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Relative Efficiency of Esterified Rubber Seed Oil in a Hydrodynamic Cavitation Reactor and Purification via Distillation Column

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High local pressure and temperature can be generated by the sudden collapse of cavities which contributed to minimising the mass transfer between methanol and rubber seed oil phase in an acid esterification pre-treatment process. The reaction is carried out in a 50 L/batch pilot scale reactor with an induced pressure of 1-3.5 bar around the orifice plate to generate the cavitational field. The double diaphragm pump is the key component to dissipate the energy in the hydrodynamic cavitation process. Four orifice plates with the various designs were studied for hydrodynamic cavitation process. In this regard, cavitation number effect, concentration effect and relative esterified efficiencies for all orifice plates were studied on various upstream pressure. It has been found that the plate with 21 holes of 1mm diameter with an inlet pressure of 3 bar gave a comprehensive result for the relative esterified efficiency of $0.005x10^{-5}J^{-1}$. The relative efficiency of hydrodynamic cavitation process is fourfold higher than the mechanical stirring conventional process which makes it energy efficient. The final product from hydrodynamic cavitation process was purified via pilot scale distillation column of 5 L/batch capacity to further commence the transesterification process. The effects of temperature, pressure and packing height on distillation have been studied. The purified product properties such as moisture content, acid value and higher heating value were measured. It was found that purified product can be utilised for transesterification reaction for biodiesel production as a greener fuel.

1. Introduction

Biodiesel research has been expanding tremendously for last few decades for the development of cleaner and greener fuel (Bokhari et al., 2015). Higher production and operational costs created major hurdles for replacement of biodiesel with fossil diesel (Chuah et al., 2015a). Feedstock selection and its cost constraint are the major contributors (70 - 95 %) towards the total biodiesel production cost (Bokhari et al., 2016). Sustainable feedstock, such as non-edible rubber seed oil (RSO) provides a potential solution to reducing the production cost with no direct competition for human food (Ahmad et al., 2014). Malaysia has the largest rubber seed plantations after palm oil which was estimated at 1,022,700 ha plantation area with 300 kg/ha seeds generation annually (Ng et al., 2013).

Approximately 306,810 t of rubber seeds are available for biodiesel production annually (Bokhari et al., 2014). The acid value of RSO is significantly high could be due to its elevated free fatty acid contents (Gimbun et al., 2013). Acid esterification process is usually adopted prior to biodiesel production to reduce the acid value of RSO. The longer reaction time of acid esterification process will further add cost to the overall production cost. Intensification technologies could have a potential to lower the reaction time at a significant level. Several intensification technologies studied include as microwave, ultrasound and hydrodynamic cavitation (HC) (Ghayal et al., 2013). HC has been adopted for biodiesel production by researchers on a laboratory scale with successful conversion of methyl esters within just a few minutes (Chuah et al., 2015d).

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HC process is an effective technology which lower the reaction time of acid esterification process with better esterified efficiency (Bokhari et al., 2016). HC technology used the phenomena of cavities which were produced with the aid of orifice plate and a destructive force dissipated in the system through the pump. Sudden upstream pressure drop and recovered downstream pressure caused growth and collision of bubbles (Gole et al., 2013). Higher intensity of bubbles creates elevated energies densities due to huge turbulence. The mass transfer between RSO and alcohol phase was reduced due to growth and collapse of cavities of higher kinetic energy (Yusup et al., 2015). Treated RSO and biodiesel have impurities such as water, catalyst and methanol (Stojković et al., 2014).

Chemistry of esterification showed that it has water formation during the reaction. Without proper removal of water from the esterified product, transesterification reaction leads towards a lower yield of biodiesel production (Chuah et al., 2015b). Purification via water washings are several disadvantages and added extra cost to the process (Ferrero et al., 2014). Implementation of distillation is most reluctant for removing of recalcitrant impurities from the esterified product. Distillation under vacuum results in a pure esterified product for further transesterification process. Implementation of purification section needs to be significant. Once established, it will give effective purification and results in the least contaminant product which is acceptable for the commercial level (Zean Consultants, 2010).

