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Synthesis of Biomass-Derived Gasoline Fuel Oxygenates by Microwave Irradiation

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Additional information is available at the end of the chapter

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1. Introduction

Recent concerns about climate change and problems associated with the use of fossil-derived fuels and nuclear energy have inspired researchers to seriously explore environmentally benign and economically viable renewable energy and fuels. As potential solution to reduce fossil-derived carbon dioxide (CO₂) emissions from gasoline-run automobiles, addition of biomass-derived oxygenates was proposed. Bioethanol has been considered, however, ether oxygenates such as ethyl *tert*-butyl ether (hereby referred to as ETBE), has gained popularity over ethanol (EtOH) due to its superior properties which blend well with gasoline [1]. ETBE also outranks MTBE as an octane enhancer due to its low blending Reid vapor pressure. Moreover, ETBE is a better option because it is derived from EtOH which can be obtained from biomass. ETBE is produced from the reaction of isobutene (IB) and EtOH, however, the current supply of IB, which is mostly derived from non-renewable crude oil, may not be sufficient to cope up with the expected high demand in the future. For this reason, alternative routes for its synthesis are also currently being explored. *tert*-Butyl alcohol (TBA), which can also be derived from biomass can be employed instead of IB [2]. Research for the development of efficient and energy-saving methods for the production of these gasoline oxygenates had gained significant momentum over the past few years. The application of microwave technology was proposed for the synthesis of the above mentioned gasoline oxygenate.

Microwave technology relies on the use of electromagnetic waves to generate heat by the oscillation of molecules upon microwave absorption. Unlike the conventional heating, the heat is generated within the material, thus rapid heating occurs. Other than the advantages of rapid heating, microwave effects on reaction likely occur, thus obtaining dramatic increase

in the yield even at low temperatures. The benefits of using microwave irradiation to the synthesis of the abovementioned biofuels include energy efficiency, development of a compact process, rapid heating and instant on-off process (instant heating-cooling process), among others.

In this chapter, syntheses of ether oxygenates by microwave irradiation will be discussed and summarized, focusing on our recent studies on microwave-assisted heterogeneously catalyzed processes.

2. Common gasoline oxygenates and their production processes

Gasoline oxygenates such as methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME) and *tert*-amyl ethyl ether (TAEE) are produced commercially by the reaction of olefins (IB and isoamylenes) or C4-C7 hydrocarbons with MeOH or EtOH, in the presence of homogeneous catalysts (e.g. H₂SO₄) or a heterogeneous catalysts (e. g. ion-exchange resin) as shown in Figure 1, in case of ETBE.

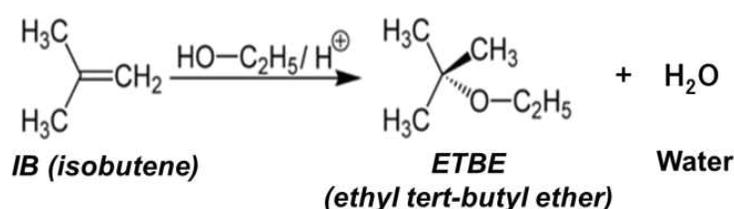


Figure 1. Reaction scheme for ETBE synthesis using IB as a reactant

The differences of blending characteristics of the ether oxygenates are summarized in Table 1.

Property	MTBE	TAME	ETBE	EtOH
Blending Rvp (psi)	8.0	2.5	4.4	18.0
Octane blending	110	105	112	115
Boiling point (K)	328	358	345	351
Oxygen content (wt%)	18.2	15.7	15.7	34.7
Solubility in water	4.3	1.15	1.20	Infinite
Fungibility in gasoline				
distribution system	High	High	High	Low

Table 1. Comparison of blending characteristics of various gasoline oxygenates

Brockwell et al. [3] discussed the process schemes for the production of these ethers. The schemes generally consist of primary reactor, distillation column and additional column to purify the products (e. g. extractor). Due to the upsurge of the demand for gasoline oxygenates, the MTBE process having a world production capacity of 20 million tons per year in 1994 [4] is the most established one. With legislations banning MTBE, it is assumed that the currently existing processes for the production of MTBE can be converted for ETBE production. Similarly, the processes can be integrated for MTBE and TAME production, since these ethers are both produced from MeOH [3].

Some of the patented processes for the production of ether oxygenates are reported in "Refining 1996" [5]. The main features of each process are summarized here.

2.1. CDTECH process

The CDTECH process utilizes C4s and alcohol as feed to a fixed-bed downflow adiabatic reactor. The equilibrium-converted reactor effluent is introduced to the reactive distillation column where the reaction continues. Concurrently, ether is separated from unreacted C4s as the bottom product.

In case of MTBE, the reactive distillation column overhead is washed in an extractor with a countercurrent H₂O stream to extract MeOH. The H₂O extract stream is sent to a MeOH recovery column to recover both MeOH and H₂O for recycle.

