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Pilot Scale Intensification of Pistacia Khinjuk Oil via Chemical Interesterification using Hydrodynamic Cavitation Technology

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Intensifying the reaction of non-edible *Pistacia khinjuk* oil with methyl acetate utilising potassium methoxide as a catalyst with hydrodynamic cavitation is a sustainable way of biodiesel synthesis. The objective of current study is to intensify the non-edible oil in the hydrodynamic caviation pilot reactor for the production of cleaner and greener biofuel. There were experimental tests with differently designed plates on the numerous upstream pressure ranges. It was noted that at the molar ratio of 1:17, catalyst concentration of 1.0 wt% and temperature of 55 °C, the maximum (98 %) production of *Pistacia khinjuk* methyl ester was observed utilising hydrodynamic cavitation reactor. In the presence of orifice plates, greater conversion compared to conventional methods was also observed. The Pistacia khinjuk oil methyl ester was characterised as per international standards. All tests passed the international tests and would be utilised as a substitute for fossil originated diesel.

1. Introduction

Due to severe environmental contamination, the development of renewable energy sources has become essential in recent years (Patil and Baral, 2021). Biomass has a potential candidate for clean energy. Biodiesel is a renewable fuel produced mainly through a methanol transesterification reaction from triglycerides contained in oleaginous plants and lipids and algae (Bokhari et al., 2014). A potential alternative to transesterification is the interesterification of triglycerides with alkyl acetate since triacetin is produced instead of glycerol. Contrary to enzymatic and supercritical reactions, the chemical interesterification process has reduced operating costs and may be performed at moderate reaction conditions. This reaction usually processes glycerol as a waste product. Interesterification with the methyl acetate is a successful alternative to transesterification since triacetin instead of glycerol is produced. Unlike transesterification, one ester exchanges its alcohol group with another ester during the interesterification event. The absence of alcohol as a reaction leads to a transformation of the reaction mix from polar to non-polar and the catalysts' insolubility (typically alkaline methoxides, alkali metals or alloys). Three consecutive reversible reactions are made up of this complicated reaction (Ogunkunle and Ahmed, 2019). Triacetin is primarily used in polymers and explosives as plasticisers and gelatinising agents. Triacetin has been discovered to be a gasoline additive or even a formulation for biodiesel (Subhedar and Gogate, 2016). Compared to the enzymes or hypercritical conditions, the low cost of employing alkaline methoxides is of special importance for chemical interest. This reaction, however, was not widely examined. The ester interchange reaction of triglycerides, an industry reaction utilised primarily to improve the thermal behaviour, microstructure, polymorphism, and crystallisation properties of fats and oils, has been the focus of most studies on chemical interesterification (Kashyap et al., 2019). This interesting analysis of lipids has been examined for the first time utilising alkaline earth metals and alkaline metals (tin, cadmium, plum), zinc, and compounds as catalysts at different temperatures (Amen et al., 2020). Sodium methoxide is the most common catalyst used in industrial operations (Syafiuddin et al., 2020).
Current research analyses the potential of *Pistacia khinjuk* oil (PiKSO) as an abnormal feedstock for the manufacture of biodiesel, a generally under-used oil seed feedstock. *Pistacia khinjuk* (Anacardia ceae/cashew family) is one of the genus Pistacia. Because of the economic worth of its members, Pistachia vera is an

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important genus. PiKSO is an Iranian-Turanian native region with planting in Pakistan, Afghanistan, Syria, Iran and Turkey. The Pistacia trees have a length between 2 – 5 m (Asif et al., 2017)
Even in annual rainfall of 100-600 mm, these trees are extremely suited to radiate, low nutrition soils, hot and arid climates. PiKSO trees may also be able to resist the most severe weather. *Pistacia khinjuk* is the greatest species cultivable in many different climates zones. Due to its dispersal in severe climatic areas and between local populations, it is a rich gene pool species. Anemophilia is another important feature that adds to its diversity. *Pistacia khinjuk* trees have been found to occupy around 1.5 – 3 acres every 106 ha in various places of Iran, with waste being their seeds. There is an oil of approximately 60 % The usage of PiKSO, under these conditions, has a stronger potential for a future source of renewable energy (Asif et al., 2017).A detailed analysis of current literature shows that there has been no investigation of the application of cavitational reactors to intensify biodiesel and triacetin synthesis via the reaction interesterification pathway (Rezania et al., 2019).
This work focuses on the enhancement of the interesterification process through a hydrodynamic reactor based on cavitation events generated by pressures created by incident orifice plates. In the presence of potassium methoxide as a catalyst with a cavitational environment, the interesterification reaction of the preselected PiKSO was carried out. Potassium methoxide has been chosen as a catalyst for the interesterification reaction because it produces more biodiesel than other catalysts such as potassium or sodium hydroxide in the interesterification reaction. Experiments were conducted on potassium methoxide to evaluate the dependence of biodiesel yield from PiKSO at varied inlet pressure and comparison with conventional stirring. In order to match international fuel criteria, the attributes of synthesised biodiesel were examined.

