

Review

Supercritical fluids technology for clean biofuel production

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Abstract

Biofuels are liquid or gaseous fuels that are predominantly produced from biomass for transport sector applications. As biofuels are renewable, sustainable, carbon neutral and environmentally benign, they have been proposed as promising alternative fuels for gasoline and diesel engines. This paper reviews state-of-the-art application of the supercritical fluid (SCF) technique in biofuels production that includes biodiesel from vegetable oils via the transesterification process, bio-hydrogen from the gasification and bio-oil from the liquefaction of biomass, with biodiesel production as the main focus. The global biofuel situation and biofuel economics are also reviewed. The SCF has been shown to be a promising technique for future large-scale biofuel production, especially for biodiesel production from waste oil and fat. Compared with conventional biofuel production methods, the SCF technology possesses a number of advantages that includes fast kinetics, high fuel production rate, ease of continuous operation and elimination of the necessity of catalysts. The harsh operation environment, i.e. the high temperature and high pressure, and its request on the materials and associated cost are the main concerns for its wide application.

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1. Introduction

Concerns about global climate change due to the emission of greenhouse gases, and the projected decline in world oil production has placed energy as the single most important problem facing humanity in the next 50 years [1]. Securing clean, affordable energy for the long term becomes one of the biggest challenges in modern societies. Increasing use of energy generated from renewable resources including biomass, wind energy, hydroelectric power and solar energy will become viable, where geographical and climatic prerequisites are favorable. Such regions, however, seldom coincide with areas of high energy consumption, i.e. industrial and city regions with

a high population density. Various sources including hydrogen, biofuels and batteries have been proposed as secondary energy carriers for the future transport sector.

To become replacement fuels for the future transport sector, the candidates would have to meet a number of criteria that include (1) abundance with enough resources that could replace petroleum-based fuels in the long term; (2) zero or low carbon emission with minimum detrimental effect to the environment; (3) applicable to most running vehicles based on existing infrastructures; and (4) economically viable. Hydrogen fuel is difficult to become a reality in the short term as today's production is dependent on crude oils or natural gas as raw material, or electricity that are from fossil fuels, together with other significant technology and economic challenges in hydrogen storage, transportation and utilization. Electric and hybrid vehicles are proposed as more viable alternatives to hydrogen vehi-

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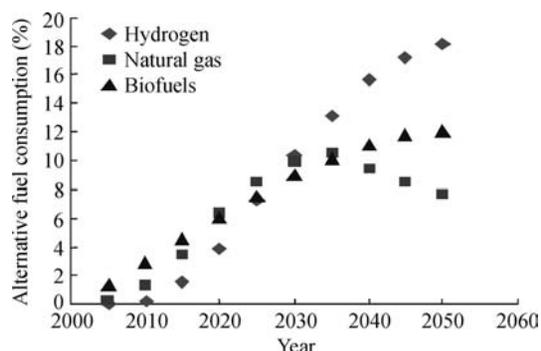


Fig. 1. Prediction of shares in the automobile market for three alternative fuels [7].

cles for transportation, particularly in the short term [2,3]; however they suffer another serious problem: limited resource of heavy metals needed for batteries. Biofuels are liquid or gaseous fuels for the transport sector that are predominantly produced from biomass. Biomass has been recognized as a major world renewable energy source to supplement declining fossil fuel resources [4] and currently supply $\sim 10\%$ of our global energy needs with expected fast growth in the near future, i.e. it would account for as much as 50% of the US's total energy consumption by 2050 [5]. Biofuels can be produced from a variety of bio-feedstocks, they are renewable, sustainable, biodegradable, carbon neutral for the whole life cycle and environmentally friendly so as to encourage green fields and the agriculture industry, as well as applicable to running vehicles with or without slight modifications. Various bio-origin fuels including bio-ethanol, biodiesel and bio-hydrogen appear to be attractive options for the future transport sector.

The decline of fossil fuel resources and the increasing price of petroleum products have led to a major interest in expanding the use of biofuels. This has been reflected by the US's commitment of threefold increase in bioenergy in 10 years time, and the EU's new biofuel targets of reaching a minimum share of $\sim 5.75\%$ of the transport fuel market by the end of 2010 [6]. The shares of alternative fuels, biofuels, hydrogen and natural gas compared to the total automotive fuel consumption in the world are shown in Fig. 1 as a futuristic view [7]. The production of biofuels is expected to rise steadily in the next few decades.

Conventionally, biofuel production is based on two routes: either thermochemical conversion or biochemical conversion, as illustrated in Fig. 2. The thermochemical conversion route can be applied to wood, straw and refuse through the gasification, liquefaction and pyrolysis processes to produce syn-gas, syn-oil and biochemicals. Biochemical conversion predominantly refers to bio-ethanol and biodiesel production through acid and enzyme hydrolysis and/or fermentation from different sets of feedstocks that include wood, wheat and sugar beet. In terms of absolute fuel costs, thermochemical conversion offers low-cost products with some mature technologies. Biochemical

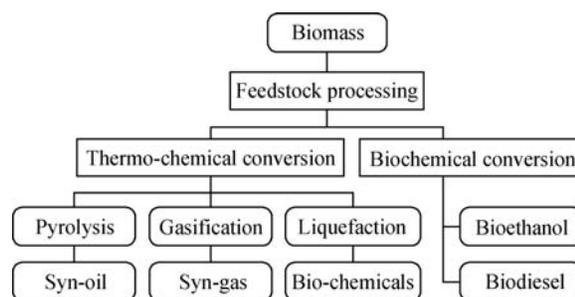


Fig. 2. Conventional biomass conversion routes [8].

routes are more expensive. With strong competition from the global fuel market, there is a growing trend towards employing modern technologies for efficient biomass conversion. The supercritical fluids (SCFs) technique is one of the most promising ones.

