

Pre-Blended Methyl Esters Production from Crude Palm and Rubber Seed Oil Via Hydrodynamic Cavitation Reactor

Suzana Yusup^{a*}, Awais Bokhari^b, Lai Fatt Chuah^c, Junaid Ahmad^d

^{a,b,c,d} Biomass Processing Lab, Centre of Biofuel and Biochemical Research (CBBR), Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750, Tronoh, Perak, Malaysia.
drsuzana_yusuf@petronas.com.my

Variety of transesterification processes was widely investigated for biodiesel production to enhance the fuel quality. Energy and reaction time are the major constraints to develop a more economically process with better product quality. Hydrodynamic cavitation possesses lessen the reaction time based on conversion of feedstock to biodiesel. Current study utilized pre-blended equi-volume mixture of crude palm and rubber seed oil as the feedstock. Rubber seed oil as a non-edible feedstock for biodiesel helps to reduce the dependency on crude palm oil. The esterification and transesterification process were carried out at mini scale pilot plant with hydrodynamic cavitation reactor. The cavities were produced in the reactor by passing the fluid (methanol, oil and catalyst) under reduced pressure through constriction (orifice) at higher velocity and these cavities will collapse due to recovered pressure. The sudden collapse of cavities under pressure increased the mass transfer between oil, methanol and catalyst. This mass transfer limitation in conventional transesterification processes was overcome by hydrodynamic cavitation and hence lesser reaction time achieved. In this research the conversion of fatty acid methyl esters up to 90% was observed in 20 minutes. The produced methyl esters were analyzed for its low temperature fuel properties and it meets the international standards of EN 14214 and ASTM D 6751.

1. Introduction

To avoid any distortion, the world emphasis is focus on search for the alternative and renewable energy sources. The search for renewable fuels offers environmental, sustainable and economic benefits. Transportation sector is the second most energy consuming sector after industry. A 30% of the globe delivered energy utilized by transportation sector from which 80% is consumed by highway transport. This sector is covers 60% of world fuel demand and it is expected as the strongest mounting energy demand sector (Atabani et al., 2013) . Almost 97.6% of the transportation around the world relies on the fossil based liquid fuels and the remaining 2.4% consumes gaseous fossil fuels. Fossil fuel contribution to world energy market is projected to decline 35-30% in year 2035 and is expected to be a major source of energy. The peak productions of fossil fuels are still conjecture but in 2005 French economics revealed that it may transpire in 2013. However World Energy Forum (WEF) predicted that the fossil fuel will be come to its peak production in next 10 decades (Lim and Lee, 2012)

In view of the rapidly growing industry and human population, the exploration of renewable fuels from aboriginal energy resources plays a crucial role. Malaysia as an agricultural country has huge potential for local seed oil production (Ahmad , et al., 2014). Particularly, palm oil and non-edible oil such as rubber seed oil can be economically converted into methyl esters. Vegetable oils can be used as an alternative for petroleum diesel either by blending them directly with fuel or by enhancing their properties through a number of available technologies (Ng et al., 2012).

Palm biomass availability significantly increased from 1.3 tons to 5 million tons from the year 1975-2011. The palm plantations covered 14% area of total Malaysian land. But this sector still have sustainable and labor

shortage challenges. The edible oil sectors is dwindling if it excessively utilized as a biofuel. Palm plantations continuously increasing at the rate of 4.4% per annum to fulfill both local and international demands. On the other side, Malaysia has huge number of rubber seeds plantations which are still ignored and un-utilized as sustainable fuel at commercial level. Rubber seed as non edible oil has better low temperature properties and great potential to replace palm oil methyl esters and uplift Malaysian economy (Bokhari et al., 2014). Existing conventional technologies to produce methyl esters are mostly based on synthesizing it from natural oils and from a single type of oil such as corn oil, linseed oil, palm oil, soybean oil, rapeseed oil. (Khan et al., 2010) describe a method for preparing esters oil from rubber seed oil. Most of the technologies are designed for the transesterification of methyl esters in crude palm oil, which may lead to food crisis. One solution is to search and explore a non-edible oil source for esters production (Yusup and Khan, 2010).