This scheme can provide overall IB conversions of up to 99.99% for MTBE process. Conversion is slightly less for ETBE than MTBE. For TAME and TAEE, isoamylenes conversions of 95%+ are achievable.

2.2. ETHERMAX process (by Huls AG and UOP)

This process which uses reactive distillation technology is developed by combined expertise of Huls AG and UOP. The feed consists of MeOH or EtOH and hydrocarbon streams containing reactive tertiary olefins such as isoamylenes and IB. Reaction takes place over an acidic ion exchange resin at mild temperature and moderate pressure.

In the MTBE case, feed first passes through an optional water wash system to remove the resin contaminants. The majority of the reaction is carried out in a simple fixed-bed reactor. The reactor effluent feeds the reactive distillation column containing a proprietary packing where simultaneous reaction of the remaining IB and distillation occur.

Overhead from the reactive distillation column is routed to MeOH recovery, a simple countercurrent extraction column using H₂O, and a MeOH-H₂O distillation column. The recovered MeOH is recycled to the reactor section. Hydrocarbon raffinate is typically sent to a downstream alkylation or oligomerization unit.

2.3. NExTAME and NExETHERS process (by Bechtel and Neste)

In the NExTAME process, the feed is typically light fluid catalytic cracker (FCC) gasoline and/or a light pyrolysis gasoline fraction from which the diolefins are removed by selective

hydrogenation. It is an integrated process consisting of reactors and a distillation tower. Etherification is carried out close to the thermodynamic equilibrium in the reactors from where the reaction product is directed into a distillation tower. A side stream containing unreacted tertiary olefins and alcohol is recycled back into the reactors. This proprietary technology leads to a high conversion of a broad range of olefins and alcohol. The process does not require a separate alcohol recovery section.

Similar to NExTAME, the NExETHERS process consists of fixed bed reactors and two distillation towers. In fixed bed reactors, the etherification synthesis is completed to the thermodynamic equilibrium in the reactors. The reaction product is then directed into the main fractionator. The bottom product of the main fractionator comprises the ether product. A side stream containing unreacted tertiary olefins and unreacted alcohol is recycled back into the etherification section. The second tower is used to recycle the rest of the excess alcohol and to remove oxygenates from C4 cut which can be directed for alkylation without any further oxygenate removal or drying.

2.4. Institutfrançais du pétrole process

The process includes alcohol purification, hydrocarbon purification and a main reaction that uses acid resins. The reactants are converted at temperatures lower than 90 °C and pressures lower than 2 MPa. Then, the main effluents are purified for further applications or recycle.

The reactor column uses CATACOL technology that combines catalysis (in a well-controlled liquid phase) and distillation in separated sections.

2.5. Phillips Etherification process (by Philips Petroleum Co.)

This process uses olefins (i. e. isoamylene and IB) to react with EtOH or MeOH over acidic ion-exchange resin. Mixed olefins from a fluid catalytic cracking unit (FCCU) or steam cracker, along with fresh alcohol are fed to the reactor section. The reactor operation is liquid phase at mild temperature and pressure.

In case of MTBE, high purity MTBE is removed as a bottom product from the fractionator and all the unreacted MeOH is taken overhead. The overhead product is then stripped of MeOH in an extractor using H₂O. The extract is sent to the fractionator, while the denuded H₂O are returned to the MeOH extractor.

2.6. Snamprogetti process (by Snamprogetti SpA)

Similar to Philips Etherification Process, ethers are produced by the addition of alcohol to reactive olefins in the presence of an ion exchange resin at mild temperature and pressure.

The feed passes through two reactors in series – an isothermal tubular reactor and an adiabatic drum reactor. The second reactor effluent goes to the product fractionation tower where the ether product leaves the bottom stream and hydrocarbon is recovered overhead.

In the MTBE process, MeOH in the overhead stream is extracted with H₂O in the MeOH removal tower. The extract from the bottom enters the MeOH-H₂O fractionator, while the MeOH overhead is recycled to reactor feed.

3. Catalysts for synthesis of ether oxygenates

In commercial practice, cation-exchange resins (*e. g.* Bowex 50w, Amberlyst 15 (A15), Lewatit SPC 118 or Nacite) which are sulphonated copolymers of styrene and divinylbenzene (DVB), the cross-linking agent, are used as fixed-bed catalysts for etherification reaction [4].

Other catalysts such as HPA [6] and zeolites [7] are also being considered. Le Van Mao et al. [8] studied the synthesis of MTBE over triflic acid loaded Y-type zeolites. Ahmed et al. [9] developed MFI-type zeolites which were synthesized by the rapid crystallization method for production of MTBE. Collignon et al. [10] evaluated several acid zeolites, including H-Beta (ZB25, ZB75, ZBF, ZBSC), US-Y (CBV760) and ion-exchange resin (Amberlyst 15) for the liquid phase synthesis of MTBE. From all of the works, it was found that all zeolites appear to be as active as Amberlyst 15 but the zeolite catalysts produce less by-products and are more thermally stable than the resin catalyst.