2. Materials and methods

2.1 Materials

Mature PiKSO seeds were obtained from several sections of Balochistan in Pakistan's southwest area. For several days' seeds have been dried in the presence of sunlight and hot temperature. The dry seeds were afterwards stored in a controlled laboratory environment to prevent moist impacts. Seeds were dried in an oven overnight at 60°C before the oil content estimate was made. The approximately 45 wt% oil yield was achieved. With the help of a mechanical oil expelling system, the oil was extracted. All the analytical grade chemicals utilised in this study were purchased from Merck, Germany. The detail and purity of the analytical grade chemicals have been reported in previous study (Asif et al., 2017). The oil characterisation results are presented in Table 1.

Table1: Properties of PiKSO

S no.	Properties	*Pistacia khinjuk oil*
1	pH	4.60
2	Freezing point (°C)	-19.0
3	The moisture content of seed (wt%)	0.20
4	Density at 15 °C (g/cm^3)	0.88
5	Viscosity (mm^2/s)	14.17
6	Ash content of seed (wt%)	0.55
7	Free fatty acid (wt%)	2.00
8	Acid value (mg KOH/g)	4.25
9	Molecular weight (g/mol)	874.66
10	Oxidation stability (h)	14.0
11	Flash point (°C)	270
12	Cetane No.	50.0

2.2 Cavitation reactor setup

Chemical interesterification reaction in a 50 L double jacket hydrodynamic cavitation (HC) reactor consisting of borosilicate glass was performed on a pilot scale. A double diaphragm pump was used to control the system's upstream pressure and circulate the reaction mixture in a narrow loop across the orifice plate. The plates were names as Plate1 (1 hole of 4.58 mm), Plate2 (21 holes with each 1 mm dia), Plate 3 (9 holes with 2 mm dia) and Plate 4 (5 holes with 4 mm dia) (Chuah et al., 2016). The double diaphragm pump is the main energy control system for a whole HC pilot plant. There were two lines of the downstream part of the pump. Valves at the mainline and circumference were controlled by the upstream pressure and fluid flow through a hole plate (Chuah et al., 2017). Figure 1 shows the HC pilot reactor scheme setup. The mass flow rates were between 2 - 8 L/min at the main and bypass lines, with the inlet pressure adjusted to 1 - 3.5 bar. The entire pilot plant has pressure

gauges and flowmeters. HC heat is dispersed by heating oil, which is around the area of the two jacket glasses. For a period of time, the digital temperature controller kept the desired temperature.
Experiments have been conducted at 1:7 molar ratio and 1.0 wt% at 50 °C for plate opening and pressure optimisation inlet. The experiments at pilot scale have been conducted on the pre-determined lab scale optimum above stated values (Asif et al., 2017). A specified amount of PiKSO and methyl acetate has been charged to the HC reactor. By cycling the reactants closely using pumping energy, uniform mixing was obtained. When the catalyst was introduced to the system, the initiating reaction point was examined (Chuah et al., 2015a). A liquid-form methanol potassium methoxide catalyst has been delivered that has a positive effect since it has been dissolved entirely with PiKSO and methyl acetate. The issues of catalyst mixing and reduced biodiesel efficiency were caused by solid potassium methoxide. The passing reaction mixture developed higher pressures of up to 3.5 bar in order to build constructive conditions for various newly developed orifice geometries. In order to check the course of a reaction, the known amount of the sample was removed from the system. Samples collected were gravitationally separated and contaminants cleaned with hot ionised water. With a rotating vacuum evaporator, the residual methyl acetate and water in the biodiesel have been evaporated off.