Reduction in saturated fatty acids from crude palm oil resulted from blending can lower the pour point of biodiesel produced (Martins et al., 2013). On that basis, we can recommend that methyl esters produced from the blended oil can also enhance the low temperature properties. Thus our intention is to develop a prototype-scale of hydrodynamic reactor for production of 30 L/batch biodiesel in a continuous mode from a blended feedstock of crude palm oil and rubber seed oil. With the successful implementation of the prototype scale, the proposed technology can further be upgraded for in-depth hydrodynamic technology research. (Gole et al., 2013) successfully reduced the acid value and produced methyl esters from Nagchampa oil using hydrodynamic technology at different pressure and flow rates. (Ghayal et al., 2013) used frying oil to optimize the reaction conditions using cavitation reactor and found it to be energy efficient technology.

Compared to the existing technologies, current innovative method is capable to reduce the acid value of equi-volume pre-blended crude palm and rubber seed oil by increasing the purity of the final product of methyl esters in efficient and economic way. The produced methyl esters were analyzed for the fuel properties according to international biodiesel standards of EN 14214 and ASTM D6751.

2. Materials and Methodology

2.1 Materials

The raw crude palm oil was purchased from Felcra Palm Oil Industry and Plantation, Seri Iskandar, Malaysia. While, rubber seed oil was imported from Vietnam. All the chemicals and reagents used for analysis are of analytical grade were attained through Merck Chemicals (Darmstadt, Germany). Methyl esters standards for gas Chromatography (GC) were purchased from Sigma Scientific Chemicals (St. Louis, MO, USA).

2.2 Hydrodynamics Reactors Configuration

The 50 L/batch hydrodynamic reactors are connected to diaphragm pumps for re-circulation of fluid in the reactors. The centrifugal compressor system supplied air to the pumps for their operation. The pumps are the main equipment which dissipates energy through hydrodynamic cavitation reactors. A maximum pressure of 3 bar was exerted by the pumps to the fluid when it passes through the orifice plate of 1mm hole and 20mm thick, placed between flange. The bottom of reactor is connected to suction side of pump discharged the fluid from top of the reactor passing through orifice plate. The pump pressure regulated with the valves controls the flow rate of air through the pump. The flow rates and pressure was monitored with the help of gauges installed with the reactor assembly. Esterification reactor is made up of see through double jacketed glass material and heat was provided with help of pre-heated silicon oil circulating at the internal side of the jacket. Similarly, transesterification reactor composed of stainless steel and heated with the help of external heating source. Both reactors were connected to condensers to avoid methanol losses.

2.3 Experimental Procedure

The crude palm and rubber seed oil was pre-blend at equi-volume ratio and its acid value was determined according to method proposed by AOCS (American Oil Chemist Society). The feedstock was pre-treated in the acid esterification hydrodynamic reactor following the pre-determined optimized conditions from our previous research work (Khan et al., 2010). For pre-treatment, the feedstock was initially heated to 70°C with the help of silicon oil circulating around the reactor. Methanol and sulphuric acid as the catalyst were added to the esterification reactor when temperature attain to its desired level. As the reaction progressed, small amount of samples were collected from downstream valve at regular interval of time to monitor its acidity. In the second step of neutralization the feedstock was transferred from esterification to transesterification hydrodynamic reactor for further proceed to produce methyl esters production. In second reactor, sodium hydroxide was used a catalyst to carry out reaction of esterified product. After reaction, the heavier phase layer of glycerol was separated from the transesterified product and deionized warm water was used for

washings to remove impurities from the product. During the reaction, methyl esters samples were also collected at specific time interval in order to analyze the methyl esters conversion. Methyl esters were analyzed quantitatively by GC FID (Gas Chromatography Flame Ionization Detector).

3. Results and Discussion

3.1 Esterification In Hydrodynamic Reactor

Higher content of free fatty acid (FFA) present in the feedstock was reduced by acid esterification process in order to avoid any saponification reaction and hydrolysis. If higher FFA feedstock undergoes direct base transesterification reaction, saponification reaction will occur. Generally, FFA content of feedstock below 1% gives favourable transesterification reaction in the presence of base catalyst. Optimization of process is considered to be beneficial from economic and smooth operational point of view. Acid esterification under hydrodynamic cavitation was run at pre-determined optimized conditions following conventional method at laboratory scale (Khan et al., 2010). According to optimize conditions, this pre-blended run in hydrodynamic reactor was carried out at methanol to oil molar ratio of 15:1, catalyst concentration of 10wt % and reaction temperature of 65°C. The FFA content of the reaction was continuously monitored at specific time interval until equilibrium was attained. Figure 1 shows the decrement of FFA content w.r.t reaction time at optimized conditions for hydrodynamic cavitation reaction compared with the conventional approach.