4. Direct synthesis of ETBE from TBA and EtOH

As a replacement for IB, TBA was first used in the synthesis of ETBE over 80 years ago utilizing concentrated H₂SO₄ as a catalyst as shown in reaction scheme in Figure 2 [11]. Habernicht et al. [12] suggested that TBA was preferred over IB as a reactant for ETBE synthesis at elevated pressures and temperatures. The reason for this is that the protonated IB (the key component in ETBE formation) forms only from TBA (not IB) under the conditions employed. Yin et al. [13] also studied liquid-phase synthesis of ETBE from TBA and EtOH catalyzed by ion-exchange resin and heteropoly acid (HPA) at mild pressures and temperatures. Knifton et al. [7] also investigated different types of zeolites catalysts for direct synthesis of ETBE from TBA and EtOH. At temperature ranges of 40-140 °C and pressure ranges of 0.1-7 MPa, liquid-phase synthesis of ETBE resulted to a 40-70 % yield and 65-95 % selectivity.

In our previous work, reactive distillation, a configuration in which the reactive section was located inside the column, was employed to continuously synthesize ETBE from bioethanol and TBA using Amberlyst 15 in pellet form as a catalyst. Results under standard operating conditions indicated that ETBE at about 60 mol% could be obtained in the distillate, and almost pure water in the residue. The conversion of TBA and the selectivity of ETBE were 99.9 and 35.9 %, respectively. The effects of operating conditions on conversion and selectivity were also investigated. Further purification of the distillate using the residue results in 95 mol% ETBE. Simulation of the process was also carried out using ASPEN PLUS simulator, and results showed good agreement with the obtained experimental results as shown in Figure 3 [14].

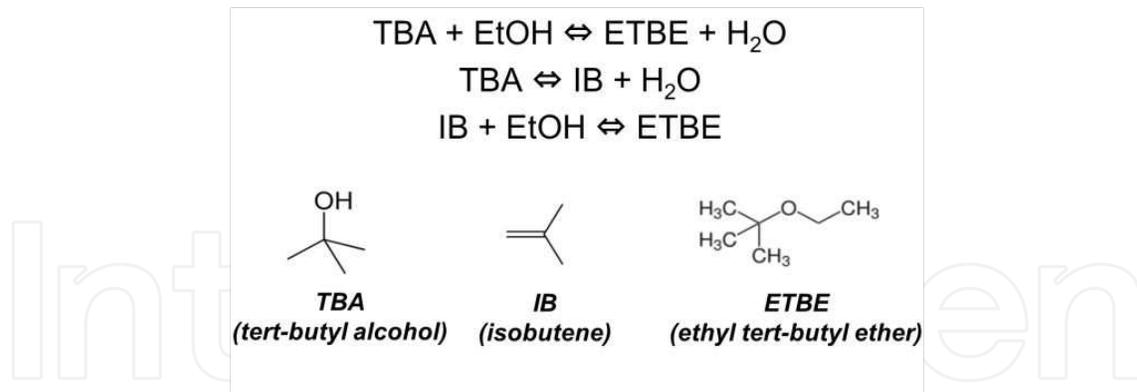


Figure 2. Reaction scheme of ETBE synthesis utilizing TBA instead of IB as a reactant