2. Supercritical fluids technique

In general, when a mixture of liquid and gas at equilibrium is heated, thermal expansion causes the liquid to become less dense. At the same time, the gas becomes denser as pressure increases. At the critical point, the densities of the two phases become identical and the distinction between them disappears. A supercritical status is defined as the fluids' temperature and pressure above its critical temperature, T_c , and critical pressure, P_c . In the gas–liquid transition regime, the SCF presents a combination of properties of gases and liquids, which makes them very suitable for the development of new processes that cannot be carried out with conventional liquid or gaseous fluids. The critical parameters of some common fluids are illustrated in Table 1.

Due to the creation of a homogeneous reaction environment, supercritical fluids possess a number of unique advantages including increased species mixing, heat and mass transfer, fast reaction typically at a few minutes level, are environmentally benign, and have good scalability, as well as being simple and easy for continuous production. The unique properties at supercritical conditions, i.e. strong dependence of the solubility of a material in a supercritical fluid to its density and good contact between oxidants and reactants, make SCFs ideal for separation and extraction of useful products and for oxidation of organic materials. However, these also have some limitations related to the harsh operation environment and their effect on the materials. Corrosion and salt deposition are the two main challenges for most of the industrial applications, especially for supercritical water (SCW) [10–12]. SCW is favorable for corrosion due to the presence of high pH values, high concentrations of dissolved oxygen, ionic inorganic species and high temperature–pressure variations. Metal oxides can be formed due to the reduced salt solubility, which could form stable solid particles that cause equipment fouling, plugging and erosion. A number of

Table 1
Critical property of various solvents [9].

Solvent	Molecular weight (g/mol)	Critical temperature (K)	Critical pressure (MPa)	Density (kg/l)
Carbon dioxide	44.01	304.1	7.38	469
Water	18.02	647.3	22.12	348
Methane	16.04	190.4	4.60	162
Ethane	30.07	305.3	4.87	203
Propane	44.09	369.8	4.25	217
Methanol	32.04	512.6	8.09	272
Ethanol	46.07	513.9	6.14	276
Acetone	58.08	508.1	4.70	278

plants could not meet their designed performance and some have been closed for these reasons [13]. Besides these, the high energy intensity to reach supercritical status is another big problem for the SCF technology, which could be solved with better heat recycling and improved system design.

Despite these limitations, the SCF technique has been proved to be an environmentally benign medium for a number of chemical and related processes in the last few decades. Many new processes and products including the fractionation of products, dyeing of fibres, treatment of contaminated solids, production of powders in micro/nanometer sizes and novel reactions [14,15] have also been developed using the unique physical and chemical properties of supercritical fluids. For the energy industry, supercritical fluids techniques have been used for coal-fired power plants [16], direct liquefaction or indirect liquefaction through gasification process for manufacturing synthesized gas, synthesized oil and chemical products, as well as advanced nuclear systems. For a instance, supercritical water reactors (SCWRs), have a high thermal efficiency of ~45% in comparison with current light water reactors which have a thermal efficiency of ~33% [17]. More recently, there has been an emerging application of supercritical fluids techniques for clean and high throughput biofuel production. Compared with conventional thermochemical and biochemical methods, the SCF technology possesses a number of advantages such as a high fuel conversion rate, quick reaction, clean production, easy and continuous operation, and elimination of the necessity of catalysts. This paper will review state-of-the-art biofuel production using the SCF technique, with the main focus

on biodiesel production through the transesterification process. Bio-hydrogen production through the gasification process and bio-oil production from the liquefaction process of biomass will also be reviewed shortly.

3. SCFs for biodiesel production

3.1. Biodiesel production

Vegetable oil has been widely used for a long time. Even the first diesel engine, named by the German scientist, Rudolph Diesel, was successfully run on peanut oil ~100 years ago. The thermo-physical properties of vegetable oil, mostly viscosity and volatility, however, limit its direct application on diesel engines. A general list of properties of vegetable oils from different sources is shown in Table 2. The viscosity value for most vegetable oils is at a range of 35–60 cSt, which is much higher than that of standard diesel fuels (~4 cSt). This high viscosity can result in problems in pumping and fuel spray processes such as the atomization and penetration effect. The low volatility of vegetable oils can result in a high flash point, which will produce a number of problems including injector choking, piston ring sticking, high carbon deposition, and lubrication oil dilution and oil degradation [19]. The reactivity of unsaturated hydrocarbon chains can also bring other problems. The combination of all these factors makes the direct application of vegetable oil unfeasible.

There has been, however, a renewed interest in vegetable oil for the transport sector recently due to the increasing price of crude oil and environmental concerns. It could, in the long run, substitute some fraction of petroleum dis-

Table 2
Properties of the vegetable oils [18].

Vegetable oil	Kinematics viscosity (mm ² /s)	Cetane number	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (kg/l)	Lower heating value (MJ/kg)
Peanut	4.9	54	5	–	176	0.883	33.6
Soya bean	4.5	45	1	–7	178	0.885	33.5
Babassu	3.6	63	4	–	127	0.875	31.8
Palm	5.7	62	13	–	164	0.880	33.5
Sunflower	4.6	49	1	–	183	0.860	33.5
Tallow	–	–	12	9	96	–	–
Diesel	3.06	50	–	–16	76	0.855	43.8
20% biodiesel blend	3.2	51	–	–16	128	0.859	43.2

tillates. However, economically it is not a competitive fuel at the moment due to the lack of practical on-farm processing technology and relatively high associated cost. For meeting environmental and energy security concerns, acceptable alternative fuels for the transport sector have to demonstrate that they do not sacrifice the engines' operating performance. Vegetable oils have to be modified to bring their combustion-related properties closer to their petroleum-derived counterparts. The fuel modification for vegetable oils is mainly aimed at reducing their viscosity and increasing their volatility. Dilution, micro-emulsion, pyrolysis (thermal cracking) and transesterification to biodiesel have been frequently used. Among all these techniques, the most successful one is to convert vegetable oils to biodiesel through the transesterification process [20].

