

INFLUENCE ON PROCESS PARAMETERS IN TRANSESTERIFICATION OF VEGETABLE AND WASTE OIL – A REVIEW

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ABSTRACT

Biodiesel, produced from vegetable oils and animal fats, is one of the most promising solutions to the ever increasing demand of diesel, providing a technology for production of fuel of similar properties to that of conventional petrodiesel but from renewable resources. In European countries biodiesel is primarily manufactured from rape seed oil, in Asia it is mainly produced from palm oil, and in the US the main raw material is soybean oil. As these resources to some extent compete with food production, use of waste oils such as waste cooking and frying oils are more obvious sustainable resource for biodiesel production. In this study over 60 papers on biodiesel production from edible vegetable oils (palm oil, soybean oil, canola oil and sunflower oil) and on biodiesel production from waste frying oil have been reviewed. The reported yields are ranging from around 60% to 100% depending on the conversion method. The different methods used under right conditions generally give high yields; therefore the choice of transesterification method depends very much on availability and local prices for raw materials. As the sustainability should be considered first when producing biofuels, waste oils should probably be chosen over the clean oils and ethanol might be a better choice for the alcohol than methanol. But at the same time, the process should consume a minimum of energy and in reality the least expensive process will be most favorable for industrialization.

Keywords: *Biodiesel, transesterification, waste cooking oil, vegetable oil.*

1. INTRODUCTION

Diesel engines are very common around the world and considering OEM diesel research and long term planning these engines will confine for decades to come. They are used in the automotive and marine industries, power generation, and agriculture. The reliance of these engines on diesel fuel has made countries and communities more dependent on the local and global availability of diesel fuel. Biodiesel, produced from vegetable oils and animal fats, is one of the most promising solutions to the ever increasing demand of diesel. It is providing a fuel of similar or outperforming properties to conventional fossil diesel from renewable resources and has been an important research subject for developing countries. Because plants utilise carbon dioxide from the atmosphere during growth, biodiesel is contributing much less to global warming than conventional fossil based fuels. Biodiesel can be produced from many different types of plants, of which some offers advantages compared to conventional plants, such as *Jatropha* that thrives in tropical climate [1] and *karanja* which is tolerant to salinity and can grow in different types of soil [1]. These crops are giving opportunities for developing countries to contribute to the future energy solutions. As biodiesel and petrodiesel mixtures require additives before use in current diesel engines, biodiesel has several other advantages such as reduction of most exhaust emissions (hydrocarbons and CO), higher flash point, and excellent lubricity [3]. The world production of biodiesel has grown from 1 billion litres in 2001 to approximately billion litres in 2007 9 [4], of which the major part is produced from pure vegetable oils. In Europe biodiesel is primarily extracted from rape seed oil whereas the US the main raw material is soybean oil [5]. In future energy solutions, it is important to consider the constraint of using farmland for energy production. Therefore, use of waste oils such as waste cooking and frying oils could be an important resource for biodiesel production. Proper disposal of used cooking oil is also an important waste management concern. Oil is lighter than water and tends to spread into thin and broad membranes which hinder the oxygenation of water. Furthermore, these oils constitute a health risk to humans if leached into water supplies or used improperly in the food chain. Most of the toxic compounds in the waste cooking oil are oxidation products from fatty acids, especially from polyunsaturated fatty acids. These polar compounds are preferentially partitioned within the crude glycerol phase during the biodiesel production process, with a further concentration during the glycerol purification step. Thus, the use of waste cooking oil as a raw material for biodiesel production instead of its management as a toxic residue will reduce waste treatment costs. In the US, the estimated annual amount of waste oil collected from restaurants and fast food chains is 1.134 million tons [6] and in Europe the collected amount for recycling is approximately 0.7-1.0 million tonnes per year [7]. Traditionally, these oils were used in animal feed products; this practise, however, has now been banned in EU (in 2002) due to the harmful compounds that are produced during the frying of the oils [7]. The oil

consumption in Thailand was monitored in 2002; the overall consumption was 38,000,000 litres, of which 16,500,000 litres of used cooking oils were collected [8]. A study estimated that the average American produces annually 4.1 kilograms of yellow grease (used frying oils from deep fryers) and 5.9 kilograms of trap grease (the trapped portions from drains and sewage systems) [9]. In Japan, the annual production of waste cooking oil is 400.000 to 600.000 tons [10]. In China, waste cooking oil is now collected by environmental protection agency authorized by the local governments in the main cities of China. It is estimated that the waste cooking oil collected in Guangzhou, the third biggest city in China, is more than 20.000 tons per year, suggesting the national production of waste oil can offset a large portion of fossil resources [11]. Despite the technological advancement made in biodiesel production in recent years, the cost of biodiesel is still higher than petroleum based diesel. While tapping on lower cost on raw material biodiesel from waste oil will definitely promote the economical viability of the overall process [12].

Vegetable oils are primarily composed of triacylglycerols – a form of unsaturated lipids comprised of 3 fatty acid molecules attached to one glycerol molecule, and to a lesser extent diacylglycerols and monoacylglycerol. The degree of unsaturation in the fatty acid molecules affects its reactivity, and can result in an increased tendency to undergo oxidative degradation, resulting in decreased lubricity and gum formation in the internal combustion engine [13]. Waste frying and cooking oil may contain high amounts of free fatty acids (FFA), which can cause a problem in base catalysed biodiesel production due to formation of soap when the alkaline catalyst reacts with the FFA's.

2. THE TRANSESTERIFICATION PROCESS

Transesterification is a reaction wherein vegetable oil or fats react with alcohol, in the presence of a catalyst, to form alkyl esters and glycerol. The resulted type of ester depends on the used alcohol and the composition of fatty acids in the vegetable oils. The transesterification reaction causes exchanging of the original organic group R" of an ester with the organic group R' of an alcohol to produce alkyl ester and glycerin. Fig. 1 depicts all the possible reactions that can take place inside the reactor.

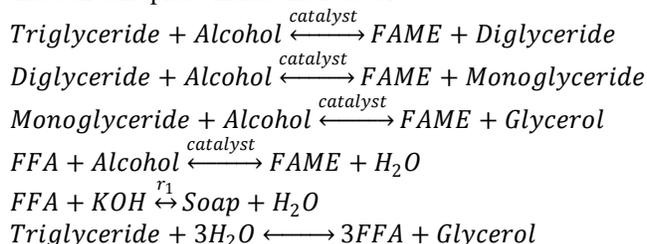


Fig 1. Transesterification process and possible side reactions (esterification of FFA, Saponification of FFA's, and alcoholysis of triglycerides).