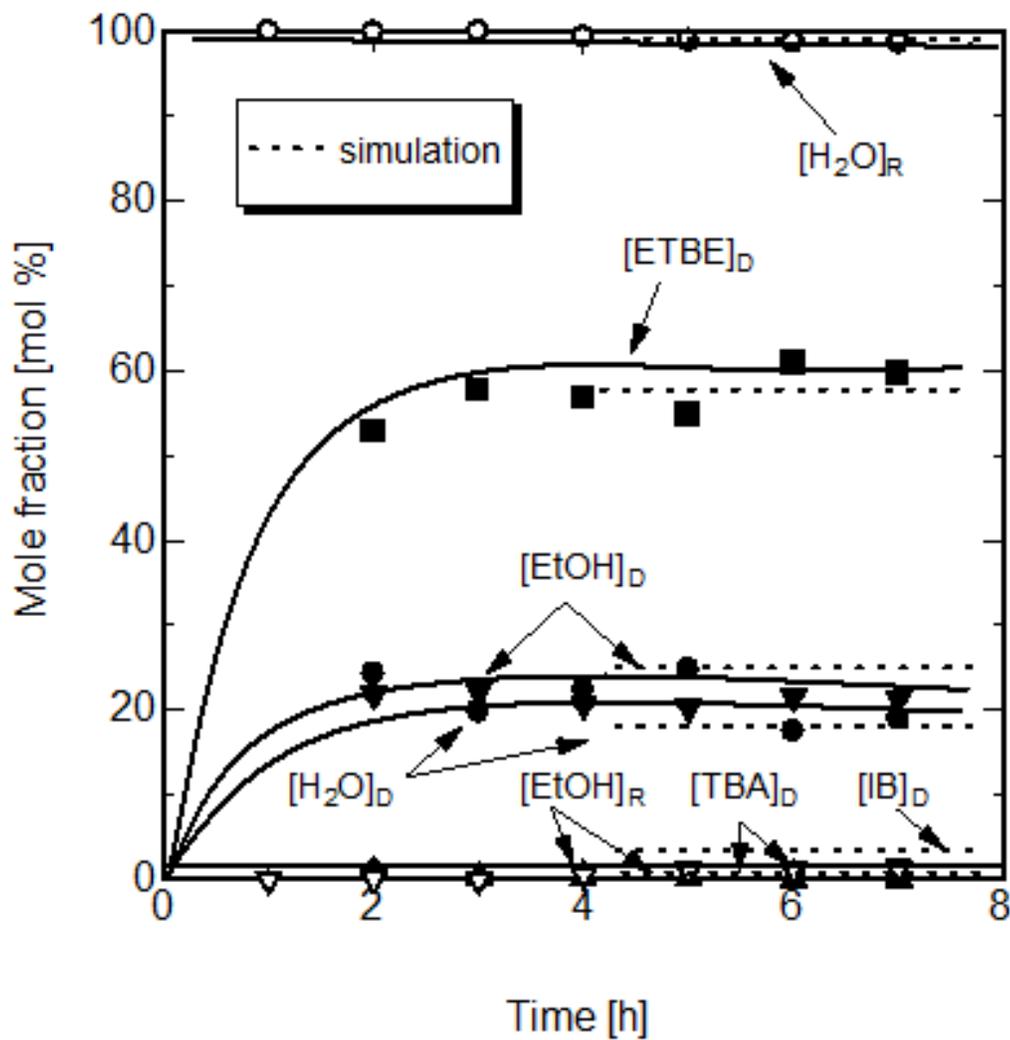


Figure 3. Comparison of concentration profiles of distillate and residue at standard operating conditions (Total feed molar flowrate = 4.13×10^{-3} mol/s, Reflux ratio = 7.0, Catalyst = 0.1 kg, Feed molar ratio = 1:1:38 (TBA:EtOH:H₂O))

5. Fundamentals of microwave technology and its benefits

Microwave technology utilizes 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 [15].

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 [16].

Other than the above mentioned advantages of rapid, internal and selective heating, microwave non-thermal effects on reaction likely occur, obtaining dramatic increase in the yield even at milder conditions. The microwave non-thermal effect is defined as the system response to electromagnetic energy not attributed to temperature variation [17]. 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 [18] comparing them with the thermal effects. The review of Jacob et al [19] 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.

6. Advantages of microwave technology as applied to the solid-catalyzed synthesis of oxygenates from biomass-derived alcohols

Most alcohols, especially the ones used as raw materials for the synthesis of ether oxygenates, have very high microwave absorptivity. Table 2 shows attained temperatures if 50 ml of typical alcohols at room temperature is heated for 1 min at microwave power of 560 W and frequency of 2.45 GHz [15]. The data indicate the benefits of using microwave irradiation, such as effective and efficient use of energy, to the synthesis of ether oxygenates. Reac-

tion relying on microwave can also be easily terminated by turning the supply of microwave irradiation off, thus further reaction or decomposition of the target compounds can be avoided resulting into higher selectivity. Also, reaction could reach completion in shorter time due to rapid heating, thus development of a compact process for a more efficient energy utilization could be possible.

Solvent	T (°C)	Boiling point (°C)
Methanol	81	100
Ethanol	78	78
1-Propanol	97	97
1-Butanol	109	117
1-Pentanol	106	137
1-Hexanol	92	158

Table 2. Attained temperatures of 50 ml of several solvents when heated from room temperature for 1 min at 560 W and 2.45 GHz

Using solid catalysts, instead of homogeneous ones, rapid heating on the surface of the catalysts likely occur upon microwave irradiation. Due this localized heating, the actual temperature at which reaction takes place may be higher than the measured bulk temperature as depicted in Figure 4, thus significantly increasing reaction rates compared to those with the conventional heating.