Current research focused on reducing the acid value of high free fatty acid RSO with an aid of pilot scale HC technology with the capacity of 50 L/batch. Four different orifice plates with an upstream pressure of 1-3.5 bar were studied. Relative esterified efficiency was calculated on each orifice plate with different upstream pressure. Pilot scale distillation column technology with a capacity of 5L/batch under high vacuum was used for purification of the esterified treated product. The distillation column was employed for purification of the esterified product by removing the water and methanol content. Thus, contaminants free esterified product will be beneficial for transesterification reaction with enhanced methyl esters conversion.

2. Materials and Methodology

2.1 Materials

The RSO was procured from Kinetic Chemicals (M) Sdn. Bhd. Malaysia. All the analytical standards chemicals were delivered by Merck, Malaysia. Bhd. Malaysia. The acid value of RSO was found to be 72.36 mg KOH/g oil by following AOCS Cd 3d-63 method. All the major properties of RSO were mentioned in our previous research work (Chuah et al., 2015b). On optimized conditions, the pre-blended run in the hydrodynamic reactor was carried out at methanol to oil molar ratio of 8:1, a catalyst concentration of 10wt % and the reaction temperature of 55 ^{o}C (Bokhari et al., 2016). The HC configuration, process flow, orifice plate design configuration and experimental procedure (Chuah et al., 2016).

2.2 Vacuum Distillation Column Configuration and Process

The schematic diagram of pilot distillation column with 5 L capacity is shown in Figure 1. The distillation column is a packed column made up of glass and can be operated between 0.1 - 2 bar of pressure at a maximum temperature of 200 ^{o}C. Pall rings were used as packings. The height of the column is 2 m with the diameter of 150 mm. The column is connected with four flasks of capacity 4 L. Two feeding flasks were connected with reboiler until 100 ^{o}C. Other two flasks were for distillate and bottom product. The re-boiler is connected to bottom phase flask with maximum operating temperature of 200 ^{o}C. The feed was entered into a column with the help of two dosing pumps.

All column is equipped with flow rate controllers with indicators to measure and adjust the flow rate. The three-way valve is provided in the column to adjust the feed point and reflux. Sampling ports are provided at each stage for sample analysis. The unit was provided with instrumentation and control system for monitoring and controlling the distillation process such as temperature, pressure and flow rates. The esterified product from the HC reactor was feed into the distillation unit from the middle line of the column which flowing down through packings and collected at the bottom of the re-boiler. The heat was supplied to the re-boiler to generate methanol and water vapours. The vapours moved up the column, condensed and collected in reflux flask. The vacuum is created in a unit with the help of vacuum pump. The esterified product after purification was transferred to product vessel through perist pump.

3. Results and Discussion

3.1 Relative Esterified Efficiency of Hydrodynamic Cavitation Technology

The parameter which expresses the required pumping energy for dissipating in the HC system to reduce acid value in terms of absolute variation of acid value concentration is known as relative esterified efficiency shown in Eq(1).

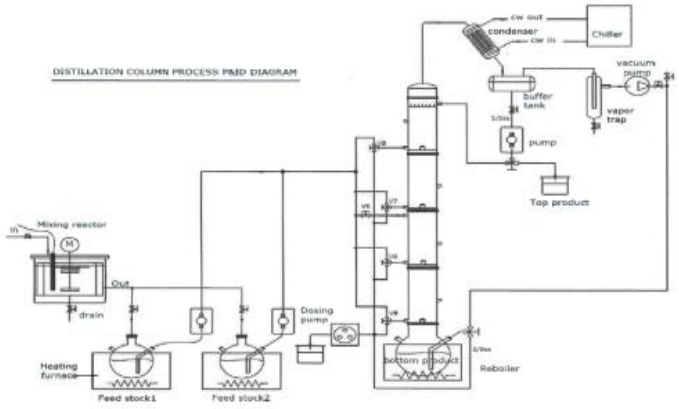

Figure 1: Process flow of distillation column

$$\text{Relative esterified efficiency} = \frac{\text{Variation of relative concentration}}{\text{Pumping Power}} \quad J^{-1} \tag{1}$$

Acid value relative concentration varies with respect to reaction for specific orifice plate at different upstream pressure. So relative esterified efficiency is the function of time and its magnitude varies during esterification process.

