selected for its availability as a non-utilised feedstock. Therefore, the use of low-cost XSO has been considered a promising non-edible feedstock, particularly under HC, to reduce overall biodiesel production cost.

2. Materials and Methods

2.1 Materials

Xanthium spinosum seeds were collected from wild plantations of the Punjab and Sindh region of Pakistan. Oil was extracted conventionally by using mechanical expellers. Engine-driven screw press was used to extract oil. It is extracted about 68 to 80wt.% of oil from seeds. The oil from the mechanical expeller required further treatment of filtration and degumming. Table 1 displays the properties of XSO. Anhydrous methanol, potash hydroxide pellets, sulphuric acid, anhydrous sulphate sodium, toluene, 2-propanol, phenolphthalein, hydrochloric acid and acetone have been obtained from Merck and have been obtained from this commodity. The analytical reagent grade was all organic compounds.

Table 1: Properties of XSO

S no.	Properties	<i>Xanthium spinosum</i> oil (XSO)
1.	pH	4.7
2.	Freezing point (°C)	-21
3.	The moisture content of seed (wt.%)	7.6wt.%
4.	Density at 15°C (g/cm ³)	0.903
5.	Viscosity (mm ² /s)	16.22
6.	Ash content of seed (m/m wt.%)	1.69
7.	Free fatty acid (wt.%)	2.3

2.2 Cavitation Reactor Setup

The 50 L hydrodynamic control cavitation reactor is linked to the diaphragm pump in adjacent proximity loops termed the batch vessel. The pump, a primary energy release mechanism for a hydrodynamic cavitation reactor, was provided by compressed air with the power of 4kW. The air supplied was compressed. For calculating upstream input pressure and downstream recovery pressure, the scale of the pressure P1 and P2 have been used. Effects of the alcohol molar ratio (4 - 7), the catalyst concentration and the reaction temperature were estimated. The HC diagram is illustrated in Figure 1. By passing the fluid glycerine through the reactor retaining tank jacket, the XSO was heated to a proper temperature. The identified weight was added in the known amount of alcohol. The 10 L reactor blend was transmitted to the adjusted hole plate with respect to the optimised inlet pressure of 2 bar for the experimental constructional setup. By gravity regulation, the collected sample in the separating funnel must be withdrawn in order to ensure separation of by-product. The by-products and catalyst have been released by opening the valve at the bottom of the reactor. For waste

catalysts and other by-products, deionised hot water was used to wash at 40 °C until the pH of the water was neutral. The leftover methanol and water were evaporated under the rotary vacuum evaporator. The substance has been packed with 15 g of anhydrous sodium sulphate to ensure that the sample has no water. GC-FID analysis measured the conversion efficiency of the collected products for interval reaction duration. Tests were repeated three intervals to assess the extent and reproductiveness of the results.

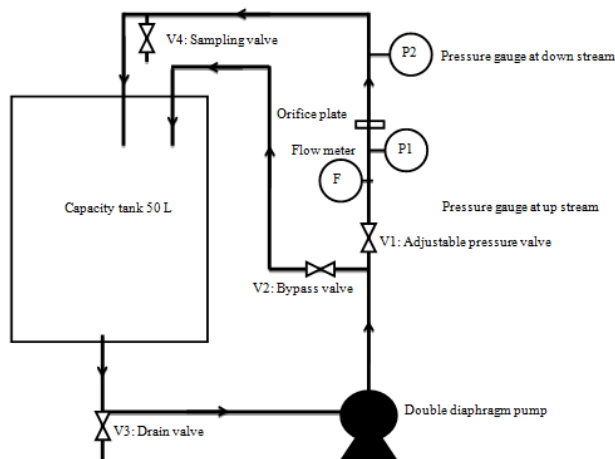


Figure 1: HC setup

3. Results and Discussion

3.1 Effect of Solvent on methyl ester production

The molar ratio of methanol is one of the utmost factors for the conversion of methyl ester. Stoichiometrically, 3 mol of alcohol is needed to generate 3 mol of ester and 1 mol of by-product in transesterification reactions (Ghayal et al., 2013). However, due to the transesterification reversible aspect of the reaction, a higher molar ratio would be desirable for the target product to achieve a higher yield and conversion. The results of the alcohol ratios of 4 to 7 and a 1 wt.% of catalyst (base) at 60 °C were evaluated in support of the reaction time in this article. The observations are seen in Figure 2. The rise of the molar oil-methanol ratio has been found to contribute to improved conversion. The molar ratio increased from 1:4 to 1:6 to an increased transition in 15 min of response time with conversion of 45.2 to 98.1 wt.%. The spike in the volume of methanol may be due to cavities formed in an oil-solvent mixture in HC.

