Microwave-Assisted Synthesis of Biofuels

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1. Introduction

Environmentally benign and economically viable alternatives to fossil derived fuels are seriously being explored due to increasing global demand for energy, coupled with the threats posed by the recent climate changes. As potential alternatives, biodiesel and biomass-derivable ethyl *tert*-butyl ether (ETBE) are being pursued. Research for the development of efficient and energy-saving methods for the production of these two promising biofuels had gained significant momentum over the past few years.

Literature searches on published articles having "biodiesel" on its title using *JST Plus/JMEDPlus/JST17580* database resulted to heavy turnouts. The trend follows the graph shown in Fig. 1 in terms of annual publication of related articles. Similar searches including those appearing in abstracts and keywords using SCOPUS database, resulted to more than 6,800 hits. The data clearly indicates a dramatically increasing global interest on research, development and analysis related to biodiesel production, especially during the past decade, due primarily to the motivation of reducing fossil-derived carbon dioxide emissions to the atmosphere.

Biodiesel is a mixture of fatty acid methyl esters produced from the transesterification of plant oils or animal fats with methanol over alkali or acid catalysts as shown in Fig. 2. As reported in the book edited by Saka (2006), the conventional method for its production utilizes homogeneous alkali catalysts, such as NaOH and KOH, in a batch mode (Fig. 3). Post treatment procedures after reaction require neutralization of catalysts and their removal from the products utilizing enormous amount of water. Alternative methods to avoid the problems and high costs of treating wastewater associated with the process are being explored. Moreover, the demand for biodiesel is highly expected to increase, and a more efficient continuous process is being sought with the purpose of reducing capital or production costs.

Several review articles have already been published discussing various alternative production methods for biodiesel. The most noteworthy is the review article published by Ma and Hanna (1999) focusing on the transesterification process, its mechanism, kinetics and effects of reaction parameters such as moisture and free fatty acid contents, molar ratio, reaction time and temperature among many others. Moreover, the source of raw materials and manufacturing costs take the major hurdle in the commercialization of biodiesel, thus alternative sources such as the use of waste cooking oil has long been considered. Kulkarni and Dalai (2006) had reviewed published articles related to the utilization of waste cooking
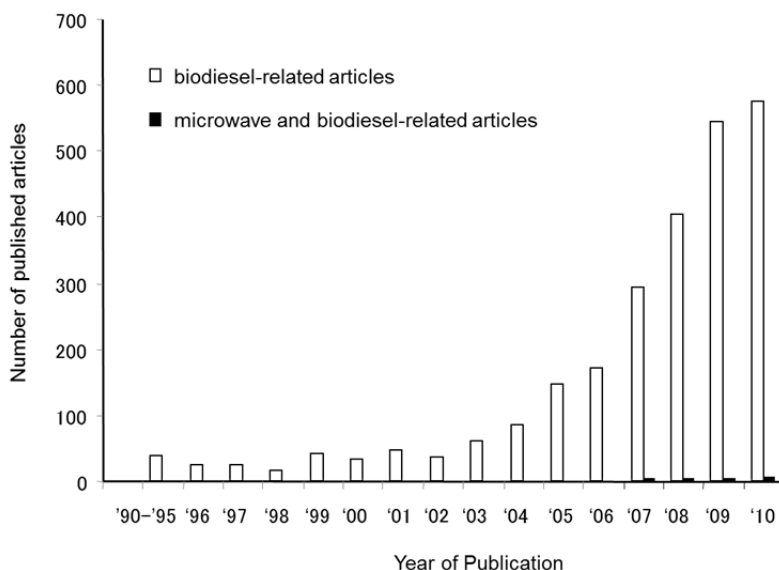
Fig. 1. Trends of biodiesel and microwave related publications based on searches using JST Plus/JMED/JST17580 database

oil as an economic source for biodiesel, showing different methods for the transesterification of oil and the performance of obtained biodiesel in a commercial diesel engine. They concluded that the biodiesel obtained from waste cooking oil gives better engine performance and less emission when tested on commercial diesel engines. Among the many techniques presented, including the use of enzymes, two-step method (acid-catalyzed followed by alkaline-catalyzed step) and supercritical methanol, no particular method was recommended to be superior. In addition, similar reviews on different techniques for the production of biodiesel from waste vegetable oil have been written and summarized by Refaat et al. (2010). Each technique presented has its advantages and drawbacks, and the choice of suitable method depends primarily on its economic viability.
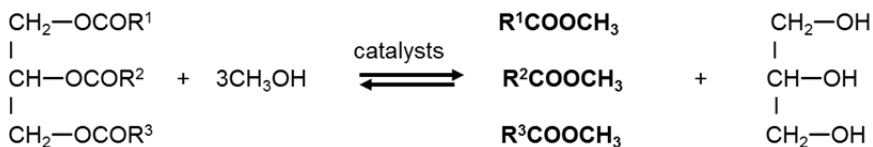
Fig. 2. Reaction mechanism of transesterification of plant oil for biodiesel production
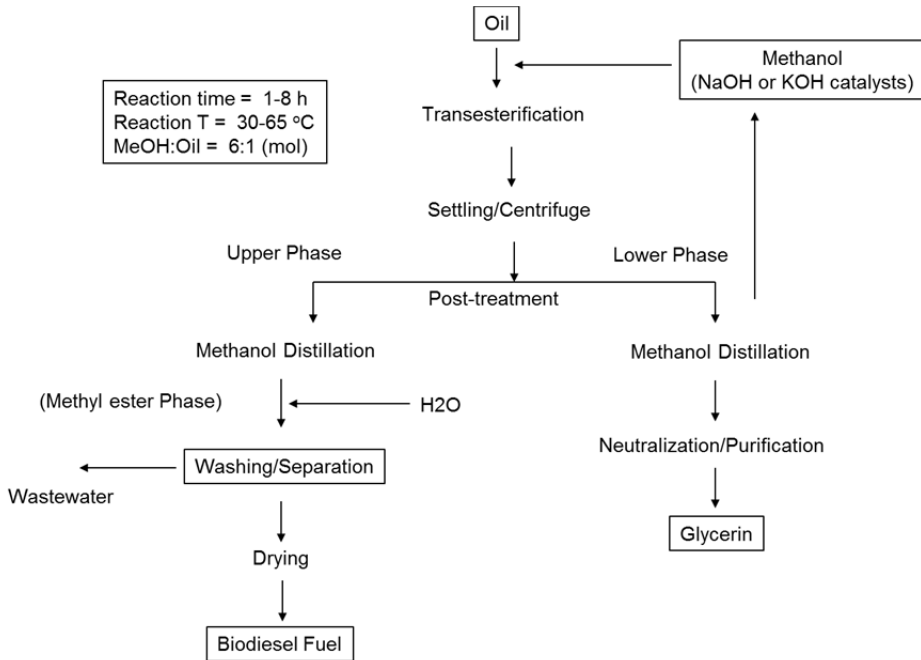
Fig. 3. Conventional alkaline-wash water process for production of biodiesel (Saka, 1996)

Aside from biodiesel, ETBE, which had been previously considered as a replacement for lead as gasoline octane booster, has also gained popularity over ethanol as biofuel due to its superior properties which blend well with gasoline. ETBE also outranks MTBE as an octane enhancer due to its low blending Reid vapor pressure, beside, ETBE is a better option because it is derived from ethanol (EtOH) which can be obtained from renewable resources like biomass. ETBE is produced from the reaction of isobutene (IB) and EtOH, however, the supply of IB, which is mostly derived from non-renewable crude oil, may become limited, and for this reason, alternative routes for its synthesis are also currently being explored. *tert*-Butyl alcohol (TBA), a major byproduct of propylene oxide production from isobutane and propylene, can be employed instead of IB as a reactant (Yang and Goto, 1997). With suitable enzyme catalysts, TBA can also be possibly produced from biomass sources similar to that used for bioethanol production. The prospects are high for the use of these two biomass-derivable lower alcohols for the production of suitable fuel for conventional engines running on gasoline.