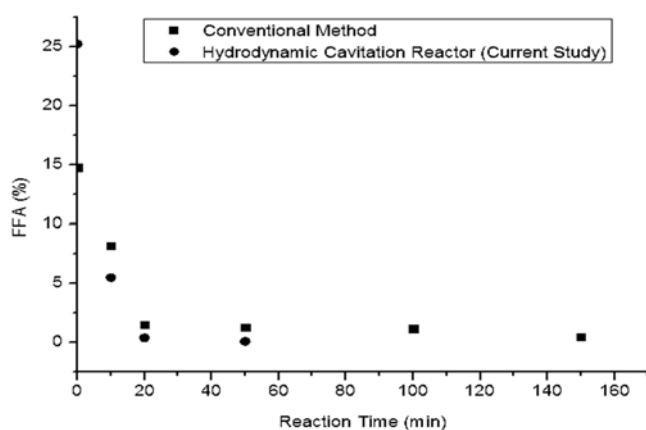


Figure 1: Comparative FFA reduction of conventional and hydrodynamic cavitation technology

It has been clearly shown from Figure 1, that hydrodynamic approach takes lesser reaction time to decrease FFA content from 25.24% to 0.2% within 50 minutes. However, conventional approach takes more reaction time to decrease FFA content to the desired level. Similarly, conventional approach needs higher temperature to carry out reaction but hydrodynamic cavitation reactor successfully produce effectual results at ambient temperature. Hydrodynamic cavitation attributed to give successful output because it eliminates mass transfer hurdle between oil and methanol phase. Sudden pressure drop at the hole of orifice plate caused cavities of higher velocities which gave large interfacial surface area for reaction between oil and methanol immiscible phase. Emulsion characteristics between oil and methanol phase determined the esterification reaction rate. The effective purpose of hydrodynamic cavitation is to break emulsion bonding between oil and methanol phase and thus to increase the esterification rate. Another most effective benefit of hydrodynamic cavitation is lesser energy requirement per mole of product produced (Gole et al. 2013).

3.2 Base Transesterification In Hydrodynamic Reactor

Base transesterification requires excess methanol to keep the reaction path towards methyl esters production in a similar way esterification process needs. For effective process operation, this process also operated at optimized conditions found by conventional method at laboratory scale. The esterified product with FFA content less than 1% from esterification hydrodynamic reactor was shifted to transesterification hydrodynamic reactor with the help of a pump. Heating jacket around transesterification reactor was turned on maintain reaction temperature at 55°C for methyl esters production. Methanol and potassium hydroxide pellets were mixed together with the help of mixture in methanol/catalyst feeding tank. Methanol with molar ratio of 8:1 and potassium hydroxide at 2 wt % at 55°C was used in this reaction according to optimize conditions found. The

emphasis to operate process at optimized conditions since it helps to shifts the reaction equilibrium towards methyl esters production side and prevent separation difficulty of methyl esters from by-product. Figure 2 shows the comparative methyl esters conversion at same optimum conditions based on previous conventional study and current hydrodynamic cavitation technology. From Figure 2 it's clearly shown that hydrodynamic cavitation takes lesser reaction time to give maximum methyl esters conversion at similar optimum conditions used for conventional method (Yusup and Khan, 2010). Current study results are comparable with other researcher's work which clearly proves that hydrodynamic technology intensify the methyl esters conversion with lesser reaction time and it is energy efficient (Gole et al., 2013). Hydrodynamic dynamic and cavitation technology physically boost up the reaction to 50%. Less intensive operation requirements make this process ease to scale up to commercial level (Ghayal et al., 2013).