Biodiesel is the methyl or ethyl ester of fatty acids made from virgin or used vegetable oils (both edible and non-edible) and animal fat. Biodiesel has combustion-related properties similar to those of petroleum diesel; it also operates in compression ignition (diesel) engines and requires very little or no engine modifications. Biodiesel can be blended in any proportion with petroleum diesel to create a biodiesel blend or can be used in its pure form. It can be stored just like petroleum-derived diesel and hence does not require a separate infrastructure. The use of biodiesel in conventional diesel engines can result in substantial reduction in emission of unburned hydrocarbons, carbon monoxide and particulate matters.

In chemical terms, transesterification is the process of exchanging the alkoxy group of an ester compound by another alcohol. The reactions are often catalyzed by an acid or a base. Transesterification is crucial for producing biodiesel from biolipids. The transesterification process is the reaction of a triglyceride (fat/oil) with a bioalcohol to form esters and glycerol [19,21,22]. The transesterification reaction can be initiated with or without a catalyst by using primary or secondary monohydric aliphatic alcohols having 1–8 carbon atoms, as shown below,

Triglycerides + Monohydric alcohol

→ Glycerin + Mono-alkyl

and a typical transesterification process is schematically shown in Fig. 3.

For biodiesel production, the transesterification can be conducted in either the presence or absence of a catalyst. The usual catalysts used are alkalis (NaOH, KOH), acids (sulfuric acid, HCl) and enzymes (lipases). The kinetics of acid-catalyzed and alkali-catalyzed reactions has been well

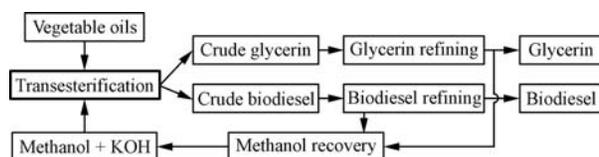


Fig. 3. Basic scheme for biodiesel production via transesterification.

studied and these processes have been commercialized [23], and some reviews on biodiesel production are also available [18]. The typical catalytic transesterification process includes the transesterification reaction, recovery of un-reacted reactants, purification of the esters, separation of glycerol and the separation of the catalyst from the reactants and products, as shown in Fig. 3. Due to the need for vigorous stirring to mix the oil and alcohol and separate the catalysts after the reaction, the catalytic processes have a high production cost and are energy intensive [24,25].

The supercritical fluids technique can be used to synthesize biodiesel through the transesterification of vegetable oils without using any catalysts. Compared to the conventional catalytic processes, the SCF technique possesses a number of notable advantages such as easy separation, fast reaction and being environmentally friendly. This is primarily because alcohols and oil can co-exist in a single phase under supercritical conditions. The increased solubility of organic matters and the homogeneous environment make the transesterification process favorable. Compared with the catalytic transesterification process, relatively fewer investigations have been explored through the supercritical fluids route. The research on the topic was pioneered in Japan [18,26–31], and recently it has enjoyed a sustained strong development in Europe [8,21,32–34], China [35–37] and India [24,38]. Most of these studies were conducted under laboratory conditions, and there is still a lack of consensus on the mechanisms of the reaction. Most of the transesterification methods via the SCF techniques are based on the batch production method [21,24,29,35]; very few are based on the continuous production of biodiesel based on a flow loop [37], whose development is still at the beginning.

3.2. Biodiesel production from SCF transesterification

A number of parameters can affect the methyl ester yield during the transesterification reaction such as the reaction temperature and pressure, alcoholic types, molar ratio of alcohol to vegetable oil, residence time, water and free fatty acid content, solvents and catalysts, and operation modes. Examples of the influence of these parameters on the biodiesel production are reviewed below.

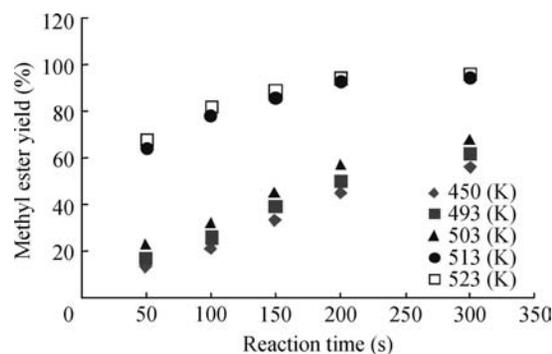


Fig. 4. Biodiesel conversion from hazelnut kernel oil [32].

3.2.1. Temperature and residence time effect

It was observed that an increase in the reaction temperature, especially supercritical temperatures, had a favorable influence on the ester conversion. Fig. 4 shows a typical example of the relationship between the biodiesel conversion and the reaction temperature for hazelnut kernel oil at a molar ratio of vegetable oil to methyl alcohol of 1:41 [32]. Table 1 shows that the critical temperature of methanol is 512.6 K, there is a big jump in the conversion rate as the temperature increases from sub-supercritical conditions (503 K) to the supercritical temperature. Nearly 100% conversion is achieved in about 6 min. This is a significant achievement compared with the conventional catalytic transesterification processes, which generally take a few hours to reach equilibrium and are difficult to achieve a complete conversion.