The synthesis route for ETBE production employing *tert*-butyl alcohol (TBA) instead of IB has long been investigated by Norris and Rigby (1932) using concentrated sulfuric acid as catalyst. Recently, Habenicht et al. (1995) investigated the reaction at elevated temperatures and pressures. Yin et al. (1995) introduced the use of heterogeneous catalysts such as ion-exchange resin and heteropoly acid. Matouq et al. (1996) applied an advanced method of reactive distillation, utilizing low-grade alcohol catalyzed by potassium hydrogen sulfate ($KHSO_4$). Results showed that ETBE could be produced from the reaction, and that the reactive distillation column was a good choice to separate ETBE from the reacting mixture. In subsequent works, pervaporation technique was incorporated at the bottom of

the column to remove the water byproducts, shifting the equilibrium forward, resulting to better yields (Matouq et al., 1997, Yang & Goto, 1997). The works were further extended on the utilization of ethanol at a concentration as low as that obtained from the fermentation of biomass (about 2.67 mol% in aqueous solution) (Roukas et al., 1995). Almost complete conversion of TBA was obtained, with ETBE selectivity of about 36% (Quitain et al., 1999).

In this chapter, works on the application of microwave irradiation to the syntheses of these two most promising biofuels by microwave irradiation will be discussed and summarized, focusing on our recent studies on microwave-assisted heterogeneously catalyzed processes.

2. Fundamentals of microwave irradiation

For rapid synthesis of the two abovementioned biofuels, the application of microwave technology has been proposed. Microwave technology relies on the use of electromagnetic waves to generate heat by the oscillation of molecules upon microwave absorption. The electromagnetic spectrum for microwaves is in between infrared radiation and radiofrequencies of 30 GHz to 300 MHz, respectively, corresponding to wavelengths of 1cm to 1 m. Domestic and industrial microwave systems are required to operate at either 12.2 cm (2.45 GHz) or 33.3 cm (900 MHz) in order not to interfere with the wavelength ranges being utilized for RADAR transmissions and telecommunications (Mingos & Baghurst, 1997).

In microwave-assisted heating, unlike the conventional methods, the heat is generated within the material, thus rapid heating occurs. As a result of this rapid heating, many microwave-assisted organic reactions are accelerated, incomparable with those obtained using the conventional methods. Thus, higher yields and selectivity of target compounds can be obtained at shorter reaction times. In addition, many reactions not possible using the conventional heating methods, had been reported to occur under microwave heating. Some very useful information on the fundamentals of microwave-enhanced chemistry, its sample preparation and applications are well presented in the book edited by Kingston and Haswell (1997).

Other than the advantages of rapid heating, microwave non-thermal effects on reaction likely occur, obtaining dramatic increase in the yield even at milder conditions. Although doubts are cast on the true existence of non-thermal effects, some evidences had been reported and postulates had also been made by several researchers. These were summarized in a review article published by de la Hoz et al. (2005) comparing them with the thermal effects. The review of Jacob et al. (1995) on thermal and non-thermal interaction of microwaves with materials attributed some interesting results on specific microwave effects. Evidences on reaction rate enhancement due to some reasons other than the thermal effects such as "hotspots" or localized heating, molecular agitation, improved transport properties were discussed. They suggested that due to the interaction of microwave with the materials, heating cannot be simply treated as that similar to the conventional methods as there are a lot of possible mechanisms of activation of materials that might possibly occur.

The abovementioned thermal and non-thermal effects of microwave irradiation offer enormous benefits to the synthesis of biofuels including energy efficiency, development of a compact process, rapid heating and instant on-off process (instant heating-cooling process), among many other possible advantages.

3. Previous studies on the application of microwave irradiation to the synthesis of biofuels

Due to the benefits and advantages accompanying the use of microwave irradiation, its applications to organic synthesis increased significantly in recent years. However, unlike the momentum that biodiesel research has gained over the past decade, the application of microwave for its production is still in its infancy. The pioneering work on this topic was reported by Breccia et al. (1999), on the use of a domestic microwave apparatus for the synthesis of biodiesel by reaction between methanol and commercial seed oils. In this work, they found that the reaction was practically complete in less than 2 min under microwave irradiation. Activities of several catalysts such as sodium methylate, sodium hydroxide, sodium carbonate, sulfuric acid, benzensulfonic acid and boron carbide were briefly discussed. Boron carbide, which actively absorbs microwave, was reported to be the most effective and promising catalyst for the transesterification. Results of preliminary experiments using a laboratory scale plant for continuous process was also reported, and based on a few obtained data, they concluded that the application of MW both in continuous and batch-wise process was proven to be practical on an industrial scale.

Upon the introduction of scientific microwave apparatus in the market, its use for the investigation of biodiesel synthesis started in 2004, based on the works of Mazzocchia et al. (2004) on the application of heterogeneous catalysts. The catalysts used were mostly zeolites, and the reaction was allowed to proceed at 170 ^{o}C for 2h in a sealed vessel. However, only moderate conversions were obtained using this technique.

Research on the use of scientific microwave apparatus was then conducted by the group of Leadbeater and Stencel of the University of Connecticut in 2006 (Leadbeater & Stencel, 2006). They used a 3-kg scale reactor apparatus allowing the reaction to proceed under atmospheric conditions in few minutes. Homogeneous catalysts such as KOH and NaOH were used to accelerate the reaction. The work was extended by the same group to a continuous flow method at flowrates up to 7.2 L/min using a 4L reaction vessel. They also found out that the continuous-flow microwave method was more energy-efficient than the conventional heating methods based on rudimentary energy consumption calculations.

Similar works had been performed by the group of Hernando et al. in 2007 using homogeneous catalysts, and they were able to obtain yield above 95% in 1 min of reaction time. They even used additives such as methyl *tert*-butyl ether (MTBE) to enhance the solubility of the reactants.

Interests on the techniques spread worldwide, and several works then followed mostly on the application to various oil feedstocks. In Thailand, experiments on the use of microwave for the production of biodiesel from waste frying palm oil were reported (Lertsathapornsuk et al., 2008). In this work, domestic microwave apparatus was modified for continuous transesterification. In New Mexico, the group of Patil et al. (2009) tried the techniques on Camelina Sativa oil. In Chicago (US), Majewski et al. (2009), experimented on the transesterification of corn and soybean oil. In China, Zhang et al. (2010) worked on yellow horn oil, Yuan et al. (2009) on castor oil using sulfated activated carbon as microwave absorption catalyst, and in Taiwan, the use of nanopowder calcium oxide to the transesterification of soybean oil was reported. In the Philippines, works using Kenaf seed oil has also been reported (Rathana et al., 2010).

Recently, Leadbeater et al. (2008) applied microwave heating for both batch and continuous flow process for production of biodiesel utilizing butanol, an alcohol that can be generated

from agriculture feedstocks similar to that used for ethanol production encouraging utilization of totally renewable based feedstocks. The work was extended by collaborative research groups in Europe (2008) under supercritical conditions for a microwave-assisted catalyst-free transesterification of triglycerides (Geuens et al., 2008). Researchers from Brazil have also tried applying microwave for the activation of enzymatic catalysts used for biodiesel production (Nogueira et al., 2010).