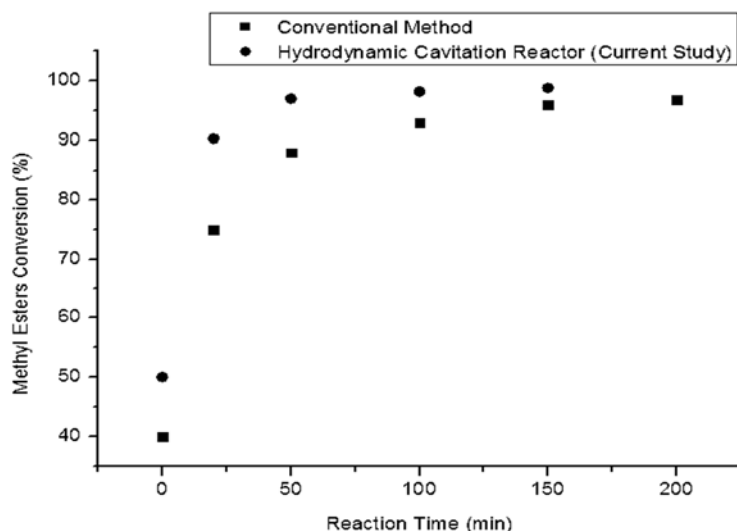


Figure2: Comparative methyl ester conversion of conventional and hydrodynamic cavitation technology

3.3 Comparative Discussion On Hydrodynamic Cavitation and Conventional Process Performance

Compared to conventional process, hydrodynamic cavitation technology required lower reaction time for processing of feedstock to methyl esters. Hydrodynamic cavities also increase the kinetic energy of the reacting molecules which prevent the needs to pre-heat the feedstock before starting reaction. Hence, no pre-heating requirement of feedstock in hydrodynamic cavitation approach reduces the overall process cost and time as compared to conventional methyl esters production method. Conventional method needs approximately 120 min to pre-heat the feedstock to desire level. By including the methyl esters process time the total time needed for complete production is almost 330min. Whereas, hydrodynamic cavitation technology required maximum process time of 130min to achieve methyl esters production according to requirements of international biodiesel standards of EN14214 and ASTM D6751. For the start up of methyl esters production, the difficult part is to initiate reaction rate by overcome the mass transfer limitations between the immiscible triglyceride and methanol phase.

Hydrodynamic cavitation technology excessively intensifies the mass transfer between this phase by producing cavities under high pressure and velocity. Similarly, this process required lower amount of energy and time to esterify the process to reduce FFA content. The yield of product per unit supplied for hydrodynamic cavitation was found to be 13.5×10^{-4} g/J and for conventional process it is 8×10^{-6} g/J. The yield for conventional process was lower because this process required pre-heating and mass transfer limitations. Whereas, hydrodynamic cavitation technology successfully initiate at ambient conditions. Later conversion of methyl esters increased by increasing reaction temperature and cavities produced by pressure overcomes mass transfer limitations. Hence, overall processing cost to produce biodiesel directly depends upon the input energy requirement. The second most important thing which directly associates with overall process cost is availability and cost of raw material feedstock. Non-edible oils as sustainable raw materials for biodiesel production positively reduce the overall process economic of biodiesel production. The overall input as well production cost of methyl esters reduced 50% by hydrodynamic cavitation as compared to conventional approach.

Table 1: Comparative methyl esters properties according to international standards for conventional and hydrodynamic cavitation technology

Test	Unit	ASTM D6751 Criteria	EN 14214 Criteria	Conventional Method (after 330 min)	Hydrodynamic Cavitation (after 15 min)	Hydrodynamic Cavitation (after 130 min)
Ester content	% (m/m)	-	96.5 min	98.113	74.8	97.6
Density@15°C	Kg/m ³	-	860-900	874	891.6	886.4
Kinematic Viscosity @ 40°C	mm ² /s	1.9-6.0	3.5-5.0	4.22	7.394	3.82
Flash Point	°C	130min	101 min	150	140	143
Sulphur Content	mg/kg	5.0 max	10.0 max	1.01	87	8.0
Water Content	mg/kg	500max	500 max	200	623	423
Oxidation Stability@ 110°C	hours	3min	6.0 min	-	1.4	8.54
Acid value	mgKOH/g	0.50max	0.50 max	0.46	8.4	0.42
Iodine Value	g iodine/100g	120max	120 max	-	90.5	90.3
Methanol Content	%(m/m)	Pass/fail	0.20 max	pass	0.09	0.01
Monoglyceride Content	%(m/m)	-	0.80 max	1.1	0.57	0.45
Diglyceride Content	%(m/m)	-	0.20 max	0.18	2.96	0.05
Triglyceride Content	%(m/m)	-	0.20 max	0.12	9.03	0.10
Cloud Point	°C	-	-	-	12	10
Pour Point	°C	-	-	-	4	3
Free Glycerine	%(m/m)	0.02max	0.02 max	0.016	0.003	0.002
Total Glycerine	%(m/m)	0.24max	0.25 max	0.195	1.511	0.10