The exchange of the organic group can be accelerated by a catalyst. The reaction happens through three consecutive reversible reactions. In the first reaction diglyceride is produced from triglycerides, then monoglyceride is produced from diglyceride in the second reaction, and finally glycerin is produced from the monoglycerides in the third reaction. An esters molecule is produced in all three reactions. Therefore, at the end of the reaction, three molecules of alkyl esters and one molecule of glycerin are obtained. Stoichiometrically, 1 mole of fatty acid is required to react with 3 moles of alcohol to produce 3 moles of the methyl ester and 1 mole of glycerol. However, in general a higher alcohol molar ratio is applied for maximum ester production depending on the oil, type of catalyst, and process parameters [14]. The process temperature is constrained to be below the boiling point of the alcohol used. Reported reaction times for typical biodiesel production ranges from 30 minutes to over 2 hours, with catalyst concentrations that vary between 0.1 and 2 % [15], [16].

2.1 Catalyst

Currently, most commercial biodiesel comes from the transesterification processes using a homogeneous alkaline catalyst, essentially NaOH or KOH as these provides a faster reaction than an acidic catalyst [17]. In homogeneous alkaline catalysed reaction, a low concentration of FFA and water is preferred to avoid side product formation and subsequent low yields. Alternatively, a pretreatment step can be applied where FFAs are converted to esters with alcohol using a strong homogeneous acid catalyst, such as sulphuric acid. It is recommended in the alkaline homogeneous transesterification process that the FFA content of the raw oil is less than 0.5-1 wt% [13]. Water in the oil is considered a precursor for soap formation and should be removed prior to transesterification [18]. The homogeneous acid catalysed process is more tolerant to FFA in the oil, as the acidic catalysts will catalyse both esterification of FFA's and transesterification of the triglycerides. Sulfuric acid, sulfonic acids, and hydrochloric acid are frequently used as acid catalysts.

The heterogeneous reaction has been reported to have even higher tolerance towards FFA's in the oils and simpler separation process compared to the homogeneous method [19]. However, the heterogeneous process has also been found to suffer from mass transfer limitations between liquid and solid phases, and the efficiency of the solid catalyst can be adversely effected by the presence of water in the oils/fat [20], [21]. Basically, there are three types of heterogeneous catalysts being used in transesterification, namely acid, base (alkali), and enzyme [21]. Many different types of heterogeneous catalysts have been reported to be suitable for transesterification of vegetable oil such as metal oxides, metal complexes, active metals loaded on supports, zeolite, resins, membranes, and lipases [21], [22], [23], [24], [25]. In heterogeneous catalysis, water acts as an inhibitor of the catalyst, but affects neither the ester yield nor the glycerol purity [18].

Enzymatic transesterification, where lipases are used as heterogeneous catalyst, have been reported to be less energy intensive than the other methods and offer advantages such as easy glycerol recovery, complete conversion of FFAs to methyl esters, and no need for waste water treatment [20]. However, this process suffers from the high cost of enzymes [26], and often a solvent is needed in order to avoid deactivation of the enzyme by un-dissolved alcohol [27]. Nevertheless, the repeated use of the immobilized enzymes and the high marked price of pure glycerol produced during the enzyme mediated transesterification could make this process competitive [25].

The supercritical alcohol technology is a non-catalytic process and the absence of a catalyst thereby renders process simplicity as far as the separation and purification of the biodiesel. In this process the alcohol is heated and pressurised to react at supercritical conditions, e.g. methanol at 239°C, 8.1 MPa. At supercritical conditions methanol and oil, which are immiscible at room temperature, form a homogeneous solution. This is due to the significant drop in methanol's solubility parameter and dielectric constant, which subsequently makes methanol a nonpolar substance. High yields of biodiesel have been achieved using short reaction times by this method [20], [28] due to the miscibility of the two phases. The drawback of the supercritical method is that a high molar ratio of alcohol to oil is needed: ~40:1 [20], [28], [29], [30].

2.2 Alcohol

Theoretically, three moles of alcohol are required for each mole of triglyceride to produce three moles of fatty acid alkyl ester and one mole of glycerol. But since transesterification is a reversible reaction, excess amounts of alcohol are used to ensure that the oils or fats will be completely converted to esters, and a higher alcohol triglyceride ratio can result in a greater ester conversion in a shorter time. Therefore maintaining a high alcohol to oil ratio is essential. The commonly employed molar ratio for two-step acid transesterification is 6:1 and 9:1 for alkali catalyzed transesterification. However, the optimum molar ratio depends on the raw oil used and its acidic value as well as other process conditions. Although, excess amount of alcohol favours the formation of alkyl esters it hinders glycerol recovery and beyond an optimal ratio it will not increase the yield but are associated with an additional cost for alcohol recovery [31], [17].

Possible alcohols that can be used in the transesterification reaction are methanol, ethanol, propanol, butanol, and amyl alcohol. Among them, methanol and ethanol are most commonly used. Methanol is more preferred due to its relatively low cost adding its physical and chemical advantages. Methanol provides a proper viscosity and boiling point and a high cetane number of the produced biodiesel [17]. Methanol has an ability to react with triglycerides quickly and the alkali catalyst is easily dissolved. As both methanol and methoxide are hazardous materials they should be handled carefully.

Ethanol can be produced from renewable agricultural resources and is non-toxic. It is starting to receive much attention as a substitute to the fossil-derived methanol. However, the formation of an emulsion after transesterification with ethanol makes the separation of esters and glycerol difficult [32]. In the case of methanol, the emulsion easily breaks down to form a lower glycerine layer and an upper methyl ester rich layer compared to the more stable layer formed by ethanol that complicates the separation process [32]. One should be aware, however, that methanol has a lower boiling point of 64.7 °C and the transesterification reaction is often carried out near this temperature.

2.3 Process conditions

For economic viability, transesterification reaction needs to be accomplished with the lowest possible temperature and time. The commonly used temperatures range from as low as room temperature to up to 65 °C. The transesterification reaction has been reported to favor increased temperature up to near the boiling point of methanol. However, increase in temperatures also promotes saponification reaction that leads to lower yield and low purity of biodiesel. Temperatures of around 300-350 °C have been considered to be optimum when using supercritical methanol [20], [26], [28].

Reported reaction times for the typical homogeneous catalysed biodiesel process range from 30 minutes to over two hours. Under heterogeneous catalysis longer reaction times may be needed, while using enzymatic catalysis can have increased reaction time of up to one to two days [33], [34]. In the beginning the reaction progresses slowly, due to the mixing and the dispersion of alcohol molecules into the oil molecules. Once the mixing occurs, the reaction proceeds very fast, while a further increase in the reaction time keeps the yield constant to certain extent. Excess time promote the reaction to proceed backwards, producing more fatty acids which eventually produce soap instead of alkyl ester. Microwave energy can be applied in biodiesel production. Microwaves provide intense localized heating that may be higher than the recorded temperature of the reaction vessel. The microwave process significantly lowers the reaction time needed for transesterification and reaction times and as low as 30 seconds were reported [10].