To date, several homogeneous, heterogeneous metal oxide and metal salt catalysts have been evaluated for the microwave-assisted synthesis of biodiesel (Breccia et al., 1999). Among the many catalysts investigated, homogeneous basic catalysts such as KOH and NaOH are the most preferred, and commonly used in the conventional process of transesterification because of its high activity even at low concentration. The production of methyl esters, with methanol as the reactant, proceeds at very high yields even under mild conditions, and reaction generally takes about an hour to complete. For the treatment of free fatty acids present in the oil feedstocks, the use of sulfuric acid is widely considered.

However, there are drawbacks on the use of these homogeneous catalysts including the tedious post treatment procedures of neutralization and washing of products resulting into enormous amount of wastewater produced in the process. Thus, the use of inexpensive heterogeneous catalysts suitable for microwave irradiation is being explored. Our group had been working on this topic since 2006, and had successfully completed application of two related Japanese patents as a result of our extensive works. The results have also been presented in various domestic and international conferences related to microwave application and biomass energy conversions (Quitain et al., 2008; Quitain et al., 2009).

In addition, for ETBE production, Tokyo Electric Co. has applied two patents using microwave irradiation. However, the reported maximum conversion at atmospheric conditions is too low at around 28%. Results of our recent research utilizing the same techniques yielded similar results. However, better conversion closed to 90% was obtained upon the application of constant microwave power, and allowing the reaction temperature to reach solvothermal conditions in a sealed vessel.

4. Advantages of heterogeneous catalysis for the synthesis of biofuels

Conventional methods of producing biodiesel normally utilize homogeneous catalysts to accelerate the reaction. At the end of the reaction, the catalyst is neutralized and removed from the products requiring enormous amount of water, which is usually about 80% of produced amount of biodiesel in mass basis. Alternative methods to avoid the problems and high costs of treating wastewater associated with the process are being explored. The use of heterogeneous catalysts offers much benefits as this would eliminate the tedious post treatment procedures of dealing with the wastewater. Besides, the use of solid catalysts accompanies easier product separation resulting to a more economical process.

Several heterogeneous catalysts including basic, acidic, acid-base and enzymes that are suitable for biodiesel production had been reviewed recently by Semwal et al. (2011). The review is very useful in the selection of suitable catalysts and the corresponding optimum conditions. Several solid catalysts have been investigated for biodiesel synthesis but their applications were limited due to lower reaction rates and unfavorable side reactions. Basic heterogeneous catalysts have also been investigated, and the catalytic activity was found to be affected by the presence of water.

Among the many reported catalysts, Ca-based solid catalysts such as CaO and Ca(OH)$_2$ had caught our interest and are deemed most promising because of their availability and low cost. Works are still in progress for modifying these types of catalysts to make them more suitable for a wide range of biofuel feedstocks.

5. Our recent works on microwave-assisted synthesis of biofuels

5.1 Biodiesel production
5.1.1 Experimental procedures

We have been investigating the application of microwave irradiation to the synthesis of biodiesel using the abovementioned Ca-based solid catalysts. In most of the experiments, rapeseed oil commercially available from Nacalai Tesque (Japan) was used. The average molecular weight of the oil was assumed to be 806 (Kusdiana & Saka, 2001). Methanol (HPLC grade), Ca(OH)$_2$ and CaO (99.9%) were purchased from Wako (Japan), while other catalysts were purchased from Sigma-Aldrich (Japan). In some experiments, commercial slaked lime in pellet form supplied by Inoue Lime Industrial Company (Kochi, Japan) was also used.
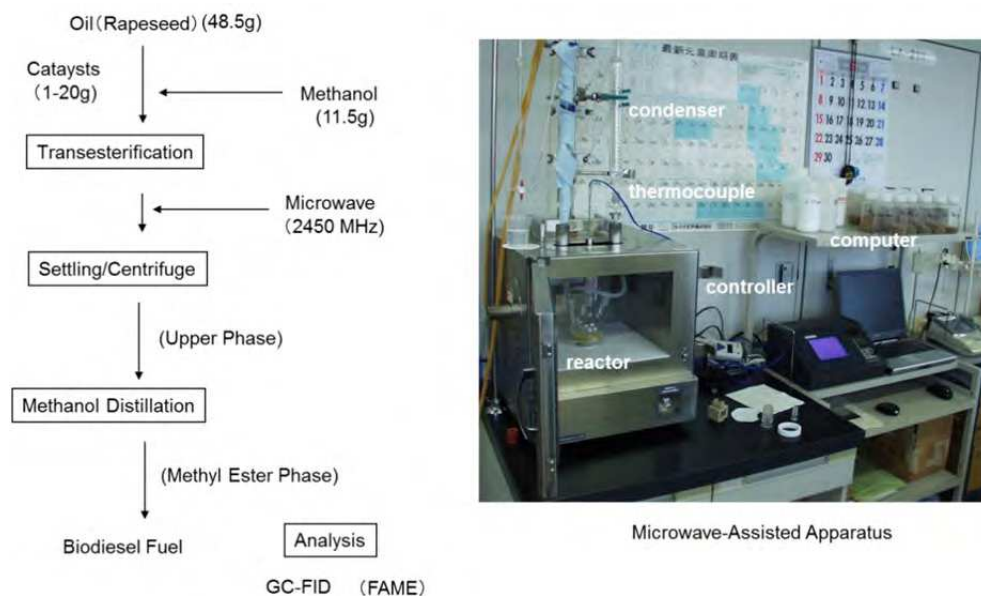

Fig. 4. Outline of experimental procedures and microwave-assisted apparatus used for batch experiments

All microwave-assisted batch experiments were performed using an in-house microwave apparatus shown in Fig. 4, working at 2.45 GHz frequency, with a power programmable from 0 to 700W. Temperature could be controlled, and the reactants could be mixed using a magnetic stirrer. Continuous experiments were performed in a similar apparatus (Shikoku Instrumentation Co. Ltd., Kagawa, Japan) design for microwave-assisted drying, but the power can be programmed to a maximum of 1500W.

In a typical batch experiment (also shown in Fig. 4), about 11.5 g methanol and 48.5 g rapeseed oil (MeOH-oil molar ratio = 6) were placed in a three-necked round bottom flask, and heated either in an oil bath or in a microwave apparatus described above. In all runs, the MeOH-oil ratio was fixed at a commonly used molar ratio of 6, which is also the ratio being employed in industrial scale production of biodiesel. The amount of catalyst was varied from 1 to 20 g. The reaction temperature was set at 60 ^{o}C, unless otherwise specified. In experiments involving constant microwave heating power, the temperature was not controlled, but the maximum attained temperature was noted.

The products were collected, then centrifuged to separate the catalysts and the glycerin phase. The unreacted MeOH in the products was then removed using a rotary evaporator at 70 ^{o}C.

The products were analyzed of its composition by a gas chromatography – flame ionization detector (GC-FID) apparatus (Shimadzu GC-14B) connected to a computer for data collection and analysis. Component separation was made in a 50m x 0.25mm CP Sil 88 capillary column (GL Science, Japan), tailor-made for FAME analysis using helium as a carrier gas. The column, detection and injection temperatures were set to 190, 300 and 270 ^{o}C, respectively. The sample injection volume was 5 μl and peak identification was made by comparing the retention time between the sample and the standard compound. FAME quantitative mixtures (GL Science, Japan) were used for peak identification and for quantitative analysis.