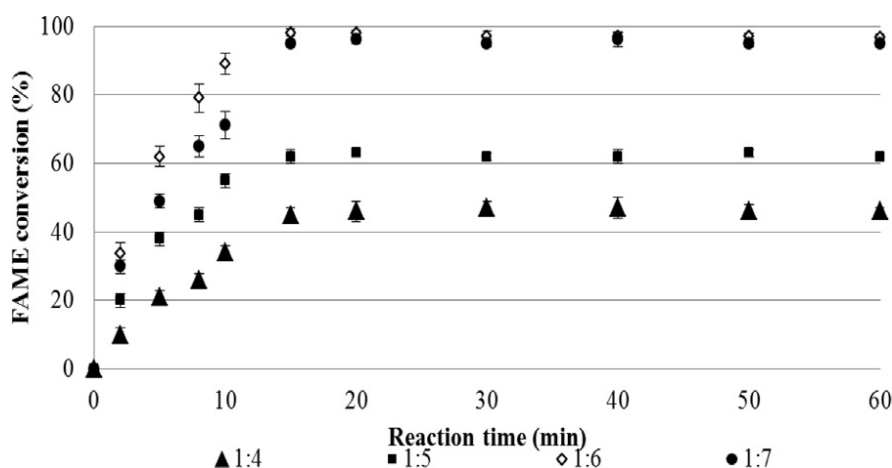


Figure 2: Effect of methanol on ester production

Tamilarasan and Sahadevan (2014) stated that high feedstock oil viscosity needed greater methanol amounts to improve methanol oil solubility. The reaction of fatty acid and base catalyst in soap formation is caused by

inadequate methanol. Away from the boundary (1:6), the volume of excess alcohol reduced marginally, which was due to dilution of the oil in methanol, from 98.1 wt.% (1:6) to 95.0 wt.% (1:7). It is detected that with a high molar ratio of 7, the parting from the by-product layer was harder because it contributes to allowing water to be absorbed by an unreacted polar hydroxyl group and monoglycerides and diglycerides to generate water. The 6 molar ratio was considered an ideal.

3.2 Effect of Catalyst on methyl ester production

The accomplishment of the reaction transformation is dependent on the concentration of the catalyst (KOH). During the washing process, the catalyst concentration caused an increased volume of wastewater (Yusup et al., 2015). The FFA can respond with base catalyst and lead to saponification, which leads to a problem of biodiesel separation. This contributes to a lower yield of the methyl ester due to chemical isolation difficulties (Ferrero et al., 2014). The results from KOH levels in a transesterification were studied, with a molar ratio (6) at 60 °C in HC ranging from 0.5wt.% to 1.25 wt.%. The effects of KOH were evaluated. The conversion of methyl ester to time at various catalyst levels is depicted in Figure 3. The conversion of methyl ester has also improved as the KOH catalyst concentration rises. The conversion rose from 63 wt.% to 98.1wt.% with the base catalyst proportion rise of 0.5 to 1.25 wt.% in 20 min. This proves that the catalyst's intervention increased the reaction rate. Triglycerides have not been converted into methyl ester with a catalyst load of less than 1.0 wt.%. However, the conversion declined slightly from 98.1 to 91.0 wt.% with a rise in the catalyst concentration from 1.0 wt. % to 1.25 wt.%. Soap formation was found above the ideal stage. Excess KOH could be due to free fats in XSOs that react primarily to KOH making the potassium soap and H₂O. This could be attributed to excessive KOH. The accumulation of an additional alkali catalyst triggered further triglyceride in the saponification process, which resulted in the appearance of elevated quantities of soap by resulting the lower conversion rate. As a result, the saponification reaction results in reducing triglycerides to methyl ester. Similar findings showed that for the transesterification of Nagchampa oil, the optimum catalyst loading was 1.0 wt.% to achieve 92.1 wt.% conversions in 25 min from (Gole et al., 2013) and for further testing 1 wt.% of catalyst (alkali) was chosen.