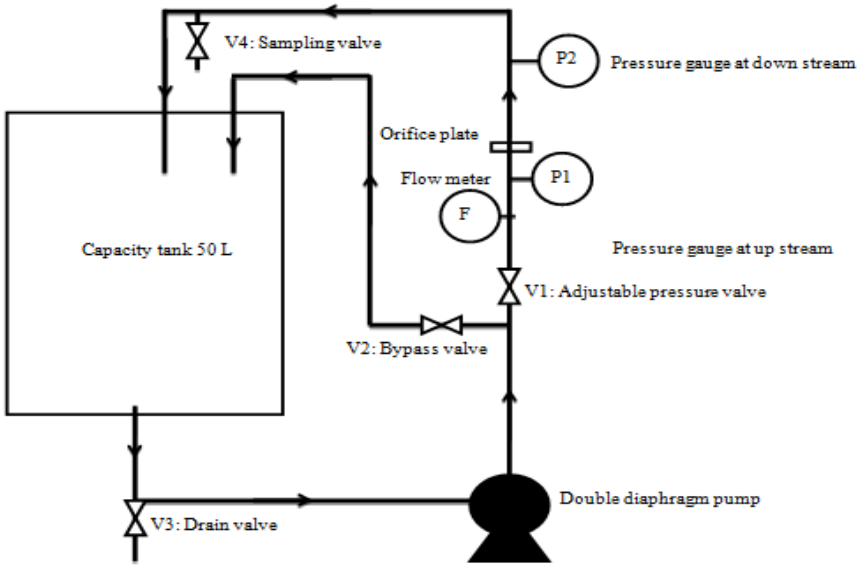

Figure 1: Interesterification reaction in a cavitation reactor

3. Results and discussion

3.1 Effect of upstream pressure in an interesterification reactor

In Figure 2, upstream pressure from between 1 and 3.5 bar at 55 °C, effects of inlet/upstream pressure for conversion of the methyl ester are demonstrated for four orifice plates of varied geometries. The increased inlet pressure from 1 to 3 bar resulted in increased interfering responses for all plates of the hole. The pressure increased from 3 to 4 bar did not influence the reaction rate considerably. It is due to the enormous voids formed on the bottom of the plate (Gole et al., 2013). The cavitation is caused by the coalescence of a great number of cavities. When the intake pressure was >4 bar, the reaction rate was slower. When the supply pressure reached 4 bar, the rate of degradation decreased. For the rest of the studies, an optimised input pressure of 3 bar was adopted. The needed time was 100, 20, 40, 60 min for plate 1, 2, 3, 4 in the optimal conversion of 98 wt%. Ghayal et al. (2013) have found that the input pressures have also increased with increased cavity collapse severity. A decrease in the impedance to mass transfer between the non-specific reactants was seen as cavities collapsed quickly happened. The abrupt collapse of cavities results in an improved transfer rate. This collapsed suddenly results in considerable fluid turbulence. The fluid rate increased led to a lesser number of cavitations.