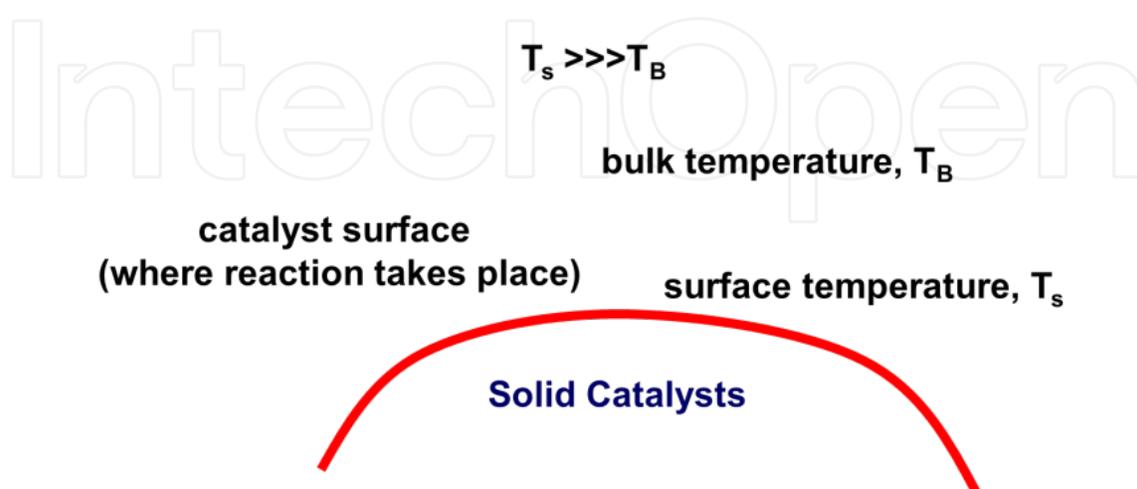


Figure 4. Phenomenon for microwave-assisted solid catalyzed reaction

7. Recent works on microwave-assisted synthesis of oxygenates

Due to the previously mentioned advantages and benefits, we applied microwave irradiation technique to the synthesis of ETBE from EtOH and TBA. Microwave-assisted experiments were performed using various microwave apparatuses working at 2.45 GHz frequency, with a power programmable from 0 to 1000W.

7.1. Batch experiments under atmospheric conditions

At first, experiments were carried out in batch mode under atmospheric pressure using the apparatus, shown as an actual image in Figure 5.

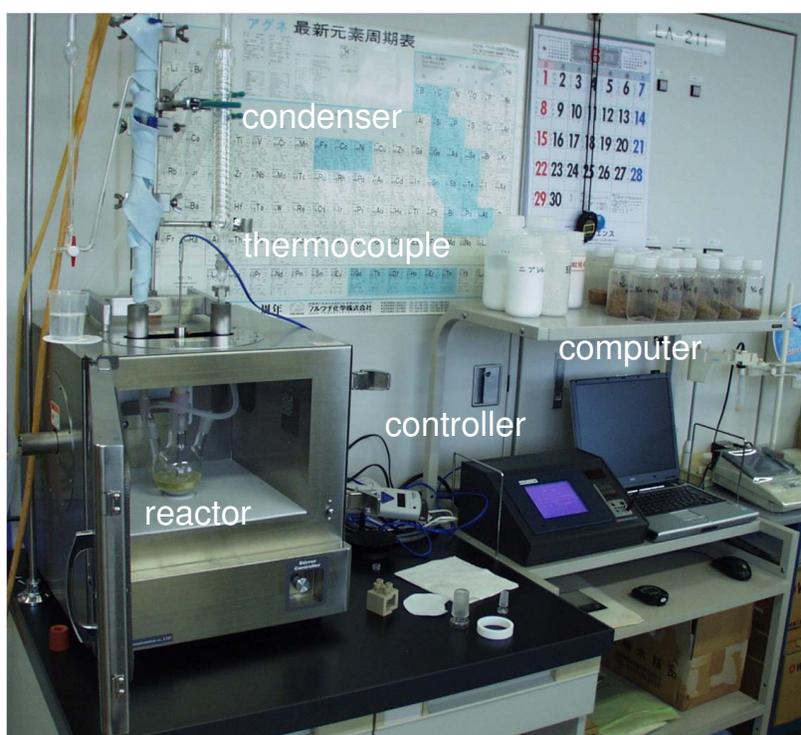


Figure 5. Microwave apparatus for batch synthesis of ETBE under atmospheric conditions (Shikoku Instrumentation Co., Ltd.)

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. Amberlyst 15, an ion exchange resin in H⁺ form was used as catalyst, unless otherwise specified. GC-FID apparatus equipped with a CP-Sil 8CB-MS (60mx0.25mm, df=0.25) column for component separation was used for the analyses of the products. Isopropanol was used as an internal standard.

Figure 6 shows typical experimental results obtained under atmospheric conditions. Experiments at atmospheric pressures using a batch reactor showed that the yield hardly increased above the 20% level. Similar results were obtained by other researchers [20,21], and the low-

er yield was likely due to the selective dehydration of TBA to IB, a highly volatile compound that easily escaped from the reaction zone. The maximum attained temperature was 80 °C, corresponding to the boiling point of the mixture.