Mixing is very important in the transesterification reaction as triglycerides are immiscible in the alcohol solution. For homogeneous transesterification, mixing of 400-1000 rpm is usually employed. However, for the heterogeneous catalysis stirring is often milder (500-100 rpm), especially when immobilized catalysts or enzymes are used. Sonochemistry, by means of ultrasound irradiation can be applied in biodiesel production. The ultrasound energy produces chemical and physical effects that arise from the collapse of cavitation bubbles. The collapse of cavitation bubbles disrupts the phase boundary in a two phase liquid system and causes emulsification by ultrasonic jets that impinge one liquid into the other [23].

3. TRANSESTERIFICATION OF PURE VEGETABLE OILS – A REVIEW

The four leading vegetable oils traded on the world market are palm oil, soybean, rapeseed, and sunflower. The world consumption for these oils is 40.8 metric tons of palm, 38.4 metric tons of soybean, 18 metric tons of rapeseed, and 10.1 metric tons of sunflower seed [35]. Generally, vegetable oil is submitted to chemical refining which comprises of the steps of degumming, neutralization, washing, bleaching, and deodorization to obtain a final product acceptable for consumption. Table 1-4 present a summary review of biodiesel production from vegetable oil. Some studies use raw oils and even in-situ extraction but most papers are on transesterification of clean refined vegetable oils (table 1-4).

Table 1: Studies on transesterification of palm oil in production of biodiesel

Method	FFA (%)	Alcohol	Molar alcohol:oil	Catalyst	Catalyst conc. (%)	Temp. (°C)	Time (h)	Agitation (rpm)	Solvent	Yield (%)	Ref.
Homo/A	-	M	40:1	H ₂ SO ₄	5	95	9	-	-	97	[37]
Homo/A	93	M	8.8:1	H ₂ SO ₄	1.83	75	1	300	-	97-99	[38]
Homo/B	-	E	5:1	KOH	1	60	2	-	-	95.8	[15]
Homo/B	-	E	5:1	KOH	1	60	2	-	-	96	[16]
Homo/B	1.7	E	8.5:1	KOH	1.5	MW	0.08	-	-	85	[32]
Hetero/A	-	M	18:1	Alum	7.09	170	12	350	-	92.5	[31]
Hetero/A	-	M	8:1	KSF	3	190	3	190-200	-	79.6	[21]
Hetero/A	5.6	M	20:1	Ar-SBA-15	6	140	4	2000	-	90	[39]
Hetero/B	-	M	30:1	Mg-Al	7	100	6	450	-	86.6	[40]
Hetero/B	-	M	11.43:1	KF/ZnO	5.52	65	9.72	-	-	89.23	[41]
Hetero/B	0.3579	M	15:1	KOH/Al ₂ O ₃	-	60	2	300	-	91.07	[17]
Hetero/B	0.3579	M	15:1	KOH/NaY	-	60	3	300	-	91.07	[17]
Hetero/B	-	M	9:1	CaO	2.8	65	1	Ultras.	-	77.3	[24]
Hetero/B	-	M	9:1	SrO	2.8	65	1	Ultras.	-	95.2	[24]
Hetero/B	-	M	9:1	BaO	2.8	65	1	Ultras.	-	95.2	[24]
Lipase	6	M	6:1	Novoz. 435	-	40	10	190	t-butanol	85	[27]
Lipase	6	M	3:1	Novoz. 435	-	40	20	190	-	91.5	[27]
Lipase	6	M	3:1	Novoz. 435	-	40	24	190	LiCl	92	[27]
Lipase	-	M	7:1	Lipase PS	-	30	72	-	-	100	[42]
SC	0.1	M	-	-	-	250	0.2	-	-	95.17	[36]
SC	-	M	30:1	-	-	360	0.3	-	-	72	[28]
SC	93	M	6:1	-	-	300	0.5	-	-	95	[26]
SC	-	M	40:1	-	-	372	0.267	-	-	81.5	[20]
SC	-	E	30:1	-	-	349	0.483	-	-	79.2	[20]

Table 2. Studies on transesterification of soy bean oil in production of biodiesel.

Method	FFA (%)	Alcohol	Molar alcohol:oil	Catalyst	Catalyst conc. (%)	Temp. (°C)	Time (h)	Agitation (rpm)	Solvent	Yield (%)	Ref.
Homo/B	-	M	9:1	NaOH	0.2	29	0.5	Ultras.	-	100	[43]
Homo/B	-	E, M	12:1	KOH	1	30	1	600	-	97.9	[44]
Hetero/A	-	M	14.9:1	La ⁺ /Zeolite	0.011	60	4	500	-	48.9	[50]
Hetero/B	-	M	6:1	Eu ₂ O ₃ /Al ₂ O ₃	10	70	8	-	-	63.2	[45]
Hetero/B	-	M	12:1	CaO	-	-	2	-	-	99	[46]
Hetero/B	-	M	12:1	CaO	8	65	3	800	-	95	[46]
Hetero/B	-	M	-	MgAl	10	60	24	600	-	97	[47]
Hetero/B	-	M	-	MgAl	10	60	5	Ultras.	-	96	[47]
Hetero/B	-	M	16:1	KI/silica.	5	70	8	-	-	90.09	[48]
Lipase/A	-	M	15:1	H ₂ SO ₄	2.5	40+50	5+12	-	-	99	[25]
SC	-	M	42:1	-	-	350	0.17	300	-	95	[30][51]
SC	-	M	42:1	-	-	300	0.5	-	Hexane	85	[30][51]
SC	-	M	42:1	-	-	300	0.33	-	CO ₂	91.6	[30][51]
SC	-	M	24:1	KOH	0.1	160	0.17	-	-	98	[30][51]

Table 3. Studies on transesterification of rape seed oil in production of biodiesel.

Method	FFA (%)	Alcohol	Molar alcohol:oil	Catalyst	Catalyst conc. (%)	Temp. (°C)	Time (h)	Agitation (rpm)	Solvent	Yield (%)	Ref.
Homo/B	-	M	9:1	NaOH	1.1	60	2	200	Hexane	98.2	[53]
Homo/B	-	M	7:1	NaOH	2	60	0.33	600/Ultras.	-	96	[23]
Hetero/B	-	M	7:1	Mg-Al	10	60	24	600	-	97	[23]
Hetero/B	-	M	7:1	Mg-Al	10	60	5	Ultras.	-	96	[2]
Hetero/B	48.8	M	9:1	D002 resin	18	60	4	-	HCl-EtOH	96	[22]
SC	-	M	42:1	-	-	300	0.25	-	-	~100	[29]

Table 4. Studies on transesterification of sunflower oil in production of biodiesel.