3.2.2. Alcohol effect

Vegetable oil can react with a number of alcohols. Fig. 5 illustrates the role of different supercritical alcohols in the fatty acid alkyl ester conversion from triglycerides [28]. The experimental results illustrated that alcohols with shorter alkyl chains gave better conversions under the same reaction time. Nearly 100% yield of alkyl esters was obtained within 15 min treatment with methanol, while it took ~45 min by ethanol and 1-propanol methods. Under a similar condition, supercritical 1-butanol and 1-octanol produced about 85% and 62% of alkyl esters, respectively, and the reaction reached a flat conversion rate of ~60% after 20 min for 1-octanol. As a consequence, the supercritical methanol method has been widely investigated for biodiesel production. Note that there is a big difference in the reaction time to reach the equilibrium status for the methanol reaction between different research groups (Figs. 4 and 5). This is common for all affecting parameters, although agreed qualitatively in general, quantitative results differ significantly among different research groups, which requires further extensive investigations.

3.2.3. Molar ratio effect

The stoichiometric ratio for the transesterification reaction requires only 3 mole of alcohol and 1 mole of triglyceride to yield 3 mole of fatty acid ester and 1 mole of

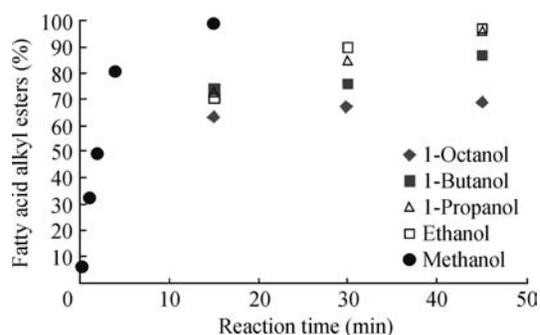


Fig. 5. Alcohol effect on biodiesel conversion [28].

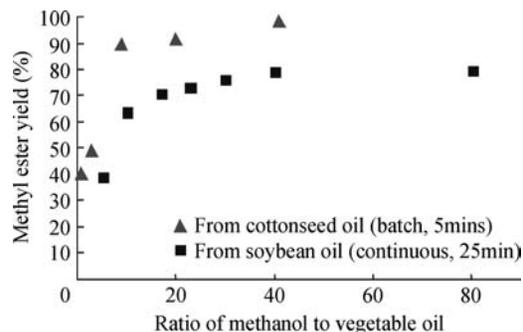


Fig. 6. Effect of molar ratio on yield of methyl ester [32,37].

glycerol. Various vegetable oils have been investigated and it was found that they can be transesterified at wide vegetable oil-alcohol molar ratios in supercritical alcohol conditions, ranging from 1:1 to 1:50 [18,29,32]. Examples of the molar ratio effect are shown in Fig. 6 for batch biodiesel production from cottonseed oil [32], and continuous biodiesel production from soybean oil based on the supercritical methanol method under 300 °C and 32 MPa conditions [37]. It is evident that higher molar ratios can result in a larger ester conversion rate in a shorter time. For soybean oil, the conversion rate reached a plateau at a ratio of ~40; further increase in the ratio did not help. Similar results have been obtained by other researchers [18,23,29]. An optimized excess of the alcohol of ~40 is therefore generally suggested in order to increase the yields of the alkyl esters and to facilitate its phase separation from the glycerol formed.

3.2.4. Water and free fatty acids effect

For biodiesel production from the conventional catalytic transesterification reaction, the presence of water can consume the catalyst, reduce catalyst efficiency and cause soap formation and frothing, which increase the biodiesel viscosity and make the glycerol separation difficult due to the formation of gels and foams [8]. For catalytic reactions, the vegetable oils/fats used as a raw material for the transesterification should be water-free, or of extremely low concentration, i.e. below 0.06%, much lower than the allowable free fatty acids content [30,39,40]. As most of the waste vegetable oils and crude oils generally contain water and free fatty acids, these problems may reduce the biodiesel production efficiency [41].

For the supercritical methanol method, optimized operation parameters have been found to be ~350 °C, ~43 MPa and residence time of ~240 s with a molar ratio of 42 in methanol for transesterification of rapeseed oil to biodiesel fuel [29]. Under supercritical conditions, free fatty acids in the oil could be simultaneously esterified. The water content effect on the yield of methyl esters by the supercritical methanol treatment was studied by Kusdiana and Saka [30] and compared with those from alkaline- and acid-catalyzed methods. Examples of water content and free fatty acid on the acid-, alkaline-catalyzed and super-

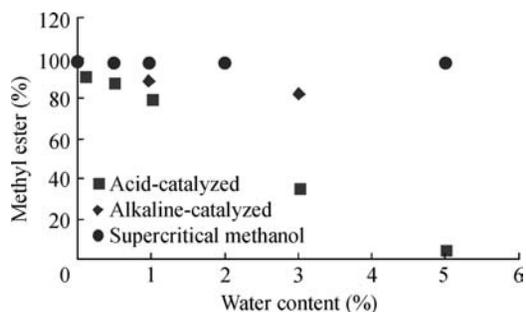


Fig. 7. Yields of methyl esters as a function of water content [30].

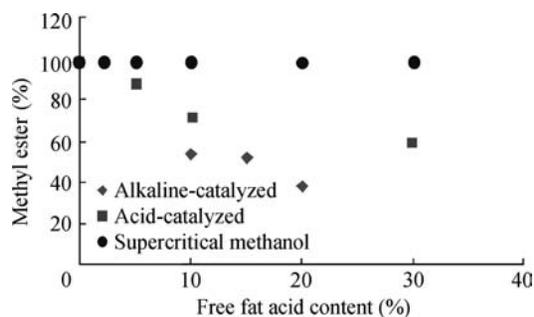


Fig. 8. Yields of methyl ester as a function of fatty acids content [30].

critical transesterification of vegetable oil are shown in Figs. 7 and 8. For acid catalytic reactions, as little as 0.1% of water addition could lead to significant reduction of the yield of methyl esters; the conversion was reduced to only ~6% when ~5% of water was added. A similar trend was also observed for the alkaline-catalyzed methods. However, the amount of water added into the reaction system did not have any significant effect on the conversion in the supercritical methanol method; and the presence of water positively affects the formation of methyl esters. In addition, compared with the alkaline-catalyzed method, a higher yield could also be obtained from free fatty acids (Fig. 8).