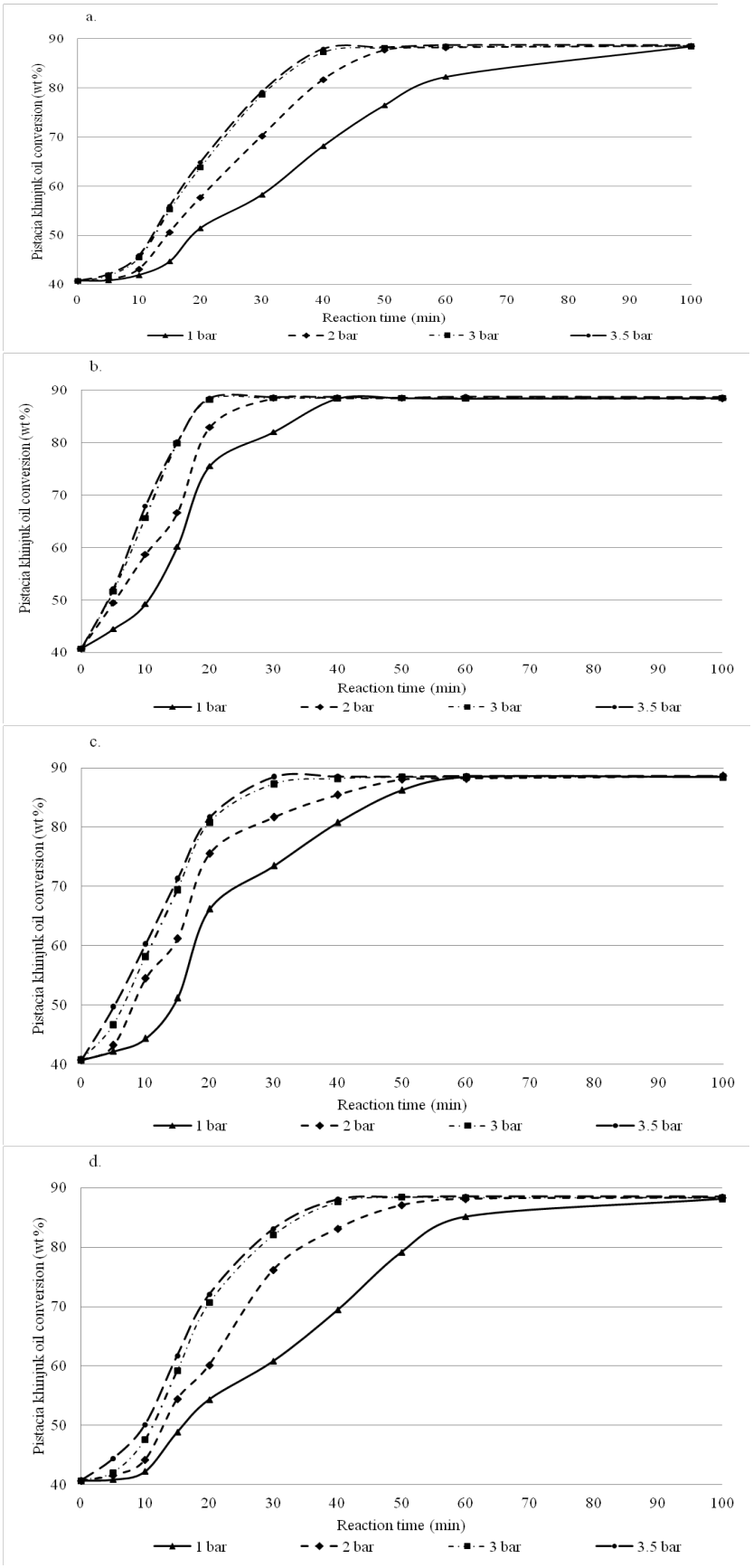

Figure 2: Effect of pressure on methyl ester conversion (a) Plate 1, (b) Plate 2, (c) Plate 3 and (d) Plate 4

The rest of the experiments with plate 2 have been performed due to conversion of maximum methyl ester at the pressure of 3 bar, compared to other plates within a short duration of 20 min. The Pistacia khinjuk oil conversion was calculated by the help of GC-FID. The fatty acid composition contain in percentage is palmitic acid, 27 palmitoleic acid, 0.61, stearic acid, 0.41, oleic acid, 22 linolenic acid, 30.86 linoleic acid, 9.99, tricosanoic acid, 27.64. The comprehensive procedure and fatty acids methyl ester calculation method is referred in previous work (Asif et al., 2017).

3.2 Comparison of cavitation with conventional stirring

The best reaction variables for chemical PiKSO interesterification with HC and conventional mechanical stirring (MS) are summarised in Table 2.

Table 2: Properties of Pistacia khinjuk oil methyl esters

Parameters	HC	MS
Optimum conditions		
Oil to methyl acetate ratio	1:17	1:17
Catalyst amount (wt %)	1.5	1.5
Temperature (°C)	55	55
RPM	-	800
Inlet pressure (bar)	3 bar	-
Time (min)	20	120

The results showed that both HC and MS interesterified methyl ester conversion to a maximum of 98 wt% in reaction time of 20 and 120 min. This is owing to the high intensity of the microturbulence produced by high-interface oscillating cavities in the HC system. HC technology affirms that mass transfer resistance during the reaction is eliminated and leads to higher conversion in less time. In MS methyl-acetate oil interface, the stirrer bar (MS) caused poor mass transfer between the immiscible reactants and a slow conversion rate. This is only possible with MS system stirrer bar (Chuah et al., 2015b). The increased conversion caused by the use of orifice plate is related to the physical consequences of the phenomenon of cavitation. Here it is vital to highlight that only the physical effects generated during the cavitation play a dominant role in intensifying the intensity of turbulence and microstreaming (Ghayal et al., 2013).
In the case of local turbulence, microcirculation and the generation of microemulsions, the increased biodiesel generation is attributable to greater area for reaction. The interface area between reactors grows considerably for the production of microemulsions between the two participating phases, allowing faster reactions and lower operating temperatures and decreasing the excess reactant level for comparable results. A further advantage of the HC technique is that for a similar or higher level of conversion level A less demand for extra methyl acetate will undoubtedly minimise the overall energy needs of the process, given that distilling methyl acetate separation is an energy-expensive operation that controls the overall economics of the biodiesel synthesis process. The ultrasonic method also provides easy product purification and the end product quality compared to the conventional approach is more appropriate.