Method	FFA (%)	Alcohol	Molar alcohol:oil	Catalyst	Catalyst conc. (%)	Temp. (°C)	Time (h)	Agitation (rpm)	Solvent	Yield (%)	Ref.
Homo/B	-	M	7:1	NaOH	2	60	0.33	600	-	95	[55]
Homo/B	-	M	7:1	NaOH	2	60	0.33	Ultras.	-	94	[55]
Homo/B	-	E	7:1	NaOH	2	60	4	600	-	88	[55]
Homo/B	-	E	7:1	NaOH	2	60	0.67	Ultras.	-	98	[55]
Homo/B	-	M	6:1	NaOH	1	60	2	600	-	97.1	[54]
Homo/B	-	M	6:1	KOH	1	60	2	600	-	86.7	[54]
Homo/B	-	M	6:1	KOCH ₃	1	60	2	600	-	90	[54]
Homo/B	-	M	6:1	NaOCH ₃	1	60	2	600	-	82.7	[54]
Homo/B	-	M	8:1	KOH	0.5	25	0.33	6000	-	~100	[56]
Hetero/B	-	M	13:1	CaO	1	60	1.5	1000	-	94	[58]
Hetero/B	-	M	15:1	KNO ₃	15	170	8	40	-	87.5	[19]
Hetero/B	-	M	30:1	K ₂ CO ₃ /Al.-O-Si	2	120	0.33	-	-	93	[59]
Hetero/B	-	M	15:1	K ₂ CO ₃ /Al-O-Si	2	120	1.67	-	-	93	[59]
Hetero/B	-	M	6:1	CaO	1	100	2.5	200	-	91	[57]
Hetero/B	-	M	6:1	CaO	1	80	5.5	200	-	91	[57]
Lipase	-	M	3:1	<i>P.fluorescens</i>	-	40	48	200	n-hexane	90	[33]
Lipase	-	M	4.5:1	<i>P.fluorescens</i>	-	40	24	200	-	>90	[33]
Lipase	-	Methyl acetate	3:1	<i>C.antarctica</i>	3	45	48	-	-	99.83	[34]

3.1 Palm oil

Palm oil is produced from *Eliaeis guineensis jacq.* (Oil palm) which is shown in fig. 2. It contains mainly lauric acid (C12:0) and over 80% w/w saturated fatty acids [16]. Palm oil is primarily produced in South-East Asia, with world producers including Malaysia, Indonesia, and Thailand [16], [36], [27]. Palm oil is cheaper than canola, rapeseed or soybean oil [37]. Several studies on transesterification of palm oil have been found in literature, using various methods (Table 1). Typically, crude palm oil contains high concentration of FFAs, and to avoid soap formation, it is removed before biodiesel production (called palm fatty acid distilled) [26]. Some studies used crude palm kernel oil with high concentration of FFA, while others used refined oil.



Fig 2. Pictures of oil crops: A: Oil palm, B: Soybean, C: Rape, D: Sunflower.

In the studies on homogeneous esterification of palm oil, both ethanol and methanol were used as a catalyst. In two studies using methanol, crude palm oil was used as raw material. In the study by Crabbe et al. [37] harsh conditions were applied with 5% sulphuric acid acting as catalyst using alcohol to oil ratio of 40:1 at 95 °C for 9 hours obtaining an ester yield of 97%. In another study, a shorter reaction time (60 min) was applied at lower temperature (75 °C) using 1.83% H₂SO₄ giving 99% yield when run in batch mode and 97% yield when run continuously [38]. Ethanol was used for transesterification of palm kernel oil using potassium hydroxide as catalyst. In one study an acid esterification step (1 wt% H₂SO₄ for 60 min and ethanol:oil 1:6) was applied before transesterification and both acid esterification and alkaline transesterification (1.5 wt% KOH for 5 min and ethanol:oil 1:8.5) was carried out by microwave (70 W) giving ester yield of 85% [32]. Nevertheless, a higher yield (96%) was obtained by the traditional process using 1% KOH for 120 minutes at 60 °C and ethanol to oil ratio of 1:5 [15], [16].

Heterogeneous catalysed transesterification of palm oil has been studied using both acid [31], [21], [39] and alkaline catalysts [40], [41], [17], [24]. In the processes using acidic catalysts, high temperatures were applied 140-170 °C [31], [21], [39]. Yields of more than 90% were achieved using high molar ratios of alcohol to oil [31], [21], [39]. A yield of 92.5% was obtained using KAl(SO₄)₂·12H₂O at high temperature and long reaction time (170 °C for 12 hours) with alcohol to oil ratio of 18:1. The alum catalyst used in this study was reported as an inexpensive, reusable, and readily available catalyst [31]. In the alkaline heterogeneous transesterification of palm oil, lower temperatures of 60-100 °C were used [40], [41], [17], [24]. Yields of more than 90% were achieved using KOH/Al₂O₃ and KOH/NaY at 60 °C for 2-3 hours with alcohol to oil ratio of 15:1. Of these two catalysts, KOH/NaY showed slightly longer reaction time (3 hours) but lower tendency to leach out the potassium [17]. In one study using three different heterogeneous alkaline catalysts (CaO, SrO, and BaO), the ester yields were significantly improved by applying ultra sonic irradiation, compared to using magnetic stirring (800 rpm). The best results were obtained with SrO and BaO; for BaO the yield was improved from 67% to 95% by the ultra sonic irradiation [24]. Ultra sonic mixing produces small cavitation spheres in the reacting medium at high local temperatures, leading to an increased interfacial area and improved mass transfer.

In enzymatic transesterification, lipases are used as a heterogeneous catalyst. In one study Novozym-435 was examined in three different set-ups using t-butanol and LiCl as solvents, compared to solvent free system with three successive additions of methanol [27]. In this study, unrefined palm oil with 6% free fatty acid was used, and it was concluded that Novozym catalyses esterification of FFA as well as transesterification of triglycerides to produce biodiesel. Low oil to methanol ratio was applied and the highest yield was obtained when using LiCl as a solvent at 40 °C for 24 hours (92% BD Yield). The highest enzyme activity was found when using t-butanol as a solvent since deactivation of the enzymes due to insoluble methanol was minimized. In another study, five different lipases were compared and amongst those Lipase PS (*Burkholderia cepacia*) was found to be superior to the others giving the highest biodiesel yields. When Lipase PS was immobilized in κ -carrageenan gel and used for transesterification at 30 °C for 72 hours at oil to methanol ratio of 7:1, 100% triglyceride conversion was achieved [42].

In non-catalytic transesterification, supercritical alcohol (SCA) is applied using high reaction temperature and high methanol to oil ratio [36]. In the study by Joelianingsih et al. [36] superheated methanol (0.1 MPa, 230-260 °C) was continuously added to palm oil at a fixed flow rate of 4 g/min. without stirring and reaction products were removed every 20 minutes. The optimum temperature was found to be 250 °C, giving biodiesel yields of 95% [36]. Another study compared the supercritical process using higher process pressure of 8.1 MPa (30:1 methanol to oil ratio, 239 °C, 20 min) with a homogeneous catalyst (6:1 ratio, 70°C, 1 hour, 0.1% NaOH) and a heterogeneous catalyst (10:1 ratio, 150 °C, 2 hour, 4% Solid montmorillonite KSF). The three setups obtained 72%, 78%, and 79% yield, respectively. The catalytic systems needed reaction times of 1-2 hours, whereas the supercritical process yield of more than 70% was achieved in only 20 minutes [28]. Yujaroen et al. [26] used a non-catalytic system with supercritical methanol at 300 °C for 30 minutes at 6:1 oil to methanol ratio for esterification of palm fatty acid distilled - a byproduct from refining of crude palm oil with free fatty acid content of 93%, aiming at finding an alternative process the traditional esterification with H₂SO₄. FAME yield of 93% was achieved. When using purified palm oil at the same conditions the requirements for methanol were higher 45:1 and only 80 % yield was obtained [41]. Kok Tat Tan et al. [20] used response surface methodology (RSM) analysis to optimize and compare supercritical methanol transesterification with supercritical ethanol transesterification. They found that the supercritical methanol achieved higher yields (81.5%) at lower reaction times compared to that of supercritical ethanol (79.2%). Optimal conditions for methanol were 40:1 methanol to oil ratio at 272 °C for 16 minutes, and for ethanol it was 33:1 methanol to oil ratio at 249 °C for 29 minutes [20].