The water-added supercritical methanol method has another feature of easier product separation, since glycerol, a co-product of transesterification, is more soluble in water than in methanol. It appears that the supercritical method is specially good for converting a variety of resources with large contents of water and free fatty acid to biodiesel, which include crude vegetable oil, waste cooking oil and animal fats.

3.2.5. Co-solvent effect

For most of the supercritical methods of biodiesel production, the reaction requires temperatures of 340–400 °C and pressures of 20–70 MPa, which is energy intensive. Such harsh operation conditions also lead to high production costs and material requirements. Various methods including co-solvents and catalysts have been investigated to reduce the reaction temperature and pressure while achieving similar conversion rates.

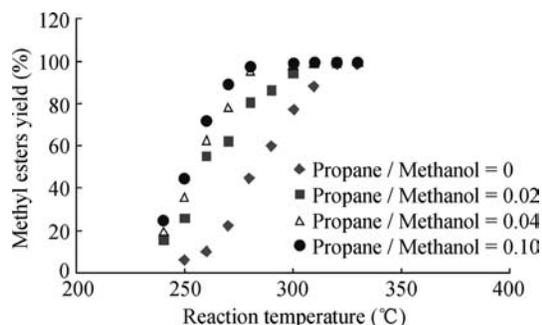


Fig. 9. Biodiesel conversions of propane and methanol under supercritical conditions [35].

It is known that the solubility of methanol decreases at supercritical conditions, being closer to that of vegetable oil at the appropriate temperature and pressure [42]. Some reports also show that the solubility of vegetable oils in methanol increases at a rate of 2–3% per 10 °C increase [39]. It would be of great interest from a practical point of view to investigate the effect of a co-solvent. This could not only increase the mutual solubility of methanol and vegetable oil at low reaction temperatures, but also possibly decrease the critical point of methanol, and allow the supercritical reaction to be carried out under milder conditions.

Using propane as the co-solvent, a study of the transesterification of soybean oil in the supercritical methanol was investigated [35]. Critical points for the binary system were determined by the content of propane in the binary system, which was found to decrease with increasing molar ratio of propane to methanol. The effect of propane on the conversion of soybean oil to methyl esters as biodiesel fuels is shown in Fig. 9. It is obvious that using propane as a co-solvent, the temperature can be reduced significantly, i.e. 330 °C for methanol only and 280 °C at propane-to-methanol molar ratio of 0.1, to reach a full conversion. As propane is easy to add and separate, the reduction of reaction temperature could make it viable for industrial applications.

3.2.6. Catalyst effect

For the conventional catalytic transesterification process, catalysts are classified as three types, alkali, acid and enzyme. Most of the reactions can be quickly preceded without the need of a catalyst under supercritical methanol and ethanol conditions. However, a few catalysts have also been introduced under such a condition in order to lower the reaction temperature and pressure, as outlined below.

Calcium oxide (CaO) has been known to catalyze reactions that require a base site. It is not dissolved in the reaction medium, and the transesterification reaction is heterogeneous. The roles of CaO in the supercritical transesterification of sunflower seed oil to biodiesel were investigated by Demirbas [33]. It was found that the addition of CaO could considerably improve the transesterification reaction. The experimental results are shown in Fig. 10 for a temperature of 525 K and a molar ratio of methanol to sunflower oil: 41:1. It can be seen that the transesterification

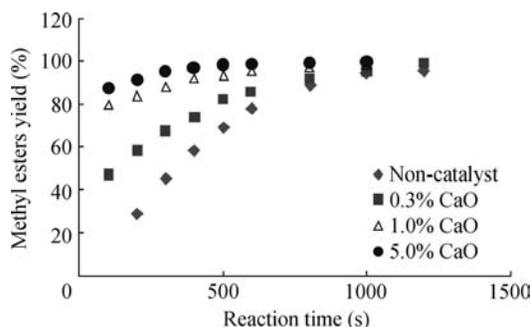


Fig. 10. Effect of CaO content on methyl ester yield [33].

rate increases evidently with increasing CaO concentrations, and the reaction time of the yield reaching plateaus of methyl ester decreases with increasing catalyst concentrations.

Temperatures and molar ratios were also found to have great influences on the catalytic supercritical transesterification. Sunflower oils could be fully converted to biodiesel in 6 min under optimum conditions, i.e. at a temperature of ~ 525 K with 3 wt% CaO and 41:1 methanol/oil molar ratio. Of note is that the catalytic transesterification ability of CaO was quite weak under ambient temperature, i.e. the yield of methyl ester was only about 5% in 3 h at 335 K. CaO appears to be a good catalyst under supercritical conditions.

Enzymatic reactions in supercritical carbon dioxide have been considered to be a practical way of achieving a better biofuel production rate. The requirement on power consumption and equipment is much lower for CO₂ SCFs than for supercritical methanol and ethanol (Table 1). The separation can also be easily achieved by the reduction of pressure, as the products and the enzyme do not dissolve in carbon dioxide at room conditions. Such an enzymatic reaction in supercritical carbon dioxide has been explored and compared with non-catalytic supercritical methods [24]. One example of experimental results is shown in Fig. 11 for the reaction at 45 °C with 3 mg of enzyme. Enzyme reactions in supercritical carbon dioxide took a much longer time and achieved only very low conversions (27–30%), whilst high conversion rates (80–100%) were typically achieved under supercritical methanol and ethanol conditions [29,32]. An improved reaction of supercritical CO₂ was developed for both edible and non-edible oils, and a maximum conversion of less than 70% can be obtained after several hours of reaction [43]. Though with

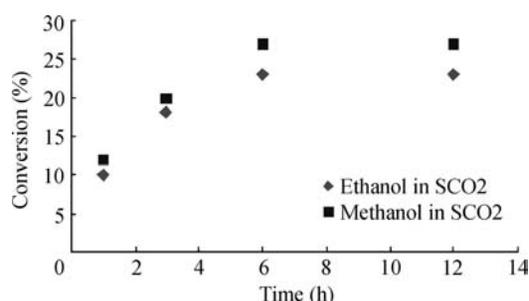


Fig. 11. Biodiesel synthesis from supercritical CO₂ [24].

low biodiesel conversions, further investigation of the enzyme's effect on the total energy consumption and benefit is still needed to assess this method.