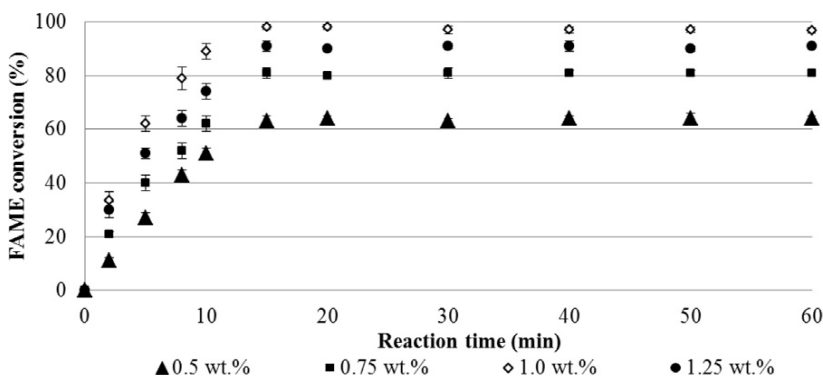


Figure 3: Effect of catalyst loading on ester production

3.3 Effect of working temperature on methyl ester production

The reaction temperature is a significant variable that influences the transesterification reaction. The optimum value was calculated with a 1:6 molar ratio of alcohol in set operating circumstances and at 1.0 wt.% catalyst loading for different transesterification temperature for observing the formation of ester. The influence on ester conversion of the working temperature is shown in Figure 4. The conversion improved dramatically from 76.0 to 98.2 wt.% in 20 min due to a rapid dispersal of solvent in the XSO and decreased viscosity of XSO with an increase in activity temperature. The conversion increased significantly by elevated temperature, which should be below the boiling point of methanol (Bokhari et al., 2015). This allows triglyceride solubility in methanol to be increased, and interaction between oil and methanol molecules progressively to be improved by increasing ester conversion. In the literature, a related pattern has also been identified. The reaction temperature of 65 °C resulted in a marginally lower conversion from 60 °C of 97.2 wt.% within 15 min (98.1 wt.%). The ester conversion pattern was higher at 65 °C than at 60 °C throughout the beginning of reaction time. That was due to the solvent that was not vaporised meritoriously at the outset of the reaction time. A double diaphragm pump recycled the oil and solvent blend through the orifice plate. Thus methanol was not vaporised inside the recirculation circuit, and the heat was released into the atmosphere. However, the conversion was marginally

lower after 15 min at 65 °C associated to 60 °C. The alcohol vaporises and forms bubbles within the device, which may avoid the reaction when the reaction temperature is greater than the bottleneck (64.6 °C).