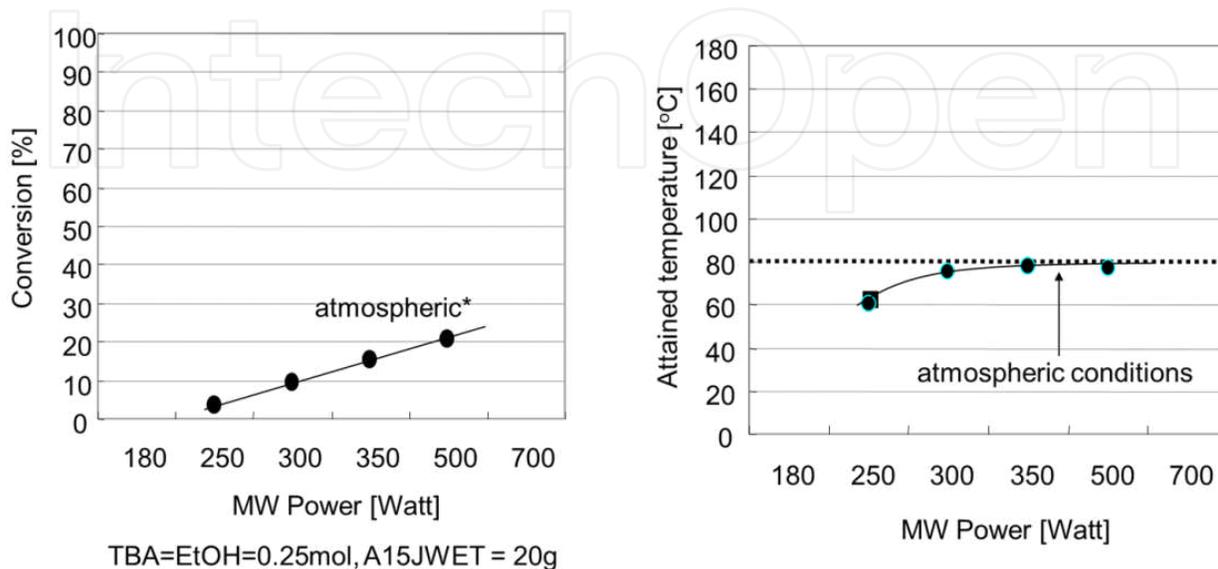


Figure 6. Typical experimental results of batch experiments carried out under atmospheric conditions

7.2. Continuous-flow experiments under atmospheric conditions

Experiments under atmospheric conditions were extended to a continuous flow system using the apparatus shown in Figure 7. A Masterflex digital pump was used to deliver the reactants into the glass reactor filled with about 50g Amberlyst 15 catalyst. The temperature was set at 70 °C. Flowrates were varied to study the effect of residence times. The residence time of the reactants inside the reactor was calculated based on the reactor void space volume and the flowrates. Products were collected continuously after certain time has elapsed, and until the system reached equilibrium.

Results in Figure 8 show that the yield increases with increasing residence time, getting maximum yield of about 30% at a microwave duty of 13%. Increasing the duty to 20% did not have any significant effect on the yield. The maximum yield of 30% obtained using this method was in agreement with our previous studies on reactive distillation [14] and the results obtained by other researchers [20]. This low yield of ETBE was likely due to the selective dehydration of TBA to IB, a highly volatile compound that easily escaped from the reaction zone. If IB could be allowed to further react with EtOH to produce ETBE, better yield could be obtained. Thus performing the experiments in a sealed reactor vessel was thought to be effective in overcoming this limitation under atmospheric conditions.



Figure 7. Microwave apparatus for continuous synthesis of ETBE (Shikoku Instrumentation Co., Ltd.)

Catalyst: Amberlyst A15JWET = 50g;
 EtOH: TBA = 1:1 (mol)

Set Temperature: 70 °C; No Stirring
 Pump: Masterflex Digital Pump

	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
Product Collection(min):	1	1	2	2	5	5	10	10
Microwave duty:	13%	20%	13%	20%	13%	20%	13%	20%
Temperature(°C):	~28	66-68	68-71	68-73	69-71	68-73	69-71	69-73

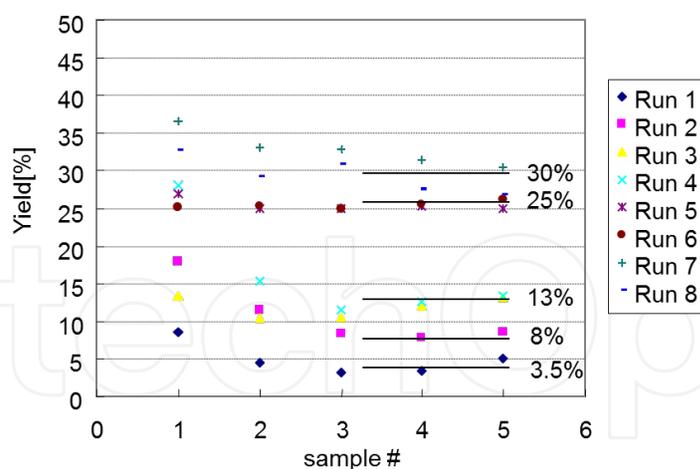


Figure 8. Typical results of continuous-flow synthesis of ETBE

7.3. Microwave-assisted pressurized synthesis of ETBE

Microwave apparatus (Microwave Accelerated Reaction System (MARS 5), CEM Corporation) shown in Figure 9 was used to study the effect of carrying out experiments in a sealed reactor under high pressure and high temperature. The microwave apparatus operates at

2.45 GHz frequency, while the microwave output can be manipulated up to maximum power of 1,200 Watts. This apparatus also consists of a fluoropolymer-coated microwave cavity, a cavity exhaust fan and tubing to vent fumes and a digital computer programmable for 100 programs consisting of up to five stages each. Inside the cavity is an alternating turntable system which can hold up to 13 reactor vessels, thus performing simultaneous experiments on 13 samples is possible.