3.2 Soybean oil

Soybeans (*Glycine soja*, the plant is depicted in Fig. 2) is the world's leading source of oil as well as by-products and protein-rich seed meal. Besides the oil content of about 20%, the high protein content (about 35%) is of special importance as a worldwide protein source. Soybeans represent 56% of the world oilseed production and almost 30% of the world vegetable oil consumption [35]. The world production of soybean oil is 219.9 Metric tons (2007) and the main producers are USA, Brazil, Argentina, China, and India [35]. Crude soybean oil contains about 88% neutral lipids, 10% phospholipids and 2% glycolipids. A summary of the studies on transesterification of soybean oil is listed in Table 2.

In homogeneous transesterification of soybean oil, high yields were obtained using NaOH and KOH as catalysts [43], [44]. The highest yield of close to 100% was obtained in the study with NaOH acting as catalyst (0.2%) using methanol at 9:1 alcohol to oil ratio at 29 °C for 30 minutes. In this study the reaction time was reduced from approximately one hour when using agitation [44], [15], [16] to half an hour using ultrasonic irradiation [43]. In the study using 1% KOH as catalyst at 30 °C for one hour, a mixture of methanol and ethanol (alcohol to oil ratio 12:1) was applied giving high yields of up to 97.9% [44]. When using these mixtures in methanol to ethanol molar ratio of 1:2 or greater enhanced fuel properties such as low temperature properties, oxidative stability, and lubricity was obtained. Other properties such as kinematic viscosity and acid value were within biodiesel standards. However, the higher price of the ethanol compared to methanol has to be considered [44].

Several recent studies on heterogeneous base catalyzed transesterification were found [45], [46], [47], [48], [49]. Georgogianni et al. [47] compared four different basic heterogeneous catalysts. MgAl hydrocalcite (10%), showed the highest activity, giving 97% biodiesel yield at 60 °C for 24 hours. Reaction times were significantly reduced by using ultrasonic irradiation to give similar yields in just 5 hours [47]. High yield of 95% was also obtained from soybean oil in another study using CaO as a solid base catalyst at 65 °C for 3 hours and 12:1 methanol to oil ratio. This study showed that a small amount of water added to the methanol increased the reaction rates compared to anhydrous conditions. The solid CaO catalyst was repeatedly used for 20 cycles without significant reduction in biodiesel yield [46]. Kouzu et al. compared CaO with other solid bases: magnesium oxide, strontium oxide, calcium hydroxide and – carbonate, and found that CaO gave the highest yield of 93% in just one hour when using 12:1 methanol to oil ratio [49]. Heterogeneous acid catalyzed transesterification of soybean oil was studied using zeolite

beta as catalyst. The catalyst was improved by modification with La^{3+} , suggested to give higher quantity of external Brønsted acid sites available for the reaction. But low conversion of triglyceride to FAME was obtained (49%) at 60 °C for 4 hours [50].

Ting et al. [25] studied the enzymatic transesterification of soybean oil combined with subsequent acid catalyzed esterification for improved biodiesel yields [25]. *C. rugosa VII* lipase immobilized on chitosan yielded 88% conversion of the oil after 5 hours at 40 °C. The oil phase was distilled to remove water and used in acid catalyzed esterification (2.5% H_2SO_4 at 50 °C for 12 hours at methanol to oil ratio of 15:1) giving a high biodiesel yield of 99% [25].

Biodiesel from soybean oil in supercritical methanol was examined by Yin et al. [51]. They obtained 95% methyl ester yield in 10 minutes using high methanol to oil ratio of 42:1 at 350 °C. However, they were able to significantly reduce the methanol to oil ratio and process conditions by adding low concentrations of KOH. When using 0.1% of KOH at 24:1 methanol to oil ratio at 160 °C for 10 minutes 98% yield was obtained [51]. This study showed that coupling supercritical conditions with catalysis offers the advantage of using less catalyst at reduced process conditions and costs [51]. The same authors also examined the effect of co-solvents such as Hexane and CO_2 and found that using 2.5% hexane improved the biodiesel yield from 62.2% to 85% at 300 °C for 30 minutes in 42:1 methanol to oil ratio and CO_2 addition improved the yield from 51.4% to 91.6% at 300 °C for 20 minutes in 42:1 methanol to oil ratio [51].

3.3 Rapeseed /Cornola oil

Rape seed oil is produced from rape (*Brassica napus*, *B. campestris*, the plant is depicted in fig. 2) and constitutes about 14% of the world consumption of vegetable oils. The total world consumption is 18 metric tons and world producers include EEC, China, India, Canada, and Japan [35] [52]. Until 15 years ago, rape oil was unsuitable for human nutrition because of its high content in erucic acid (up to about 50% of C22:1 n-9), which was shown to influence negatively the metabolism of several organs. The erucic acid-rich oil was used in Europe as a lamp oil, in the production of soaps and paints, and for cooking and in Canada as a lubricant. New varieties were developed with low erucic acid content (lower than 2%) and are known under the name Canola [52]. Rapeseed oil consists of 98% triglycerides and 1.5% free fatty acids (Yuichiro Warabi et al., 2004). Summary of the conducted studies on transesterification of rapeseed oil are listed in table 3.

Traditional homogeneous alkaline transesterification using NaOH was studied in combination with two-phase solvent extraction of oil from the rapeseeds. Oil was extracted from the ground seeds using hexane as solvent. Transesterification of the oil hexane solution was then carried out with methanol, the hexane acting as a co-solvent to make the methanol and oil form a single phase. Transesterifications were carried out at different process settings and the best biodiesel yield of 98.2% was obtained at 60°C for 120 minutes using 9:1 methanol to oil ratio and 1.1% NaOH [53]. In the study by Georgogianni et al. [23], alkaline homogeneous and heterogeneous transesterification were compared using stirring at 600 rpm in one experiment and with ultrasonic irradiation in another. For the homogeneous process, no effect of the ultrasonication was found on the yield (which in both cases was 96% after 20 minutes when using 2% NaOH at 60°C and 7:1 methanol to oil ratio [23]). In the case of the heterogeneous catalyst, MgAl hydrotalcite showed the highest activity compared to other heterogeneous catalysts (Mg/MCM-41, 10K/ZrO₂ and 20K/ZrO₂) in short process time of 5 hours without significant loss of biodiesel yield under ultrasonic irradiation. The obtained yield was 96% at 60°C and 7:1 methanol to oil ratio for 5 hours [23]. Lui and Wang [22] used a column reactor packed with cation exchange resin for transesterification of rapeseed deodorizer distillate (RODD), a by-product from refining of the rapeseed oil with high free fatty acid content of 48.8%. Different resin catalysts were compared and the amount of packed catalyst examined. The best resin D002 yielded 96% at a dosage of 18% by weight when used at optimal conditions of 60 °C for 4 hours at 9:1 to oil ratio [22].