3.2.7. Continuous production

Most of the biodiesel production via supercritical transesterification is based on the batch-type process. As the supercritical methanol method requires a high temperature of 350 °C and a pressure of 45 MPa, and in addition, as a large amount of methanol is necessary, it generally involves high labor cost, unreliable production and relatively longer time. It would be very beneficial to operate under continuous production conditions. A few continuous production systems have been developed for catalytic transesterification processes, which have resulted in increased production efficiency and quality of biodiesel [44–47].

Recently, He et al. [37] reported a continuous production process for soybean oil conversion to biodiesel through the supercritical methanol method. The experiments were operated in a 75 ml tube reactor that supplied continuous flow of soybean oil and methanol under molar ratios from 6:1 to 80:1. After the reaction, the product was cooled to room temperature, and then the crude methyl esters were obtained in a separate vessel. Similar to the supercritical batch operation, it was observed that increasing the molar ratio, reaction pressure and reaction temperature enhanced the production yield effectively. However, there is also a critical value of residence time at high reaction temperature, and the production yield will decrease if the residence time surpasses this value. Some side reactions of unsaturated fatty acid methyl esters (FAMES) also occurred when the reaction temperature was over 300 °C, which led to a big loss of the material under a pressure of 32 MPa and a molar ratio of 40:1 as is shown in Fig. 12. Under the optimal reaction condition, only a maximum production yield of 77% was observed, primarily due to the reactions of unsaturated FAMES at high temperature.

3.3. Reaction mechanism of transesterification

It was observed in many experiments that fatty acids present in the vegetable oil can be successfully converted to methyl esters under supercritical methanol conditions

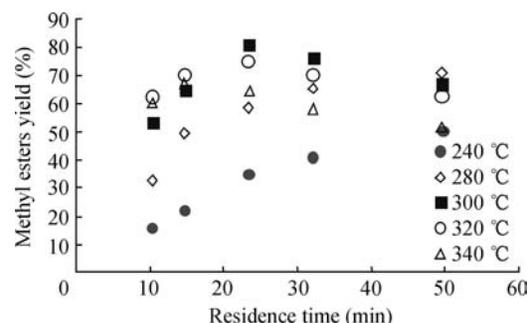


Fig. 12. Continuous synthesis of methyl esters from soybean oil [37].

[31]. Two types of reactions may exist in the supercritical method for methyl esters formation: transesterification of triglycerides and methyl esterification of fatty acids. It is expected that a higher yield can be obtained than that produced by the alkaline-catalyzed method [31].

Warabi et al. [28] studied the reactivity of transesterification of triglycerides and alkyl esterification of fatty acids in the supercritical alcohol process. In the experiments, the reaction temperature was set at 300 °C, and methanol, ethanol, 1-propanol, 1-butanol or 1-octanol was used as the reactant. It was shown that triglyceride was converted stepwise to diglyceride, monoglyceride and finally to glycerol as shown below.

Step I: triglyceride + methanol → diglyceride + methyl ester

Step II: diglyceride + methanol → monoglyceride + methyl ester

Step III: monoglyceride + methanol → glycerol + methyl ester

The formation of alkyl esters from monoglycerides is the core step that determines the reaction rate, since monoglycerides are the most stable intermediate compounds. The result also showed that transesterification of triglycerides (rapeseed oil) was slower in reaction rates than alkyl esterification of fatty acids, and the presence of saturated fatty acids such as palmitic and stearic acids had slightly lowered reactivity than that of the unsaturated fatty acids, oleic, linoleic and linolenic. Free fatty acids present in vegetable oil could be completely converted to the alkyl esters under the supercritical transesterification treatment.

3.4. Biodiesel economy

Although biodiesel has become more attractive recently because of its abundance, carbon neutral effect and environmental benefits, the economics of biodiesel is the main obstacle for the commercialization of the product and for wide distribution in transport sectors.

A review of 12 economic feasibility studies shows that for biodiesel produced from conventional catalytic methods, the projected cost from oilseed or animal fats falls within a range of US\$0.30–0.69/l [48]. This includes the meal and glycerin credits and the assumption of reduced capital investment costs by having the crushing and/or esterification facility added onto an existing grain or tallow facility. Rough costs of biodiesel from vegetable oil and waste grease are estimated to be US\$0.54–0.62/l and US\$0.34–0.42/l, respectively. With pre-tax diesel priced at US\$0.18/l in the US and US\$0.20–0.24/l in some European countries, it is difficult for biodiesel to compete with petroleum fuels without further economic and technological development breakthrough.

One reason for the non feasibility of biodiesel is the high cost of the feedstock as most of the biodiesel is currently made using soybean oil under alkaline catalyst conditions.

The high value of soybean oil as a food product makes the production of a cost-effective fuel very challenging. However, there are large amounts of low-cost oils and fats, such as restaurant waste and animal fats, that could be converted to biodiesel. As reviewed earlier, these low-cost oils and fats often contain large amounts of free fatty acids and water that cannot be converted to biodiesel by the conventional catalytic method [30]. Only the supercritical processing method could solve the problems; it offers a great advantage to eliminate the pretreatment capital and operating cost. It appears that using waste oil as a raw material and employing a continuous transesterification process under supercritical conditions, with recovery of high quality glycerol as a biodiesel by-product, are primary options to lower the cost of biodiesel.