The sealed Teflon-reactor vessel can handle pressures up to 5MPa and temperatures up to 250 °C. The reactor can be connected to the pressure and temperature control mechanisms of the MARS 5, for online monitoring and for operational safety. Some of the experiments were also carried out in a similar apparatus (Ethos) manufactured by Milestone General Co, Ltd.



Figure 9. Microwave apparatus for pressurized synthesis of ETBE in a sealed reactor vessel (MARS5, CEM Corporation, Japan)

In a typical experiment, about 0.25 mol each of the reactants (TBA and ETOH) were placed inside the vessel, and mixed with 20g of Amberlyst 15 catalysts. The reactor was sealed and connected to temperature and pressure sensors, then microwave was irradiated until the set irradiation time has elapsed. After cooling the vessel to reach a temperature below 50 °C, the reactor was opened and an aliquot part of the products was taken for analysis.

Figure 10 shows the yields of ETBE using MW at various power at irradiation time of 1 min. A maximum yield of about 87% was obtained at MW power of 350W. At this condition, the attained temperature was around 87°C as shown in Figure 11, higher than the boiling points of the two alcohols. The yield was also found to be dependent on the amount of catalysts, reaction time and microwave power.

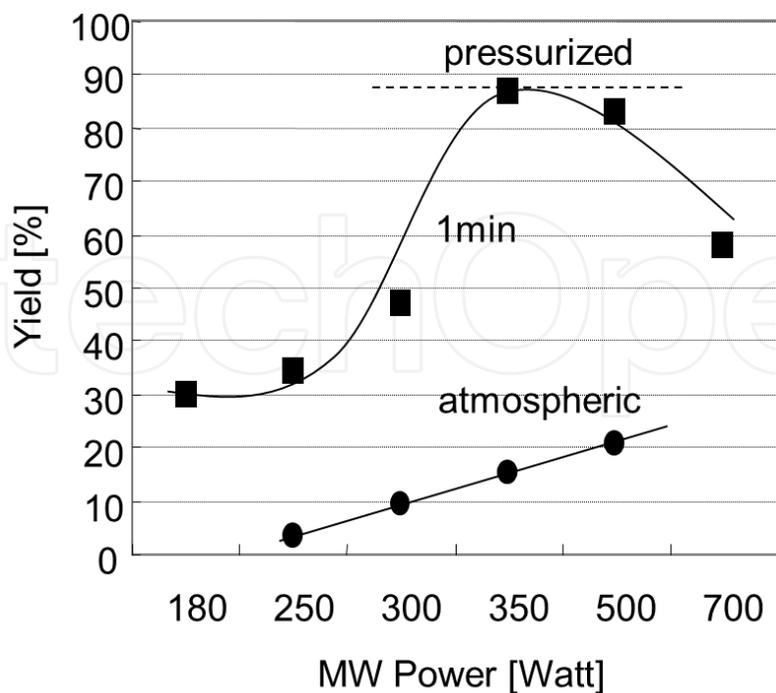


Figure 10. Yields obtained using a sealed reactor compared to those at atmospheric conditions (TBA=EtOH=0.25mol, A15 = 20g)