Supercritical transesterification of rapeseed oil was studied comparing different alcohols at supercritical temperature of 300 °C using high alcohol to oil ratios of 42:1. The highest alkyl ester yield of close to 100% was obtained in 15 minutes with methanol, while ethanol and 1-propanol required 45 minutes. Under similar conditions, supercritical 1-butanol and 1-octanol produced about 85% and 62% alkyl esters, respectively [29]. They also studied the reaction rates of the two involved reactions: transesterification of triglycerides and esterification of fatty acids and concluded that the transesterification of oil was slower than esterification of free fatty acids for all alcohols employed [29].

3.4 Sunflower oil

Sunflowers (*Helianthus annus L.*, the plant is depicted in fig. 2) are a member of the *Compositae* family, and is an important oilseed crop worldwide, yielding approximately 45-50% oil (dehulled seed mass basis). Sunflower oil is widely used for cooking and frying purposes, but is gaining attention as feedstock for biodiesel production.

Worldwide consumption of sunflower oil is 18 metric tons [35]. Rashid et al. [54] report that the crop is gaining interest in Pakistan, where efforts have been made to anchor the production of this crop increasing cultivated areas from 107,717 ha in 2002-03 to 379,204 ha in 2006-07. The current sunflower oil production in Pakistan is 240,000 tons [54]. Sunflower oil is a desirable substrate for transesterification because of the increased stability of its alkylesters when stored, and improved fuel properties. The esters of sunflower oil actually cause less injector tip fouling than diesel fuel and yield higher break thermal efficiencies, as well as lower smoke value [34]. A summary of the studies on transesterification of sunflower oil is listed in table 4.

Several studies on homogeneous alkaline transesterification of sunflower oil were found. Georgianni et al. [55] compared alkaline transesterification with NaOH using either methanol or ethanol with mechanical stirring or ultrasonic irradiation at 60°C and 7:1 alcohol to oil ratio. When using methanol no significant effect of the ultrasonication was observed, both processes yielded 94-95% after 20 minutes when using 2% NaOH. However, for ethanol use of ultrasonication left to higher ester yields of 98% in 40 minutes compared to mechanical stirring where even after 4 hours of reaction time the yield was still only 80% [55]. Rashid et al. compared four different alkaline homogeneous catalysts NaOH, KOH, KOCH₃, and NaOCH₃ using 1 wt% at 60 °C for 2 hours at 6:1 methanol to oil ratio. The highest yield of 97.1% was obtained with NaOH. Furthermore, NaOH was used at different concentrations (0.25, 0.5, 0.75, 1, 1.25, and 1.5) and methanol to oil ratios (6:1, 3:1, 9:1, 12:1, 15:1, and 18:1) the best results were 97% biodiesel yield using 1 wt% NaOH at 6:1 methanol to oil ratio [54]. In the study by Guan et al. the effect of different co-solvents (dimethyl ether, diethyl ether, tert-butyl methyl ether, and tetrahydrofuran) on the homogeneous transesterification with KOH was studied. For all co-solvents, close to 100% conversion of the oil was obtained after 20 minutes at 25 °C when using 1 wt% KOH and 8:1 methanol to oil ratio. Without co-solvents only 78% conversion was obtained at these conditions. The optimum co-solvent addition was found to be the minimum co-solvent to methanol ratio required for the complete dissolution of methanol and oil. The study concludes that DME could be an interesting co-solvent for alkaline transesterification, since it is more easily recovered from the products than the other co-solvents used in this study [56].

Heterogeneous alkaline transesterification of sunflower oil has been studied by several authors using catalysts such as CaO, K₂CO₃, KNO₃. Calcium oxide was studied at constant catalyst loading of 1% and methanol to oil ratio of 6:1 at varying temperature (60-120 °C), pressure (1-15 bars) and reaction time (1.5-5.5 hours). The maximum FAME yield of 91% was achieved both at 80 °C for 5.5 hours and at 100 °C for 2.5 hours [57]. Another study used the same catalyst at higher methanol to oil ratio (13:1) and obtained 94% yield at 60 °C for 90 minutes [58]. This study also concludes that CaO is rapidly hydrated and carbonated by contact with room air, whereas the negative effect of water on the catalyst is less important, and that re-activation by outgassing above 700°C can revert the CO₂ poisoning [58]. Kotwal et al. created a heterogeneous catalyst by loading 5 % KNO₃ on fly ash – one of the inorganic residues that arise from coal combustion processes. Being an environmental pollutant, which is constant generated in huge quantities, proper utilization with emphasis on finding new applications could be of great interest. In this study 87.5% oil conversion was achieved at 15% wt enzyme loading when using 15:1 methanol to oil ratio at 170 °C for 8 hours [19]. Lukić et al. synthesized a K₂CO₃ catalyst on alumina/silica support using sol-gel method followed by drying at elevated temperatures to obtain xerogel. This heterogeneous catalyst was used in transesterification of sunflower oil, and optimum temperature as well as methanol to oil ratio was studied. Optimal biodiesel yield of 93% was achieved in 20 minutes when using 30:1 methanol to oil ratio and in 100 minutes when using 15:1 methanol to oil ratio at 2% catalyst loading and 120°C [59].

In the study by Soumanou and Bornscheuer [33], several microbial lipases were tested for transesterification of sunflower oil and the best conversion was achieved with lipase from *Pseudomonas fluorescens*. Approximately 90% yield was achieved using this lipase at low methanol to oil ratio of 3:1 when n-hexane was used as solvent (at 40 °C for 50 hours) [33]. The same study found that more than 90% yield could be obtained in 24 hours in a solvent free system using *Pseudomonas fluorescens* lipase at slightly higher methanol to oil ratio of 1:4.5 [33]. This result could only be achieved with the *Pseudomonas fluorescens* lipase, where as lipase from *R. miehei* and *T. languginosa* gave less than 50% biodiesel yield at these conditions. This could be due to the resistance to toxic solvents, such as methanol, developed by some strains of *Pseudomonas* [33]. Another study optimized transesterification of sunflower oil using lipase from *Candida Antarctica* (Novozymes 435) and found that optimal conditions were 45 °C, 3% enzyme, and 3:1 methanol to oil ratio. At these conditions, approximately 99% yield was obtained in 50 hours [34]. This study also tested the use of acyl acceptors other than methanol in order to improve the stability and reuseability of the immobilized lipase. By using methyl acetat, instead of methanol, the biodiesel yield after the 5th reaction cycle was still 93.6% compared to 0% for methanol, 11% for 2-propanol, and 12% for n-butanol [34].