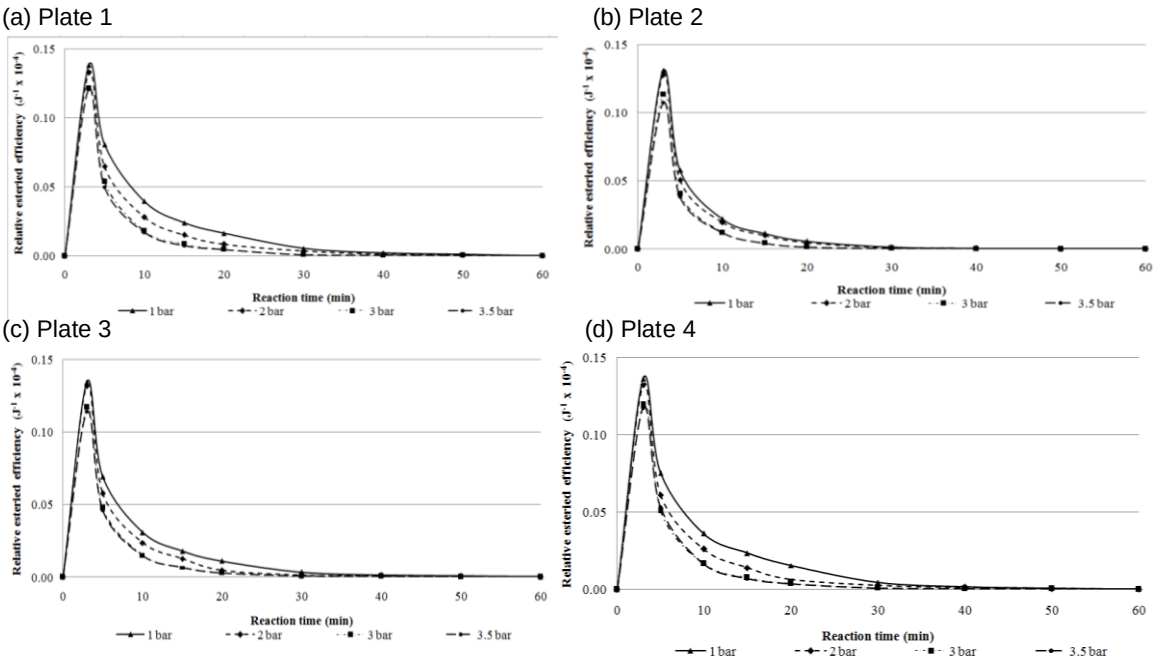

Figure 2: Relative esterified efficiency of hydrodynamic cavitation technology

Figure 2(b) depicts that orifice plate 2 with 21 holes at the upstream pressure of 3 bar shows better relative esterified efficiency. Higher intial acid value concentration led to the higher value of relative esterified efficiency. As the concentration of acid value decreased the relative esterified efficiency observed is lower. The lowest value of caviation number at this stage is observed which proves better cavitational phenomena occured (Chuah et al., 2015c). For the higher value of cavitation number, the relative esterified efficiency incresead due to the high demand of pumping energy needed at these cavitational zones. There is a marginal difference observed in relative esterified efficiency values between the upstream pressure of 3 - 3.5 bar. This could be attributed to the oulet of an orifice plate, which was accumulated with a large number of cavities and resulted in cavitational chocking (Bokhari et al., 2016).

At the pressure of 1 - 2 bar the esterified relative efficiency significantly high with a larger value of cavitation number. The relative esterified efficiency of plate 2 at 2 bar was 0.0011 x $10^{-5}J^{-1}$. It was increased by about 45.5 % compared to 3 bar and 32% compared to 1 bar of upstream pressure with a relative esterified efficiency of 0.0013 x $10^{-5}J^{-1}$. The relative esterified efficiency has also compared with mechanical stirring (MS) at the same conditions and has found that MS is four folds higher than HC. The lower the value of relative esterified efficiency, better the cavitational zone. At the lowest value of relative esterified efficiency, the acid value of RSO was reduced from 78.66 to 2.68 mg KOH/g. Sayyaadi (2015) studied the relative efficiency of enhanced cavitation-oxidation process of non-VOC aqueous solution using hydrodynamic cavitation and the results showed the effect of relative concentration of H_2O_2 injection on the relative efficiency of the system. For other orifice plates, Figure 2 shows similar phenomena of relative esterified efficiency for other orifice plates with the ranking of orifice plates i.e plate 2 > plate 3 > plate 4 > plate 1.