Very recently, such considerations have been incorporated into an economic study that was conducted to focus on converting waste cooking oil via supercritical transesterification from methanol to methyl esters [49]. The economics of three plant capacities, 125,000, 80,000 and 8000 tonnes biodiesel/year from waste cooking oil, were studied for biodiesel production under continuous supercritical transesterification conditions. The results showed that biodiesel produced by supercritical transesterification can be scaled up with high purity of methyl esters (99.8%), and almost pure glycerol (96.4%) can be attained as a by-product. The economic assessment of the biodiesel plant shows that biodiesel can be sold at US\$0.17/l (125,000 tonnes/year), US\$0.24/l (80,000 tonnes/year) and US\$0.52/l for the smallest capacity (8000 tonnes/year), which makes it a strong competitor for the catalyzed transesterification process, and also in the near future as a promising replacement fuel for petroleum.

Such an economic analysis demonstrated that biodiesel production from supercritical fluid methods could become economically competitive even to the petroleum market. Further assessments of the sensitive key factors including raw material price, plant capacity, glycerol price and capital cost, as well as different supercritical techniques, are still needed to reach an impartial conclusion. In general, though, supercritical fluids will be an interesting technical and economic alternative for future biodiesel production.

4. Supercritical gasification of biomass

4.1. Conventional hydrogen production methods

The hydrogen economy is dependent on individual parts of a hydrogen energy system, which include production, delivery, storage, conversion, and end-use applications. The economic production of hydrogen and a highly efficient conversion system, i.e. through fuel cell technology to convert chemical energy to electricity and/or thermal energy, are the two core elements. Currently over 70% of hydrogen produced is from fossil fuels, mainly steam-methane reforming (SMR). The process includes mainly three parts: (i) pretreatment of the feedstock, (ii) steam reform-

ing and water–gas shift reaction and (iii) gas purification through pressure swing adsorption (PSA). In the first part, the hydrocarbon feedstock is desulphurised using activated carbon filters, pressurized and preheated and mixed with process steam. The fresh water is softened and de-mineralized by an ion-exchange water conditioning system. In the second part, methane and steam are converted within the compact reformer furnace at approximately 900 °C with the addition of a nickel catalyst to a hydrogen-rich reformate steam according to the following reactions.

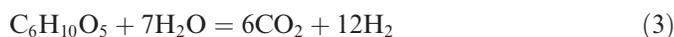


The heat required for the first reaction is generally obtained by the combustion of fuel gas and purge/tail gas from the PSA system. Following the reforming step, the synthesized gas is fed into the CO-conversion reactor to produce additional hydrogen. Heat recovery for steam or feedstock preheating takes place at different points within the process chain to optimize the energy efficiency of the reformer system. In the third part, hydrogen purification is achieved by means of PSA. The PSA unit consists of vessels filled with selected adsorbents, and could achieve hydrogen purities higher than 99.999% by volume and CO impurities of less than 1 vppm (volumetric part per million) to meet the requirement of the fuel cells. Pure hydrogen from the PSA unit is sent to the hydrogen compressor, while the PSA off-gas from recovering the adsorbents, the tailgas, is fed to the reformer burner. A recuperative burner is used with high efficiency and low nitrogen oxide emission. During a normal operation, the burner can be operated solely on the tailgas stream.

Besides SMR, water electrolysis is also a major production process where electricity is used to split water into hydrogen and oxygen molecules. While the SMR process is heavily dependent on fossil fuel supply, which is limited and causes environmental problems, the electrolysis process is very expensive and heavily depends on the supply of electricity, which again is mostly from fossil fuels. Biomass is a large potential resource for economic production of hydrogen. This interest is founded upon the expectation that hydrogen will be produced at a competitive price with conventional fossil fuels.

4.2. Gasification of biomass for hydrogen production

A similar process with SMR can be used for hydrogen production from biomass, steaming reforming of biomass.



In this reaction, natural gas is replaced by cellulose that is represented as $\text{C}_6\text{H}_{10}\text{O}_5$. In the idealized, stoichiometric equation, cellulose reacts with water to produce hydrogen and carbon dioxide. The research on the gasification of biomass began a few decades ago, and much progress has been made. The major challenges facing biomass gasification

now are to reduce and even eliminate the formation of tar and char so as to increase the conversion efficiency, and to find practical technologies to convert not only the cellulose, but also hemicellulose, lignin, protein, and extractive components of a biomass feedstock into a gas rich in hydrogen and carbon dioxide. Any production of char and tar represents an effective loss of gas.

For conventional biomass gasification under atmospheric pressure, biomass does not react directly with steam to produce the desired products. Instead, significant amounts of tar and char are formed, and the gas contains higher hydrocarbons in addition to the desired light gases [50,51]. The formation of pyrolytic char and tar during gasification sets limits on the efficient production of hydrogen from biomass under atmospheric pressure. Both the temperature and pressure effects on reducing the char and tar production have been investigated. As the temperature increased to over 800 °C, a nearly complete conversion of tar to gas could be realized [52], but the char by-product remained unconverted. For biomass gasification under high pressure, it was found that even cellulose, the most stable component of biomass, decomposes rapidly at a temperature below the critical temperature of water at a pressure above water's supercritical pressure, 22.1 MPa [53]. The char formation can be fully suppressed as temperature is further increased [54]. However, tar gasification becomes the chief obstacle for a total steam reforming of biomass.

Based on previous experiments, it has therefore been expected that complete gasification could be achieved for supercritical water under optimized operational conditions.