4. USED COOKING AND FRYING OILS IN BIODIESEL PRODUCTION – A REVIEW

Several studies on transesterification of waste cooking oils have been published. Different methods are chosen based on the properties of the waste oil. The FFA content of the waste oil varies depending on cooking, collection and storage conditions. Oils with relatively low FFA content (below 15%) are characterised as yellow grease, and those with high levels (above 15%) are characterised as brown grease [60]. The price associated with the waste cooking oils is 2-3 times less expensive than virgin vegetable oils. Consequently, the total production cost of biodiesel can be significantly reduced [10]. A summary of the conducted studies on transesterification of waste oils is listed in Table 5.

Several papers used the traditional homogeneous alkaline transesterification process on waste oils with low FFA content. In the study by Lertsathapornsuk et al. [10], waste frying palm oil was used for biodiesel production by alkaline homogeneous transesterification with ethanol and sodium hydroxide as catalyst. The process was carried out continuously by microwave. The catalyst was added in excess (3%), in order to neutralize the free fatty acids in the oil (4.5%). The conversion of the triglycerides were 82% when using 9:1 molar ratio of ethanol to oil and 97% when using 12:1 molar ratio with a equivalent residence time inside the microwave oven of 30 seconds [10]. It is argued in this study that the efficiency of the microwave in alkaline transesterification is due to direct adsorption of the radiation by the OH group of the reactant causing the local temperature around the OH group to be much higher than its environment and exceed the activation energy for transesterification [10]. In another study, potassium hydroxide was used as a catalyst for transesterification of waste frying oils collected from restaurants and shops in Ho Chi Minh City [61]. The effect of methanol to oil ratio, catalyst concentration, and reaction temperature was examined in a traditional process. Conversion of 90% was achieved at methanol to oil ratio of 8:1 at 30 °C for 2 hours when using 0.75% KOH. At higher catalyst concentration (1-1.5%) lower conversion was achieved. This could be explained by the formation of soap which hinders the separation of methyl ester phase during the washing step [61]. Taking this into consideration, the optimal catalyst concentration depends on the type of oil and the free fatty acid content of the oil. In the study by Bautista et al. [7], the potassium hydroxide and methanol transesterification of waste frying oil was optimized using response surface methodology. At fixed methanol to oil ratio of 6:1 and reaction time of 1 hour the optimal reaction conditions for waste oil containing 1.88% free fatty acids were found to be 30 °C and a minimum catalyst concentration of 1.3 wt% [7]. Alcantara et al. [62] used sodium methoxide produced from sodium metal and anhydrous methanol as catalyst for transesterification of a mixture of used olive oil and sun flower oil as well as fresh soy bean oil and tallow. High conversion were obtained (~100%) of triglycerides in all three raw materials after approximately 30 minutes at 60 °C, 1% catalyst, and 7.5:1 methanol to oil ratio [62]. In their study, triglycerides were also subjected to amidation reactions with methanol and diethylamine to produce an amide biodiesel - a fuel with enhanced ignition properties when mixed with 5% petro diesel [62].

Wang et al. described a method for waste oils with high free fatty acid content where the alkaline homogenous transesterification was combined with heterogeneous acid esterification in a two step process. This technique was applied to waste cooking oil provided by a company in China who collects oils from restaurants by the local Chinese authority. At the first step, ferric sulphate was used for esterification of free fatty acids with methanol. The ferric sulphate is insoluble in the oil and is recovered from the liquid after methanol recovery and reused. In the second step, potassium hydroxide was added to catalyse the transesterification reaction with methanol. Using this method, 97.22% conversion of free fatty acids in the oil was obtained in the first step after 4 hours using 2% catalyst at 95 °C and 10:1 methanol to oil ratio [11], [63]. However, the study does not report the overall yield after both steps. The study also showed the result of the conversion of waste oil to biodiesel by homogeneous acid esterification and transesterification and obtained more than 90% yield when using 2.5% H₂SO₄ at 95 °C for 10 hours and 20:1 oil to methanol ratio [11], [63]. Liu et al. also used a two step process in combination with radio frequency (RF) heating. Compared to microwave heating, RF heating systems are simpler to configure, have higher conversion efficiency of electricity to electromagnetic power, and is reported to have a deeper penetration into a wider array of materials, hence increasing feasibility in industrial applications [60]. The two step process was applied to waste cooking oil collected through a “Waste to Fuel” campaign run by the City of Gadsden in Alabama, USA. In the first stage the acid number of the oil was reduced from 68.2 (34.1% FFA) to 1.64 mg KOH/g using 3% H₂SO₄ and 0.8:1 methanol to oil weight ratio at 8 minutes RF heating. In the second step the esterified product reacted with 0.91% NaOH and 14.2:1 methanol to oil molar ratio under RF heating for 5 minutes. The overall conversion rate was 98.8% [60]. Patil et al. compared the two step process using ferric sulphate and potassium hydroxide to the supercritical one step process [64]. The maximum biodiesel yield obtained using the two step process at 100 °C was 96% after a total reaction time of 2 hours and 9:1 methanol to oil ratio, compared to around 80% biodiesel yield in the supercritical process at 300 °C after 20 minutes but at high methanol to oil ratio of 40:1 [64]. Enzymatic transesterification of waste frying oil was studied by Maceiras et al. [65]. The waste frying oil was collected from restaurants, filtered to remove the suspended matter, and blended into homogeneous oil. Novozyme 435 lipase was used for

transesterification with methanol. The effect of methanol to oil ratio, dosage of enzyme and reaction time was studied at 50 °C with stirring at 150 rpm. The optimal yield of 89.1% was achieved with 25:1 methanol to oil ratio using 10% enzyme based on oil, and 4 hours of reaction time [65]. Two studies were found on heterogeneous biodiesel production from waste oils using solid acidic catalysts [66], [67]. The study by Jacobsen et al. [66] tested 11 different solid acid catalysts for transesterification of waste cooking oil from Saskatoon processing Co., in Canada containing 15 wt% free fatty acids. The best yield was obtained with ZnS/Si and the reaction with this catalyst was optimised. The highest ester yield of 98% was obtained at 18:1 methanol to oil ratio and 3% catalyst at 200 °C for 10 hours. The ZnS/Si catalyst was reused several times without loss in activity [66]. Another study used $(\text{SO}_4)^{2-}/\text{TiO}_2\text{-SiO}_2$ for biodiesel production from waste oil feedstock. In this study a mixture of refined cottonseed oil and oleic acid was used to simulate the waste oil. The optimal reaction conditions were studied and the highest yield was obtained at 200 °C, when using 9:1 methanol to oil ratio and 3% of the solid catalyst. For oil with 80% FFA the yield after 4 hours at optimal conditions was approximately 95%, whereas it was approximately 85% for oils with 30% FFA [67]. The greater solubility of FFAs than cottonseed oil in methanol is one of the reasons for the higher yield in the oil with high FFA concentration [67]. The study also proposed a process for continuous biodiesel production from waste oil with high FFA using the $(\text{SO}_4)^{2-}/\text{TiO}_2\text{-SiO}_2$ catalyst. A 10,000 tonnes/year pilot plant to demonstrate this process was built in China [67].