4. Conclusions

The present work has identified the usefulness of a hydrodynamic cavitational interesterification procedure for biodiesel and triacetin manufacture from *Pistacia Khinjuk* oil. The procedure can be a valuable alternative to the most frequently used transesterification because triacetin instead of glycerol is generated as a significant addition to improve biodiesel characteristics, especially in cold settings. The results given in the current context are quite relevant since they have concentrated on one of the cheaper routes of synthesis for biodiesel production using non-edible oils that intensify considerably by employing process intensification. In the case of the cavitation technique, higher biodiesel yields were reported compared to the traditional method, and the synthesised biodiesel also improves its characteristics. In comparison to conventional and intensification processes, the surplus reactants needed are also lower, with benefits in terms of cheaper separation costs. It was initially confirmed that the synthesis of biodiesel based on the interesterification methodology has resulted in significant process intensification.

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References

Amen R., Yaseen M., Mukhtar A., Klemeš J.J., Saqib S., Ullah S., Al-Sehemi A.G., Rafiq S., Babar M., Fatt C.L., Ibrahim M., Asif S., Qureshi K.S., Akbar M.M., Bokhari A., 2020, Lead and cadmium removal from wastewater using eco-friendly biochar adsorbent derived from rice husk, wheat straw, and corncob, Cleaner Engineering and Technology 1, 100006

Asif S., Ahmad M., Bokhari A., Chuah L.F., Klemeš J.J., Akbar M.M., Sultana S., Yusup S., 2017, Methyl ester synthesis of Pistacia khinjuk seed oil by ultrasonic-assisted cavitation system, Industrial Crops and Products 108, 336-347.

Bokhari A., Yusup S., Faridi J.A., Kamil R.N.M., 2014, Blending study of palm oil methyl esters with rubber seed oil methyl esters to improve biodiesel blending properties, Chemical Engineering Transactions, 37, 571-576.

Chuah L.F., Yusup S., Abd Aziz A.R., Bokhari A., Klemeš J.J., Abdullah M.Z., 2015a, intensification of biodiesel synthesis from waste cooking oil (Palm Olein) in a hydrodynamic cavitation reactor: effect of operating parameters on methyl ester conversion, Chemical Engineering and Processing, 95, 235-240.

Chuah L.F., Aziz A.R.A., Yusup S., Bokhari A., Klemeš J.J., Abdullah, M.Z., 2015b. Performance and emission of diesel engine fuelled by waste cooking oil methyl ester derived from palm olein using hydrodynamic cavitation. Clean Technologies and Environmental Policy 17(8), 2229-2241.

Chuah L.F., Yusup S., Abd Aziz A.R., Bokhari A., Abdullah M.Z., 2016, Cleaner production of methyl ester using waste cooking oil derived from palm olein using a hydrodynamic cavitation reactor, Journal of Cleaner Production, 112 (5) 4505–4514.

Chuah L.F., Klemeš J.J., Yusup S., Bokhari A., Akbar M.M., 2017. A review of cleaner intensification technologies in biodiesel production. Journal of Cleaner Production 146, 181-193.

Ghayal D., Pandit A.B., Rathod V.K., 2013, Optimisation of biodiesel production in a hydrodynamic cavitation reactor, using used frying oil, Ultrasonics Sonochemistry, 20, 322-328.

Gole V.L., Naveen K.R., Gogate P.R., 2013, Hydrodynamic cavitation as an efficient approach for intensification of synthesis of methyl esters from sustainable feedstock, Chemical Engineering and Processing: Process Intensification, 71, 70-76.

Kashyap S.S., Gogate P.R., Joshi S.M., 2019. Ultrasound assisted synthesis of biodiesel from karanja oil by interesterification: Intensification studies and optimisation using RSM. Ultrasonics Sonochemistry 50, 36-45.

Ogunkunle O., Ahmed N.A., 2019, A review of global current scenario of biodiesel adoption and combustion in vehicular diesel engines, Energy Reports, 5, 1560-1579.

Patil A.D., Baral S.S., 2021. Process intensification of thumba methyl ester (Biodiesel) production using hydrodynamic cavitation, Chemical Engineering Research and Design, 171, 277-292.

Rezania S., Oryani B., Park J., Hashemi B., Yadav K.K., Kwon E.E., Hur J., Cho J., 2019, Review on transesterification of non-edible sources for biodiesel production with a focus on economic aspects, fuel properties and by-product applications, Energy Conversion and Management, 201, 112155.

Subhedar P.B., Gogate P.R., 2016, Ultrasound assisted intensification of biodiesel production using enzymatic interesterification, Ultrasonics Sonochemistry 29, 67-75.

Syafiuddin A., Chong J.H, Yuniarto A., Hadibarata T., 2020, The current scenario and challenges of biodiesel production in Asian countries: A review, Bioresourse Technology Reports, 12, 100608.