5.1.2 Evaluation of catalytic activities of various solid catalysts

Preliminary experiments were conducted to evaluate catalytic activities of various solid catalysts such as Amberlyst 15, Amberlite-OH, Amberlite-Acid, zeolite, sulfated zirconia (in powder and pellet forms), $Ca(OH)_2$ and CaO. Among the catalysts investigated, $Ca(OH)_2$ showed to be the most active, while CaO also gave fairly good results as shown in Fig. 5. The use of these two relatively cheap catalysts showed potential for biodiesel production, thus $Ca(OH)_2$ was used in the succeeding experiments unless otherwise specified.

5.1.3 Comparison of microwave and conventional heating

Microwave heating for the production of biodiesel in a batch mode was compared with that of the conventional. In case of the conventional method, the oil bath temperature was set at 60°C, and the mixtures of reactants and catalysts were heated for 1 min. Using microwave irradiation, the power was set at 700 W. Heating for 1 min, the bulk temperature of the mixtures did not reach 60°C in all runs.

Fig. 6 shows a remarkable increase in the yield of methyl esters using microwave heating compared to the conventional. The yield, corresponding to the amount of methyl esters in the oil phase, reached above 95% using 20g $Ca(OH)_2$.

Even if the bulk temperature did not reach 60°C, it is likely that localized heating above 60°C occurred at the surface of the catalysts, which brought about a significant increase in reaction rate, resulting into high yield. This is advantageous especially on the viewpoint of equipment design as this entails less provision for heat and pressure-resisting reactor materials.

In this proposed method, the reaction time was reduced to less than 60 sec compared to 1 to 8 h using the conventional method. In addition, the use of solid catalysts avoids the rigors and complexities of dealing with post-reaction treatments (*i. e.* neutralization of homogeneous catalysts and washing of the products with water). Furthermore, with short

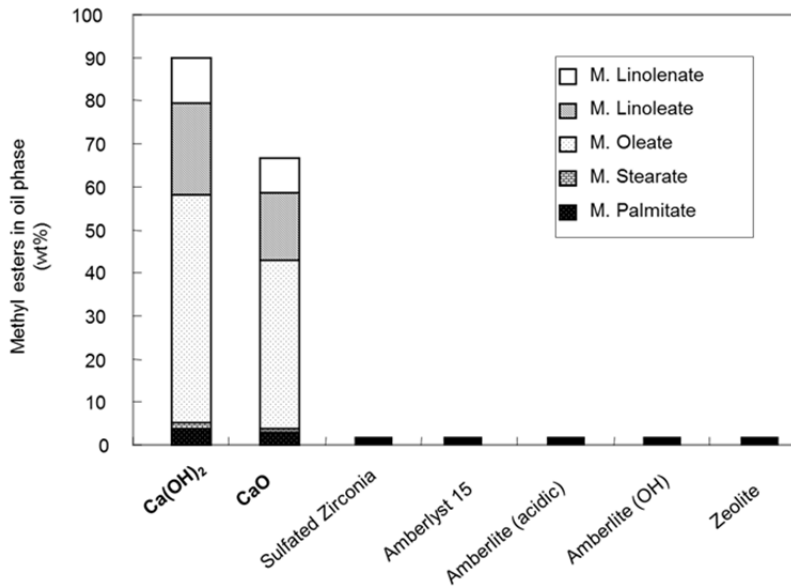reaction time, development of a continuous process is highly feasible thus reducing equipment costs.

Fig. 5. Comparison of activities of various catalysts under microwave irradiation (t = 1min, catalysts = 10g, MW = 700W)

5.1.4 Effect of operating conditions

Fig. 7 shows the effect of microwave irradiation power on the yield at various amounts of catalysts. No significant differences were observed at 140 and 350W, but the yields were comparatively high at 700W especially at 10 and 20g $Ca(OH)_2$.

Using 10g $Ca(OH)_2$, the reaction time was increased to 5 min at the same microwave power of 700W. Results showed that while the temperature increased sharply above 110 °C in just 5 min, the yield decreased to 20%. It is likely that reverse reaction took place brought about by an increase in reaction temperature and the subsequent evaporation of MeOH from the reaction zone. The same results were observed in the works of Hernando et al. (2007) on the batch tests performed with microwaves.

5.1.5 Comparison with other vegetable oils

The fatty acid compositions of various oils differ as shown in Table 1. Rapeseed oil contains mostly oleic acid, while soybean and coconut oils are rich in linoleic and lauric acids, respectively. These differences might have an effect on the transesterification of the oils, thus the results obtained using rapeseed oil were compared with that of soybean and coconut oils. Fig. 8 shows that almost similar results were obtained with different types of vegetable oils investigated, with the yield for coconut oil higher than the two other types of oil. This implies that the proposed method can be applied to any types of oil (or fat) feedstocks for biodiesel production.
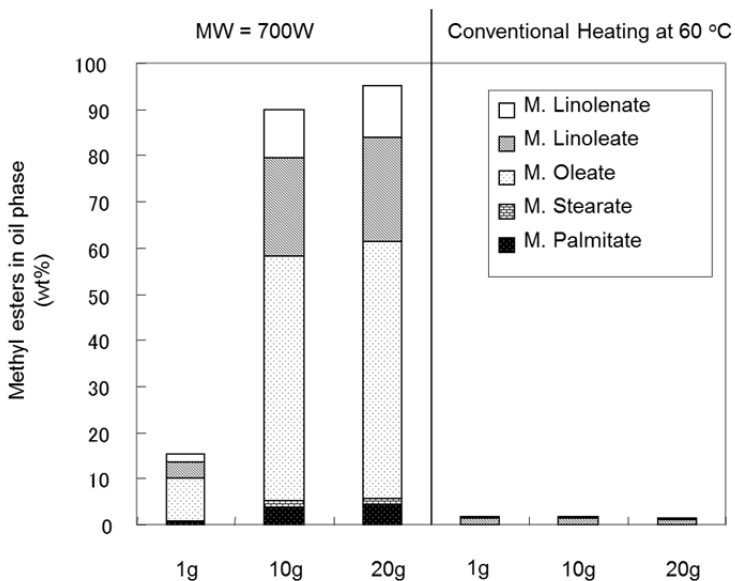
Fig. 6. Comparison of microwave and conventional heating (t = 1min, catalysts: $Ca(OH)_2$, MW = 700W)
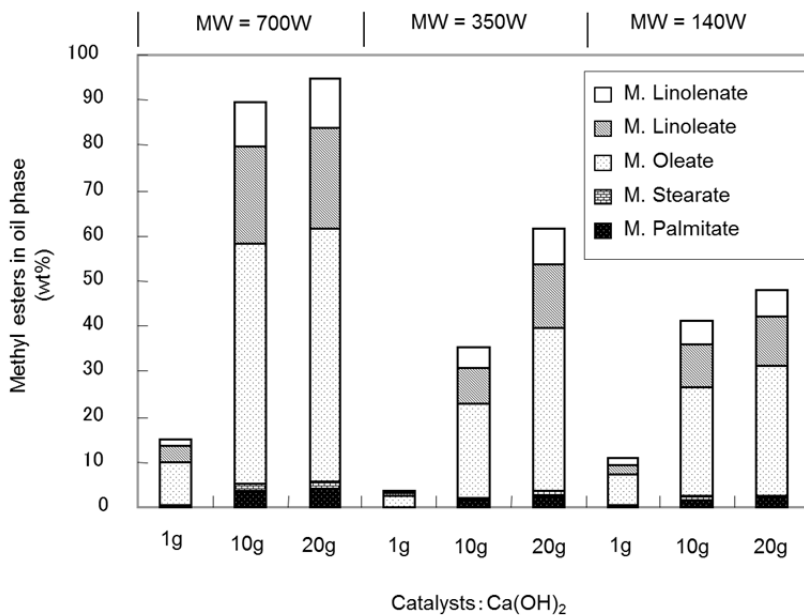