5. ECONOMICS OF BIODIESEL PRODUCTION

When comparing different processes, process economics is an important factor. Some studies were found that evaluate the economics of different systems using modelling tools such as ASPEN and Super Pro Designer. However, it is important to remember that such studies are highly dependent on the process parameters and settings used for each model.

In the study by Zhang et al. [68] the economics of four continuous biodiesel processes (including alkaline and acid catalyzed process from both virgin vegetable oil and waste oil) were compared. The four processes compared were: 1) Alkaline (NaOH) catalyzed biodiesel BD production from virgin oil, 2) Alkaline catalyzed biodiesel BD production from waste oil incl. a pretreatment step where FFA's were esterified using sulphuric acid as catalyst, 3) Acid (H_2SO_4) catalyzed BD production from waste oil using high molar ratio of methanol, 4) Acid catalyzed BD production from waste oil using hexane as extraction solvent. The study found that the break even biodiesel price for the processes was \$857 /tones for process 1, \$884 /tones for process 2, \$2,644 /tones for process 3, and \$644 /tones for process 4. Hence, even though the alkaline process using virgin oil had the lowest fixed capital cost the acid catalyzed process using waste oil was more economical feasible giving higher return and the lowest break even biodiesel price. The study also concluded that plant capacity and prices of feedstock were the most important factors affecting the economics of biodiesel [68]. Another study also compared three different processes: 1) Alkaline catalyzed biodiesel BD production from oil with 5 % FFA incl. a pretreatment step where FFA's were esterified using sulphuric acid as catalyst, 2) Acid (H_2SO_4) catalyzed BD production from oil with 5% FFA, and 3) Heterogeneous catalyzed BD production using solid resin as catalyst. This study concluded that the heterogeneous process has the lowest capital investment costs due to less equipment needed in this process. The operating cost is similar for all processes and this study also concludes that the feedstock costs is a major contributor toward operating costs (around 76-80%) – emphasizing the need to use cheap waste oil in order to make biodiesel competitive to petrochemical based diesel. The unitary costs of producing biodiesel from the three processes were found to be: \$508 /tones for process 1, \$515 /tones for process 2, and \$522 /tones for process 3 [69]. However, the selling price of the glycerol from the heterogeneous process is much higher than from the homogeneous processes due to a higher purity, making the heterogeneous process the most profitable of the three [69]. Van Kastern et al. evaluated continuous supercritical biodiesel process from waste frying oil with methanol using three different plant sizes. They found that the breakeven price of the biodiesel produced by this method was 0.17 \$/l for a 120,000 tons/year plant, 0.24 \$/l for a 80,000 tons/year plant, and 0.52 \$/l for a 8,000 tons/year plant or 0.18 \$/l for a 120,000 tons/year plant, 0.25 \$/l for a 80,000 tons/year plant, and 0.54 \$/l for a 8,000 tons/year plant if bio-ethanol was used instead of methanol [70]. From this study, it seems the supercritical method produces cheaper biodiesel compared to the homogeneous catalyzed processes. The study also identifies the key factors in biodiesel economics to be price of raw materials, plant capacity, glycerol price, and capital costs. Another study also looked at economics in relation to plant size and concluded that plants with capacity less than 15,000tons/year should be avoided as the plant cannot be profitable and preferable plant size should be greater than 50,000tons/year [71].

6. CONCLUSION

Biodiesel has great potential to offset large portion of petroleum based diesel with a sustainable and biodegradable fuel. In this study, several recent papers on biodiesel production from edible vegetable oils (palm oil, soybean oil, canola oil and sunflower oil) and some papers on biodiesel production from waste frying oil have been reviewed and

summarised in Tables 1 to 5. The reported yields are ranging from 52% up to 100%. Several different methods exist from which biodiesel can be produced with high yields; including: homogeneous and heterogeneous, acidic and alkaline catalytic transesterification, one step and two step processes, lipase (enzymatic) transesterification, and supercritical processes at which alcohol is applied at supercritical conditions without the use of catalyst. Some studies also combine methods, e.g. use of catalyst at supercritical conditions to reduce the amount of catalyst and reduced process severity and possible process costs [30], [51]. Another study combined the enzymatic transesterification with the heterogeneous acid catalyst aiming at higher yield and process costs reduction [25]. Several different process configurations were reported. In most studies transesterification is carried out in stirred tank batch reactors but the use of microwave or radio frequency heating is also reported, giving the advantage of shorter reaction times. Continuous transesterification is suggested to be the preferred method for industrial biodiesel production [67]. The method of transesterification often depends on the characteristics of the oil. For oils with high FFA concentration, an acidic catalyst is often employed for simultaneous esterification of the FFA and transesterification of the triglycerides. Alternatively, a two step process can be applied where the acid catalyst is used in the first step for FFA esterification and the faster alkaline catalyst is then used in the second step for transesterification of the triglycerides. In general, the acid process is slower than the alkaline process and requires an excess of alcohol to proceed with the reaction. For the waste oils, potassium hydroxide has been reported to be a better homogeneous catalyst than sodium hydroxide. For the clean oils, high yields are obtained in short reaction times with the traditional homogeneous alkaline transesterification with NaOH using around 6:1 molar ratio of alcohol to oil, but there are some environmental disadvantages to this process associated with neutralisation and separation of the product. The process pertain the consumption of large amounts of water and the disposal of highly basic streams. Other studies show that the heterogeneous catalyst CaO and the homogeneous catalyst NaOH are comparable with the additional advantages offered by the solid catalyst in easy product separation [46], [43]. Methanol was the preferred alcohol in most studies as the reaction is generally faster with alcohols of low molecular weight, and methanol is less costly than ethanol. However, ethanol can be derived from renewable resources and contribute to the sustainability of the produced biodiesel. In the processes where lipases are used and also in the supercritical transesterification where no catalyst is applied, a co-solvent is often used in order to overcome the low solubility of the alcohol in the triglyceride phase. Co-solvent in supercritical process allows the process to proceed under milder conditions [30], [51].

In conclusion, since all the methods used under the right conditions can give very high yields of biodiesel, the method to choose for transesterification depends very much on availability and raw material costs. In general, the sustainability should be considered when producing biofuels, hence waste oils should probably be chosen over the clean oils and ethanol might be a better choice for the alcohol than methanol. At the same time, the process should consume a minimum of energy and in reality the cheaper process would most likely be chosen for industrialization.

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