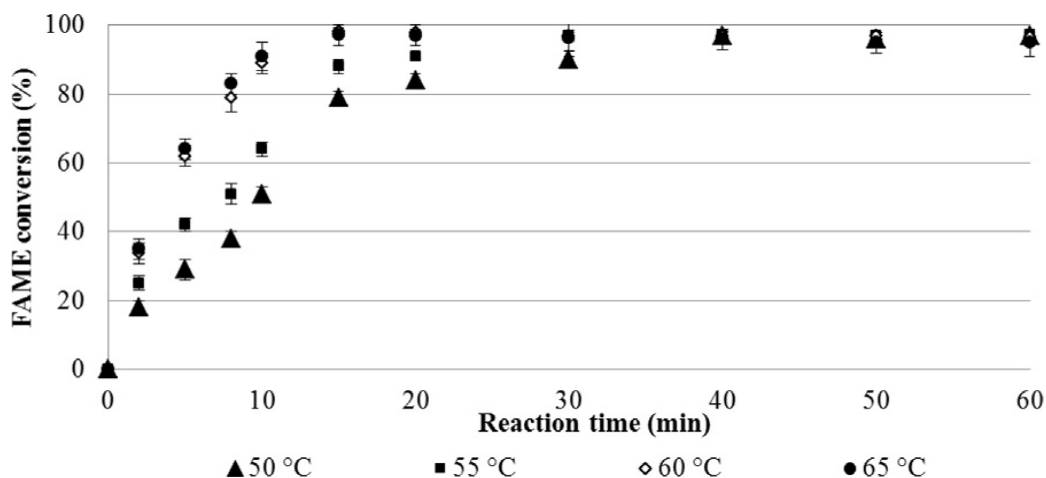


Figure 4: Effect of working temperature on biofuel production

3.4 Comparative performance of intensification with a conventional method

Optimised parameter conditions were contrasted with mechanical stirring conditions used in operating the HC reactor for biodiesel synthesis. It is seen in Figure 5 that 98.1 wt.% of HC was converted in just 15 min for HC. and 19wt. % of ester conversion was achieved in mechanical stirring in 20 min of reaction time. It is a much smaller conversion in comparison to 20 min of operation. The high strength of microturbulence produced by oscillating cavities with the elevated interfacial area may be attributed. An HC reactor is very successful in removing the resistance to mass transmission during the reaction. The oil process to the methanol-oil interface only relied on the stirrer bar that could be a restriction and ultimately resulted in a weak mass transfer between reactants. The transition rate was sluggish in conventional biodiesel synthesis. It can be observed that HC has a making efficiency of 12.50×10^{-4} g/J and a reaction rate of 15 min, which is roughly 8 times higher and 6 times more than the mechanical sprinklers (1.5×10^{-4} g/J). Gole et al. stated that subsequently 40 min of an improved reaction time, the ultrasound cavitation obtained a 93 wt.% conversion, or 2.7 fold longer than the existing HC research. In contrast with ultrasonic cavitation and mechanical stirring, the maximum efficiency and the fastest reaction time to approach desired ester conversion could be obtained with HC. The results are in the good comparison with the experimental data of Ghayal et al., (2013).

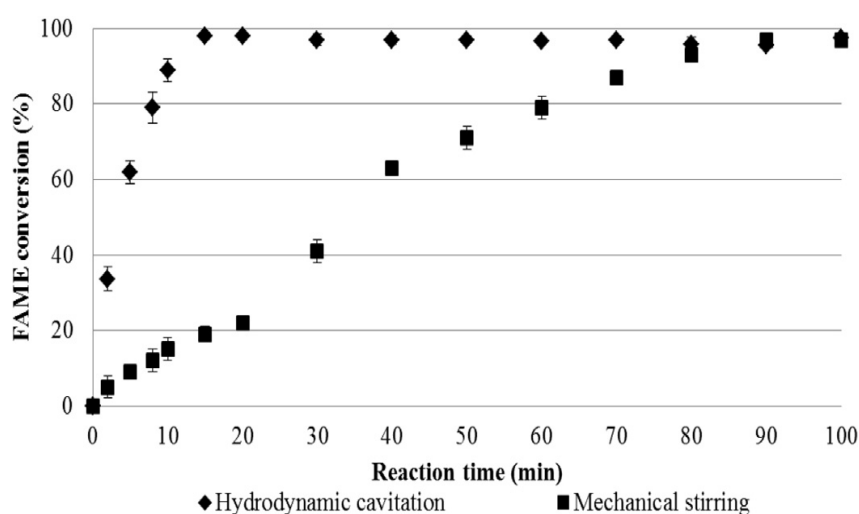


Figure 5: Comparative performance of HC with the conventional procedure of biodiesel synthesis

4. Conclusions

The present study has shown the XSO methyl ester synthesis in an HC reactor under the optimised geometric plate and inlet pressure. The XSO has been converted to respective methyl esters in a shorter reaction time in an HC reactor as compared to the conventional production approach. Optimal operational conditions for transesterification reactions are 1:6 alcohol ratio in the oil and 1.0 wt. % of catalyst. The optimisation experiments have proposed solutions for different non-edible oils in a similar process state, such as *Calophyllum inophyllum*, *Jatropha* oil, and rubber seed oil. The role of HC in the development of cavities was observed and compared to the mechanical riveting process, which successfully emulsifies oil alcohol to reduce mass transmission resistance and thus significantly increasing the conversion efficiency. The obtained results were in a good agreement in all technical aspects with other researcher's work.

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