4.3. Biomass gasification in supercritical water (SCW)

Biomass gasification in supercritical water opens a door to the realization of effective thermochemical gasification of biomass, especially wet ones, as schematically shown in Fig. 13. In general, the supercritical gasification can be categorized into two areas, low temperature gasification at 350–600 °C with the aid of some catalysts and high temperature gasification at 600–800 °C without any catalysts. For low temperature gasification, although catalysts are generally applied to enhance the reaction, complete gasification of feedstock is still difficult. Due to the high dependence of the reactivity of biomass on temperature, a complete conversion of biomass into combustible gas has become possible at higher temperatures. However, the gasification efficiency falls as the concentration of the organic feedstock increases. There are a number of parameters that affect the thermochemical conversion efficiency under supercritical conditions, which include operating pressure and temperature, different catalysts and feedstock, interactions between different components and effect of partial oxidation. A recent review by Matsumura et al. can be found in Ref. [51].

Throughout the development of the technology till to date, the possibility of biomass gasification in near- and

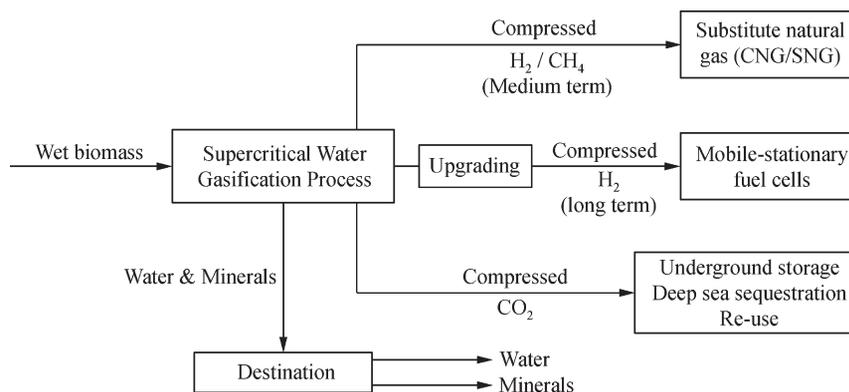


Fig. 13. Schematic of the application of supercritical water gasification [51].

supercritical water (SCW) has been demonstrated, and a complete conversion of biomass into combustible gas has been achieved. SCW may become an important technology for converting wet biomass or organic waste to a pressurized and clean medium caloric value gas with a high hydrogen content. Compared with conventional biomass gasification technologies, supercritical water gasification possesses a number of advantages that include high thermochemical conversion rate, suitable for wet feedstock such as water hyacinth and algae, high pressure products that are easy for future transportation and usage, opportunities for carbon capture, sequestration and storage, as well as to further pure hydrogen production via a further steam-methane reforming process. However, some technical breakthroughs, especially on the complete gasification of tar and char, practical difficulties of operation in harsh temperature and pressure conditions, material requirement and its associated high cost are the main barriers for the technology to become widely commercially available.

5. Supercritical liquefaction of biomass

Among the biomass energy conversion methods as shown in Fig. 1, thermochemical liquefaction is considered to be a promising method for converting biomass into higher value fuels. Compared with the gasification technique, the liquefaction process does not require a feedstock drying process, which typically requires significant heating due to the large latent heat of water vaporization. Thermochemical liquefaction can be an effective method for converting woody biomass into oil or other types of fuels.

Supercritical fluid is a candidate for the chemical conversion of lignocellulosics due to its unique properties. Supercritical water treatment for cellulosic samples has been extensively studied to obtain saccharides for subsequent fermentation to ethanol [55]. Co-liquefaction of cellulose and coal in supercritical water has also been investigated aiming for hydrogen production [56]. However, as the reaction is energy intensive to reach the supercritical status of water, a number of alcohols have been recently investigated, including methanol, ethanol and 1-propanol [27,57–60]. Using

these low critical temperature and pressure alcohols, it is possible to obtain liquid products as direct fuels. In addition, various alcohols can be produced from biomass, i.e. methanol from hydrogen and carbon monoxide gasified from biomass, and ethanol and butanol from fermentation of biomass saccharides. Various types of biofuels can be achieved by using different alcohols.

Compared with the conventional method, supercritical biomass liquefaction could offer a number of advantages such as high conversion rate, fast reaction and few or no catalysts. The techniques are still under development and interested readers may refer to the above reference for detailed information.

6. Conclusion

This paper reviews state-of-the-art applications of supercritical fluids (SCFs) technology for biofuels production, with the main focus on biodiesel production from vegetable oil via the transesterification process. Bio-hydrogen from the gasification and bio-oil from the liquefaction of biomass from the SCF route are also briefly reviewed. It shows that SCF is a promising technique for future biofuel production. Compared with conventional biofuel production methods, the SCF technology possesses a number of advantages that include fast conversion, high fuel production rate, ease of continuous operation and elimination of the necessity of catalysts. Some main conclusions can be drawn:

1. Increasing temperature and molar ratios can enhance the conversion rate and kinetics for supercritical biodiesel production from vegetable oils.
2. Among all alcohols, methanol is the best for the transesterification process. Its conversion effect could be much improved under optimized conditions and in the presence of either a co-solvent or a catalyst.
3. Water and free fatty acid have little or even positive impact on the biodiesel conversion under supercritical conditions, which make SCF especially suitable for biodiesel production from waste oil and animal fat.

4. The economic assessment shows that biodiesel produced from the SCF technology is comparable to conventional catalytic transesterification, and is competitive with petroleum-derived fuels if waste oil is used as a feedstock.
5. Supercritical fluid technology has favorable impact on biogas production via the gasification, and bio-oil production via the liquefaction of biomass.

There are, however, a number of problems associated with the SCF technology. The mechanistic understanding of the process, the harsh operation environment such as high temperature and high pressure, and its request on the materials and associated cost are the main concerns for its wide application. Future research should focus on the reduction of operating temperature and pressure while maintaining the high conversion rate.

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