Fig. 7. Dependency of yield on microwave irradiation power at various amounts of $Ca(OH)_2$ catalysts (t=1min)

Oil/Fats	Fatty Acid Composition (wt%)								
	Caprylic (C8:0)	Capric (C10:0)	Lauric (C12:0)	Myristic (C14:0)	Palmitic (C16:0)	Stearic (C18:0)	Oleic (C18:1)	Linoleic (C18:2)	Linolenic (C18:3)
Rapeseed					6	1	**58**	24	11
Soybean				0.3	7.8	2.5	26	**51**	5
Coconut	8	8	**48**	16	8.5	2.5	6.5	2	

Table 1. Fatty acid composition of various oil feedstocks investigated
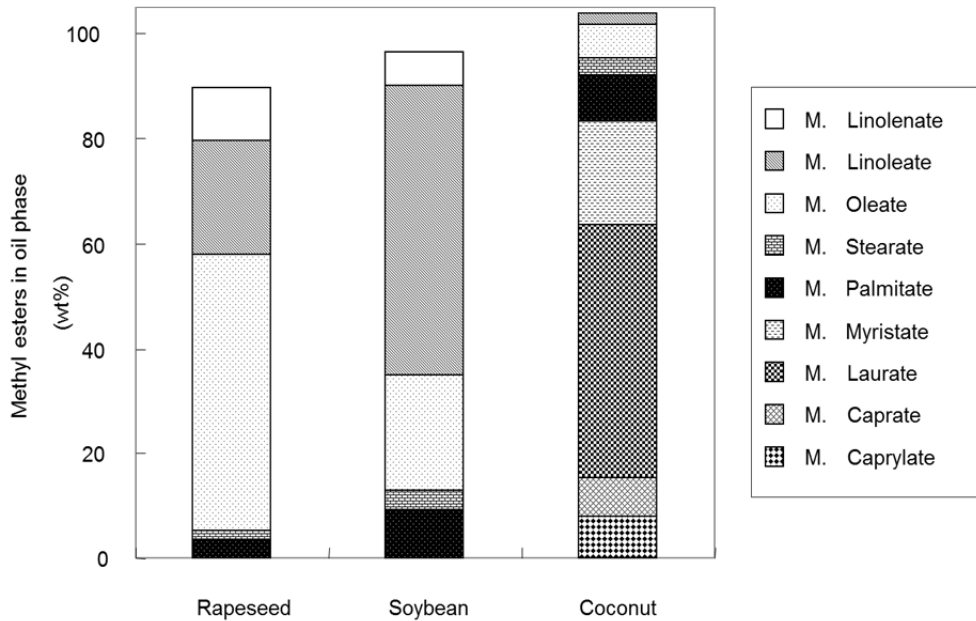
Fig. 8. Comparison of yield using various types of oil feedstocks (t = 1min, Ca(OH)2 = 10g, MW = 700W)

5.1.6 Comparison of commercial slaked lime with pure Ca(OH)$_2$ catalysts

For low-cost production of biodiesel, cheap and readily available catalysts for its production are being sought. The use of cheap commercial grade Ca(OH)$_2$ catalysts could be considered. For this purpose, the activity of the commercial slake lime pellets (supplied by Inoue Lime Co. Ltd., Kochi, Japan) containing 60% Ca(OH)$_2$ was compared with that of pure Ca(OH)$_2$. Results in Fig. 9 show that the yield was low at around 30% using the un-pretreated pellets. If pre-dried, the yield increased by more than 10%. After further pulverization, a three-fold increase in the yield was obtained using dried catalysts as a result of the increase in surface contact area. In the succeeding continuous-flow experiments, non-pulverized dried slaked lime pellets were used.
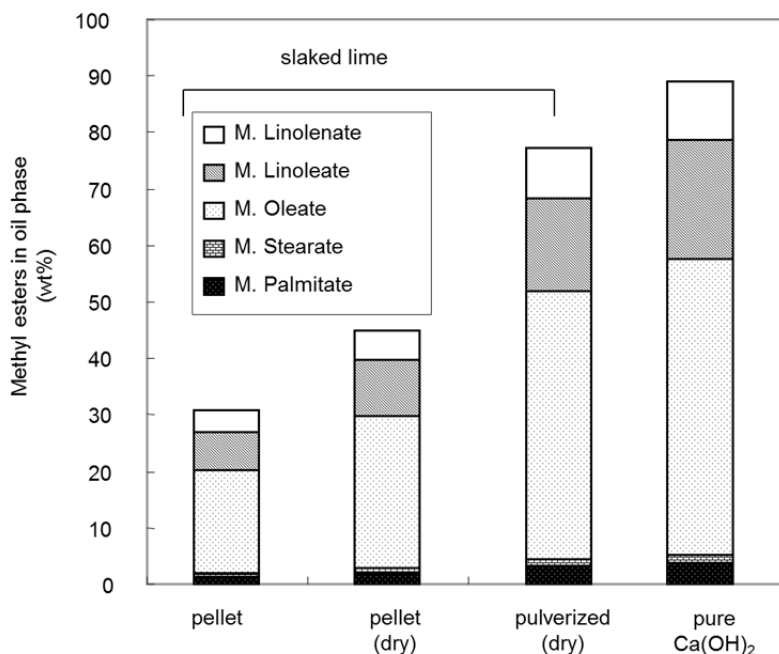
Fig. 9. Experimental results using commercial slaked lime (60% pure) compared to pure Ca(OH)$_2$ catalysts (t=1min, catalysts=10g, MW=700W)

5.1.7 Typical continuous-flow experimental methods and results

For continuous-flow experiments, about 120g of slaked lime pellets was placed in a 100-ml glass flask which served as a reactor. Slaked lime was selected based on the results of our previous work on the investigation of activities of various catalysts. Methanol and rapeseed oil (fixed at a molar ratio of 6) were vigorously mixed and allowed to pass through the reactor at various flow rates. The residence time was calculated based on the void space of the reactor after placing the catalysts.

Fig. 10 shows the typical experimental conditions and results of the continuous process for biodiesel production using microwave. The temperature was controlled at 60°C by supplying microwaves at a maximum peak of 30% corresponding to a power of about 300 W. The flow rates were varied from 12 to 50 ml/min corresponding to residence times of 7 to 1.5 min, respectively.

In runs 1 and 2, high yields were observed initially when most of the microwave irradiation were supplied and absorbed by the reactants and catalysts. However, above the set reaction temperature of 60°C, the microwave irradiation automatically ceased, which could possibly cause an intermittent lowering of the yield. If the temperature decreased below 60°C, the system automatically activated, supplying the microwave again to the reactor. The reaction reached steady state after about 8 sampling runs corresponding to a run time of about 8 and 16 mins for runs 1 and 2, respectively. Other than the thermal effects, microwave effects were evident from the experimental results, and thorough investigation would be necessary to further validate this interesting phenomenon.