Table 1 shows the comparative methyl esters product analysis according to international standards (EN14214 and ASTM D6751) for both conventional and hydrodynamic cavitation technology. Hydrodynamic cavitation process analyzed at reaction time of 130 min and 15min. It's cleared from Table 1 that 15min reaction shows 72% conversion of methyl esters but most of the properties not fall within the range of international biodiesel standards. The analysis after 130min reaction shows that all the methyl esters properties lie in range as per fulfilling international standards. The 130min reaction shows acceptable low-temperature properties and oxidation stability for methyl esters. On the other hand, conventional method

approach shows acceptable values according to international standards but it takes longer reaction time of 330min and more energy requirements. Thus the current work with hydrodynamic cavitation reactor produced methyl esters of international standards using sustainable raw material of high acid value.

4. Conclusions

Biodiesel conversion and its properties have been comparatively studied by using hydrodynamic cavitation technology. It has been proved that methyl esters conversion achieved within lesser reaction time and energy by hydrodynamic cavitation technology. The biodiesel properties has been determined at two different time intervals by hydrodynamic cavitation technology. It has been shown that hydrodynamic cavitation technology provided final product quality that meet the international standards of ASTM D674 and EN 14214 compared to conventional approached which took a longer time.

Acknowledgements

This work was financially supported by PRGS project funding (0153AB-K19), MYRA project (0153AB-J19) and Universiti Teknologi PETRONAS.

References

- Atabani A.E., Mahlia T.M.I., Masjuki H.H., Badruddin I.A., Yussof H.W., Chong W.T., Lee K.T., 2013, A comparative evaluation of physical and chemical properties of biodiesel synthesized from edible and non-edible oils and study effect of biodiesel blending, *Energy*, 58, 296-304, DOI:10.1016/j.energy.2013.05.040.
- Ahmad J., Yusup S., Bokhari A., Kamil R.N.M., 2014, Study of fuel properties of rubber seed oil based biodiesel, *Energy Conversion and Management*, 78, 266-275, DOI:10.1016/j.enconman.2013.10.056.
- 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, DOI:10.3303/CET1437096.
- Ghayal D., Pandit A.B., Rathod V.K., 2013, Optimization of biodiesel production in a hydrodynamic cavitation reactor, using used frying oil, *Ultrasonics Sonochemistry*, 20, 322-328, DOI:10.1016/j.ultsonch.2012.07.009.
- 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, DOI:10.1016/j.cep.2012.10.006.
- Khan M.A., Yusup S., Ahmad M.M., 2010, Acid Esterification of a high free fatty acid crude palm oil and crude rubber seed oil blend: Optimization and parametric analysis, *Biomass and Bioenergy*, 34, 1751-1756, DOI:10.1016/j.biombioe.2010.07.006.
- Lim S., Lee K.T., 2012, Implementation of biofuels in Malaysian transportation sector towards sustainable development: A case study of international cooperation between Malaysia and Japan, *Renewable and Sustainable Energy Reviews*, 16, 1790-1800, DOI:10.1016/j.reser.2012.01.010.
- Martins M.I., Pires R.F., Alves M.J., Hori C.E., Reis M.H.M., Cardoso V.L., 2013, Transesterification of soybean oil for biodiesel production using hydrotalcite as basic catalyst, *Chemical Engineering Transactions*, 32, 817-822, DOI:10.3303/CET1332137.
- Ng W.P.Q., Lam H.L., Yusup S., 2012, Supply network design and the utilisation of rubber seed oil as biofuel and biochemicals, *Chemical Engineering Transactions*, 29, 835-840, DOI: 10.3303/CET1229140.
- Yusup S. and Khan M A., 2010, Base catalyzed transesterification of acid treated vegetable oil blend for biodiesel production, *Biomass and Bioenergy*, 34, 1500-1504, DOI:10.1016/j.biombioe.2010.04.027.