3.2 Distillation of the Esterified Product

Three theoretical stages and a reflux ratio of 2 were employed for the purification of the esterified product. Five kg of the esterified product contains approximately 20 % of water and methanol. Methanol and water shall present in the product. Water in the product is due to several deionised warm water washing in order to clean the esterified product and the water produced in the reaction as a by-product. Distillation was carried out per batch with different parameters as shown in Table 1. It can be clearly shown that maximum product was purified at re-boiler temperature of 175 ^oC with feed inlet at 75 ^oC and vacuum pressure of 0.1 bar.

Feed was pumped into a column at the middle with a mass flow rate of 4 kg/h. The packing height throughout the column is 127 mm for this batch stage. At this stage, 95.25 % of water and methanol was recovered back as a top product. Remaining 4.75 % of the methanol and water remained in the bottom product. The packing provided the interfacial area between vapor and liquid phase which enhanced separation. A 127 mm height of packings found to be suitable for maximum purity of the esterified product. Distillate quantity becomes lesser when the packing height increased to 177.8 mm. At this packing's height, vapors from the bottom product at re-boiler faced the hurdle due to low temperature at that region. The vapors cannot reachable to the condenser for collection in distillate flask.

Table 1: Distillation of the esterified product

Distillation Parameters	Re-boiler Temperature (^oC)	100	125	150	175	200
	Feed Inlet Temperature (^oC)	20	30	55	75	100
	Vacuum Pressure Created in Column (bar)	2	1.5	1	0.1	0.1
	Feed Mass Flow (kg/h)	1	2	3	4	5
	Packing Height (mm)	63.5	63.5	127	127	177.8
	Methanol +Water in Top Product (mass) (kg)	0.132	0.258	0.491	0.762	0.615
	Bottom Product mass (kg)	0.9868	1.742	2.509	3.238	4.385
	Methanol and Water in Bottom Product (kg)	0.078	0.142	0.109	0.038	0.385

3.3 Distillation of Esterified Product

The following properties of the esterified product were determined as shown in Table 2. The acid value of distilled product was significantly reduced after purification. Methanol and water content were reduced at an acceptable minimum level at which the esterified product can be converted to biodiesel via transesterification process. Flash point of the esterified product has been reduced after the distillation process. Methanol content in the esterified product prior to distillation plays a key role in lower of the flash point value. For the safety point of handling the esterified product, its flash point should be higher (Ahmad et al., 2014). The higher acid value of the esterified product is the key factor of occurrence of saponification reaction in subsequent transesterification process (Chuah et al., 2015c).

Distilled product saponification value is lower after purification as shown by the corresponding reduction in the acid value. Cold flow properties such as cloud and pour point after distillation were significantly improved because of the lesser content of water and methanol. Impurities were present in the esterified product before distillation such as water and methanol. After distillation, the purified product density was decremented.

Table 2: Comparative esterified product properties before and after distillation process

Parameters	Unit	Before Distillation	After Distillation
Ester content	% (m/m)	29.66	29.66
Density @ 15 ^oC	(kg/m^3)	950	863
Kinematic Viscosity @ 40 ^oC	(mm^2/s)	6.6	4.2
Flash Point	(^oC)	67	145
Water Content	(mg/kg)	900	200
Acid value	(mg KOH/g)	4.2	2.64
Iodine Value	(g I_2/100g)	131.8	120
Saponification Value	(mg KOH/g)	226	201
Methanol Content	%(m/m)	11	0.02
Cloud Point	(^oC)	8	3
Pour Point	(^oC)	0.3	-1.6

4. Conclusions

HC technology successfully reduced the acid value with better relative esterified efficiency for orifice plate 2 with 21 holes of 1 mm diameter at 3 bar of upstream pressure. The relative efficiency of HC technology found to be four folds higher than MS. The esterified product has been purified in the pilot vacuum distillation column to enhance the quality. By referring to distillation parameters, temperature effects, vacuum pressure, feed flow rate and packing height have been studied. The most appropriate values obtained for the esterified product purification are critical to being further utilised for transesterification process. Some important properties of the esterified product after and before distillation have been compared. It has been found that distillation gives the most affirmative results on the esterified product, which helps in getting better quality biodiesel that met criteria of international standards.

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