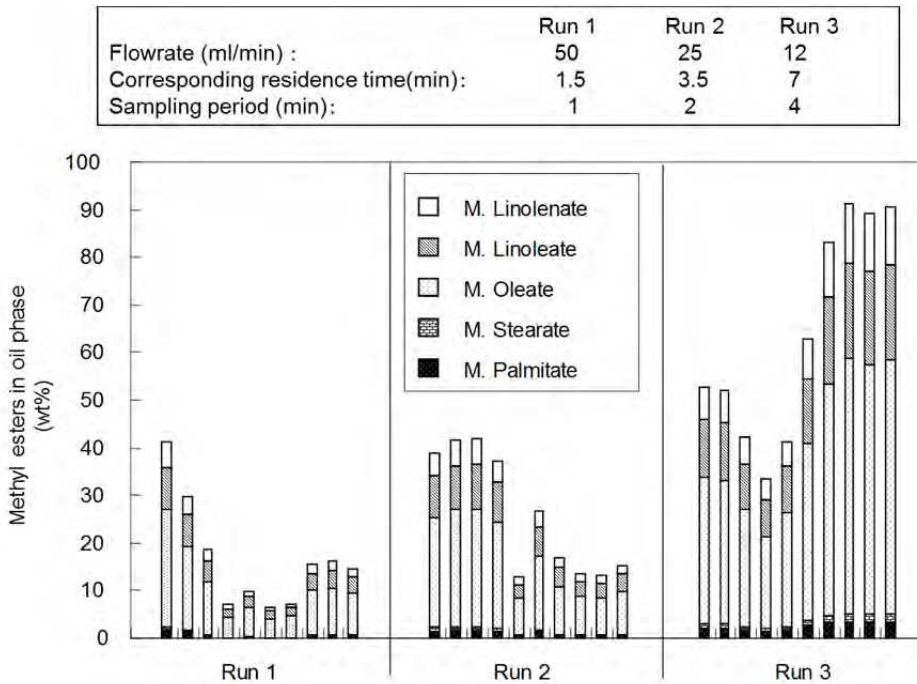|	Run 1	Run 2	Run 3
Flowrate (ml/min) :	50	25	12
Corresponding residence time(min):	1.5	3.5	7
Sampling period (min):	1	2	4

Fig. 10. Typical continuous-flow experimental results for biodiesel production under microwave irradiation

In run 3, steady state was also observed after about 8 sampling runs, and a yield above 90% was obtained in short residence time of 7 min. Mixing of the reactants and catalysts by stirring could improve the homogeneity of microwave absorption and could increase the yield. However, in the case of solid catalyst pellets, recirculation of the reactants or products back to the reactor could be a better alternative to stirring.

5.1.8 Combined reaction and separation in a single cavity

The applicability of a combined reaction and separation technique in a single microwave cavity was also investigated using a Soxhlet-extractor-inspired apparatus. In this experiment, the reactants were supplied on top of the glass reactor vessel. Once a predefined level was reached, the products were siphoned down to a distiller right below the reactor to undergo separation of unreacted MeOH from the products and glycerin under microwave irradiation. The time elapsed from the introduction of the reactants to the reactor until the moment it was siphoned to the distiller served as the residence or reaction time.

In a typical run, the temperature was controlled at 60°C by microwave irradiation at a maximum peak of 30% corresponding to about 300 W. The flow rates were varied from 12 to 50 ml/min corresponding to residence times of 20 to 6 min, respectively.

Results in Fig. 11 showed that a combination of reaction and distillation units in a single cavity could be promising for the separation of unreacted MeOH. However, results of the preliminary experiments showed that the yield was lower than those obtained using the

batch reactor. One possible reason for this was the difference in the sizes of the two reactors. It was also likely that the supplied microwave power in this experiment was not sufficient for both reaction and distillation processes to occur simultaneously and more efficiently. A rigorous investigation to optimize the process are sought in order to further validate the economic feasibility of this proposed process.
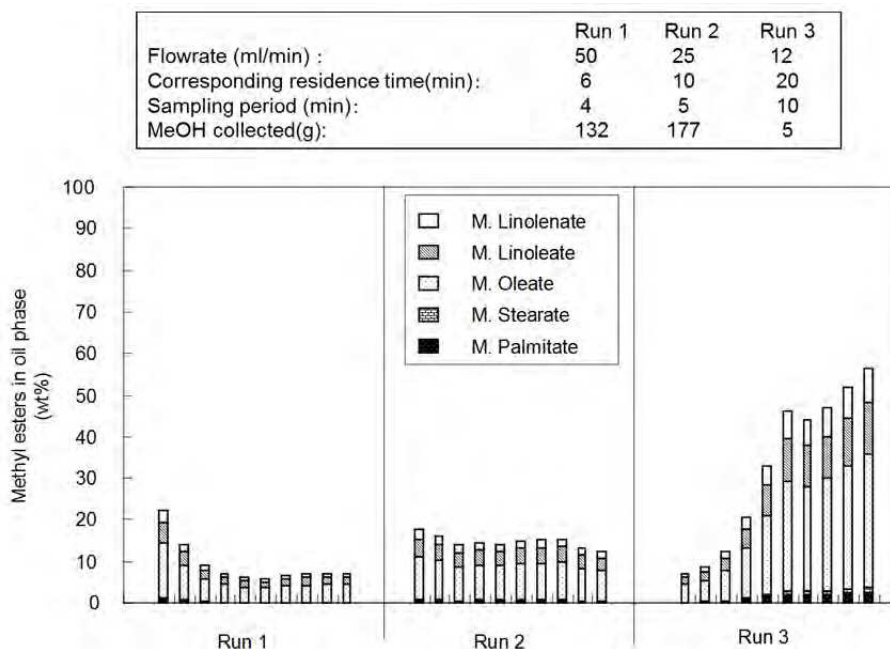

Fig. 11. Results using combined microwave-reactive distillation experiments in a single cavity.

5.1.9 Esterification of free fatty acids present in oil feedstock

Most of the oil feedstocks for biodiesel syntheses contain relatively high amount of fatty acids especially the waste cooking oil. This has become a big hurdle for industrialization of the proposed process, because the presence of fatty acids significantly affects the solubility of Ca-based catalysts in the products. Government quality standards for biodiesel require the level of Ca to be below 5 ppm, while the fatty acid content should not exceed 1wt%. Thus, pretreatment of free fatty acids in oil is necessary prior to transesterification of the triglyceride contents. In this regard, microwave irradiation was also applied to convert free fatty acids into biodiesel. Results in Fig. 12 show an 88% conversion of fatty acids in waste cooking oil in 1 min of microwave irradiation at a power of 700W using ion exchange resin as catalysts. With these results, a two-step process shown in Fig. 13 is proposed for the conversion of waste oil, or any type of oil feedstocks containing high amount of fatty acids, to biodiesel fuel. The process consists of a first step of esterification of fatty acids followed by a second step of transesterification of the triglyceride. While the two-step process seems ideal for the treatment of free fatty acids in oil, this also minimizes the solubility of Ca-based catalysts as a result of the reduction of fatty acid contents.
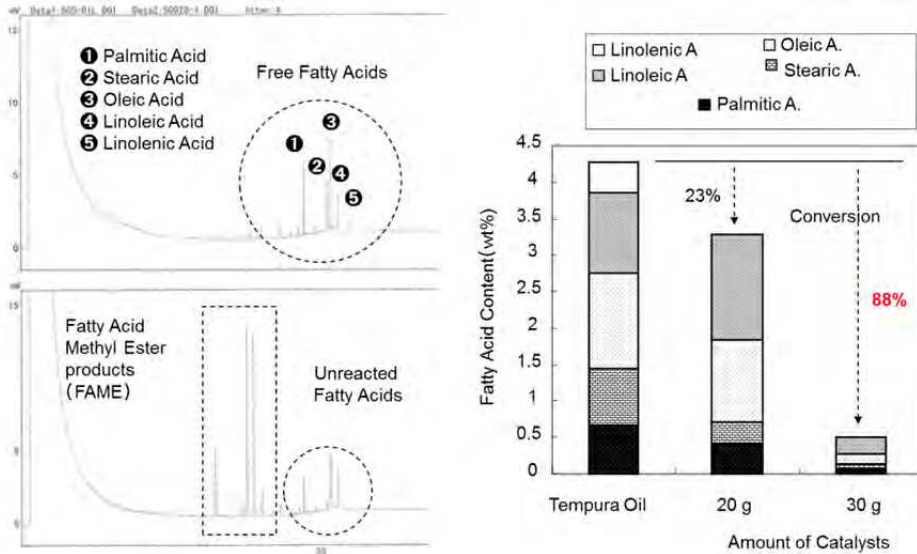
Fig. 12. Results of experiments on esterification of free fatty acids in waste oil using microwave (MWpower=700W, t = 1 min)
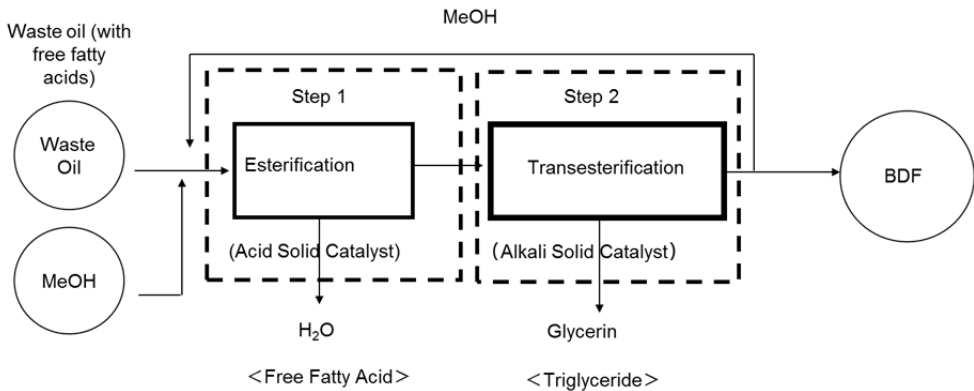

Fig. 13. Proposed two-step process for conversion of waste oil to BDF using solid catalysts under microwave irradiation

5.2 ETBE production

The method was also applied to the synthesis of ethyl *tert*-butyl ether (ETBE) from two biomass-derivable alcohols (ethanol and *tert*-butyl alcohol). ETBE, is commonly used as an additive in gasoline to increase the octane number. Recently, EtOH is the most after-sought biofuel replacement for crude-oil-derived gasoline. However, ETBE is thought to offer equal or greater air quality benefits as ethanol, while being technically and logistically less challenging. Unlike ethanol, ETBE does not induce evaporation of gasoline, which is one of the causes of smog, and does not absorb moisture from the atmosphere.

Microwave-assisted experiments were performed using the same microwave apparatus used for biodiesel synthesis, working at 2.45 GHz frequency, with a power programmable from 0 to 1000W. In a typical run, about 0.25mol of EtOH and TBA, and 20 g of catalyst were placed in a reactor vessel, and heated using a microwave apparatus described above. GC-FID was used for the analysis of the products using an internal standard.

Preliminary experiments on the evaluation of catalytic activities of various solid catalysts such as Amberlyst 15JWET, sulfated zirconia, sulfated charcoal and zeolite showed Amberlyst 15JWET to be the most effective as shown in Fig. 14. The yield of ETBE using sulfated charcoal and and zeolite is almost negligible compared to that of Amberlyst 15JWET and sulfated zirconia. Thus, Amberlyst 15JWET was used in the experiments unless otherwise specified.

Experiments at atmospheric pressure using a batch reactor showed that the yield hardly increased beyond the 20% level. The experiments were extended to continuous flow at various conditions, but the yield did not exceed 35% as shown in Fig. 15. Almost similar results were obtained by other researchers (Japanese Patent JP2007-126450), and the lower yield was likely due to the selective dehydration of TBA to IB, a highly volatile compound that could easily escape from the reaction zone. If IB could further react with EtOH to produce ETBE, better yield could be obtained. Thus, experiments using a sealed reactor vessel were conducted using another microwave apparatus (Milestone Ethos). Fig. 16 shows the conversion of EtOH to ETBE using MW at various power and irradiation time. A maximum yield of about 87% was obtained at MW power of 350W at irradiation time of 1 min. At this condition, the attained temperature was around 87°C, higher than the boiling points of the two alcohols, as shown in Fig. 17. The conversion was also found to be dependent on the amount of catalysts, reaction time and microwave power.
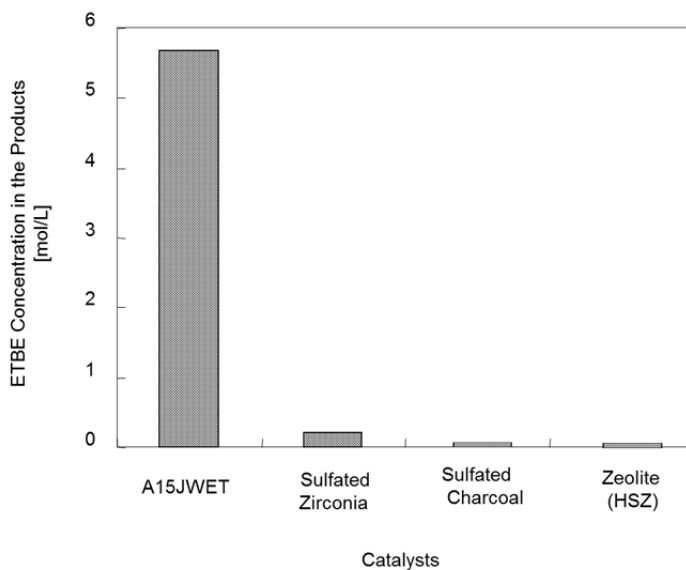

Fig. 14. Comparison of activities of various acidic heterogeneous catalysts for production of ETBE under microwave irradiation (TBA=ETOH=0.25mol, MW=350W, t=1min)

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8
Flowrate (ml/min) :	100	100	50	50	20	20	10	10
Residence time(min):	1	1	2	2	5	5	10	10
Sampling time (min):	1	1	2	2	5	5	10	10
MW duty (%):	13	20	13	20	13	20	13	20
Temperature (°C):	28	67	69	71	70	71	70	71
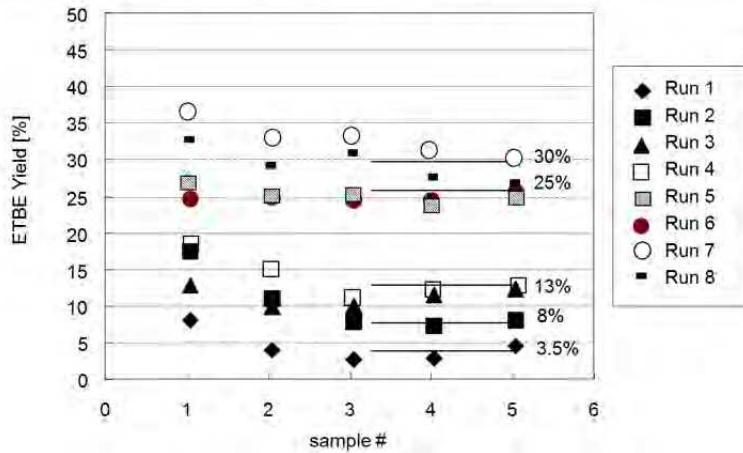
Fig. 15. Typical continuous-flow experimental results for ETBE production using A15JWET ion exchange resin catalysts under microwave irradiation
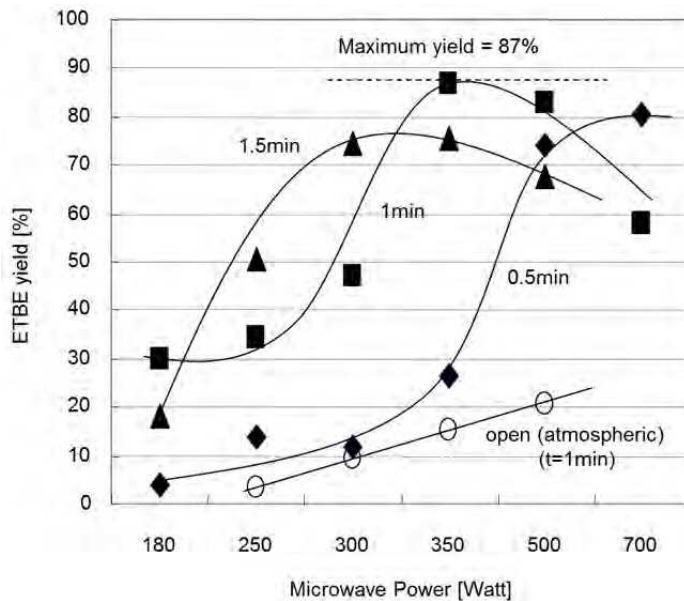

Fig. 16. Yield of ETBE at various microwave irradiation power and reaction time (closed system, TBA=EtOH=0.25mol, A15JWET = 20g)
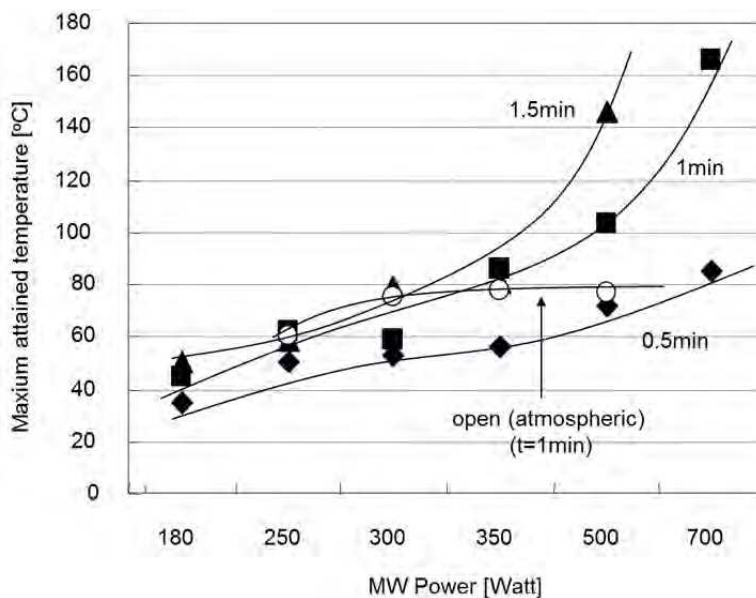
Fig. 17. Maximum attained temperature at various microwave irradiation power and reaction time (closed system, TBA=EtOH=0.25mol, A15JWET = 20g)

	Yin et al. (1995)	Quitain et al. (1999)	Ito et al. (2007) (JP2007-126450)	This Method
Heating Method	Conventional	Conventional	Microwave	Microwave
Reaction Type	batch, open	continuous reactive distillation	batch, open	batch, closed
Solid Catalyst	A15	A15 (pellet)	A15JWET	A15JWET
Reaction Conditions	T = 65°C, t = 4h	T = 75°C, t = 3h	T = 70°C, t = 0.5-4h	MW=350W, t = 1min (T = ~86°C)
g catalyst/ mol EtOH	10	~	8	80
Stirring	YES	NO	YES	NO
Yield(%)	26	38	9 ~ 28	87

Table 2. Comparison of the methods for production of ETBE from TBA and ETOH with the proposed microwave-solid catalyst method

The results of ETBE synthesis using microwave irradiation were summarized in Table 2 in comparison with the methods reported in literature. While several methods reported a conversion in the range of 9 to 38 % using the conventional heating methods, we obtained a

maximum conversion of about 87% under microwave irradiation at a power of 350 W for 1 min. At this condition, the bulk temperature reached about 86 ºC, which was above the boiling points of the two alcohols. The results imply that solvothermal condition (closed system) is ideal for ETBE synthesis because the IB generated from the dehydration of TBA can further react with EtOH to produce ETBE, resulting to higher conversion.

6. Problems associated with the proposed process

Microwave-assisted reactions offer several great advantages to the synthesis of biofuels, however, there are also some drawbacks associated with its use. Microwave could not work well with large quantities of materials, and thus could not be easily converted from laboratory to a multikilogram industrial-scale production. The penetration depth of MW irradiation into the absorbing materials is only a few centimeters, and this significantly limits scale up of the technology.

Microwave irradiation is non-homogeneous and formation of "hotspots" is likely, thus control of reaction is too difficult. Mixing may improve homogeneity, however, with the use of solid catalysts, appropriate methods of mixing remains a challenge.

Safety consideration is another factor for industrial utilization of microwave. The use of batch microwave reactors, for the processing of comparatively large volumes under pressure may not be safe because any malfunction or rupture of a large pressurized reaction vessel, which are usually made of Teflon or glass materials, may result into massive spillage causing significant operational damages to the working place and the environment.

7. Outlook and future prospects

As the demand for biofuels continue to increase in the near future, and while the search for an efficient and low-cost production process continues, the global outlook is positive for the use of microwave irradiation to the synthesis of two most promising biofuels - biodiesel and bioETBE.

To overcome the limitations for scaling up microwave-assisted technology for biodiesel production, development of a continuous process is suggested, but still poses several challenges that require detailed investigation. The future also calls for the development of cheap, effective and stable solid catalysts for the synthesis of the abovementioned fuels.

While the use of microwave irradiation offers great benefits with regards to rapid reaction or synthesis, safety is a big factor to consider in designing a large scale production plant. However, this can be avoided if multilayered compact reactors operating under microwave irradiation can be developed instead.

8. Conclusion

This chapter has presented syntheses of two most promising biofuels, *i. e.* biodiesel and bioETBE, by microwave-assisted heating. Methods for the production of the biofuels reported in literatures were reviewed, and the advantages of the proposed process of using microwave and heterogeneous catalysts were outlined and discussed. The benefits have been indicated using the results of our recent works, however there are some drawbacks that would require thorough investigation prior to its commercialization. Although the field is in its infancy, the outlook is bright for the proposed methods due to foreseen high global

demands for biofuels. The next few years should see development of continuous compact process, along with cheap, effective and stable solid catalysts.

9. Acknowledgements

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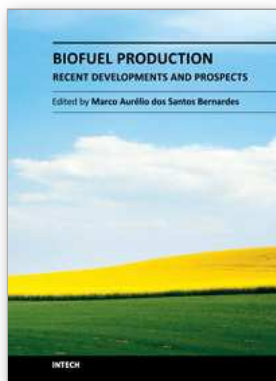
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