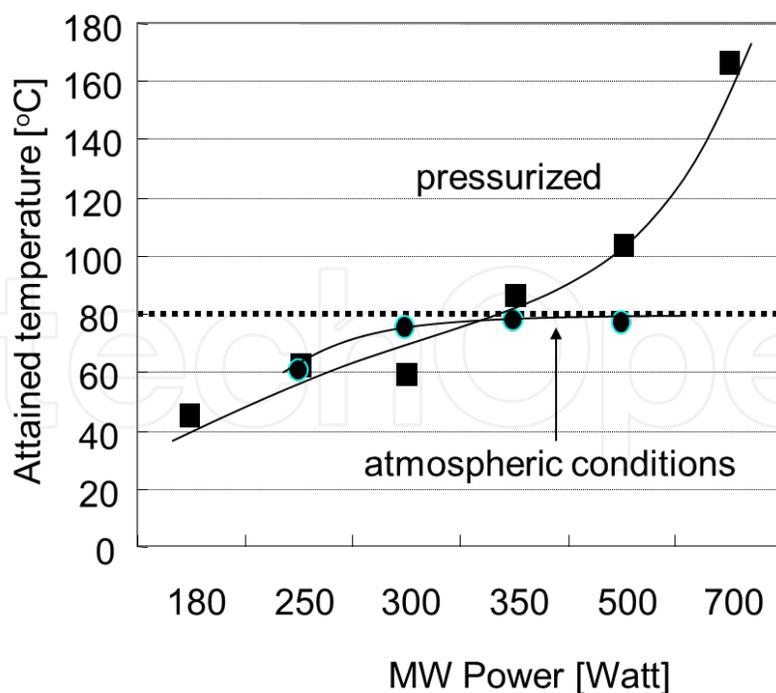


Figure 11. Attained temperature inside the pressurized vessel

7.4. Preliminary studies on combined reaction and separation inside microwave cavity

In an equilibrium reaction, simultaneous separation of obtained products will shift the reaction forward, thus further increasing the yield. In case of ETBE synthesis, simultaneous removal of the product (ETBE) and byproduct (H_2O) could increase the yield of the target compound. Preliminary studies were carried out using the apparatus shown in Figure 12. In this set-up, the catalysts were placed at the middle of the column. Initially, an equimolar mixture of TBA and EtOH was placed in a round bottom flask in B, then microwave irradiated. The products (distillates) were condensed and collected outside the cavity. After 25 min, the collected products in the distillates (D) and bottoms (B) were analyzed of its composition.

Results in Figure 13, show that the bottom consisted of mostly H_2O and unreacted EtOH, while the distillates consisted of ETBE, unreacted TBA, unreacted EtOH and H_2O indicating possibility of simultaneous separation of the products. The future will look at the control and optimization of its operation to obtain better yield of the target compound.



Figure 12. Microwave apparatus for preliminary studies on reactive separation for ETBE synthesis

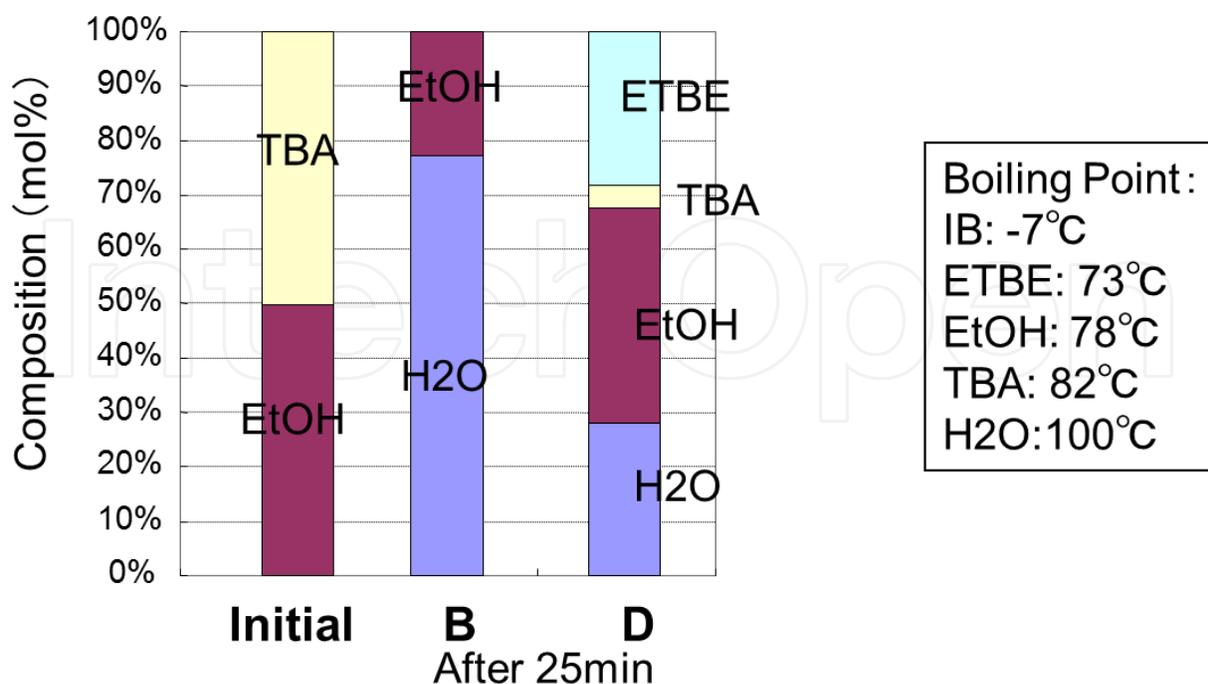


Figure 13. Results of preliminary studies on reactive separation for ETBE synthesis

8. Conclusion and future directions

Microwave irradiation was applied to syntheses of ETBE from biomass-derivable alcohols (TBA and EtOH). The maximum yield obtained under atmospheric conditions was low at around 30%, which agreed with our previous studies on reactive distillation and the results obtained by other researchers. Performing the experiments in a sealed reactor at a microwave power of 350W, and irradiation time of 1 min, the mixture reached pressurized conditions obtaining EtOH conversion closed to 90%. The conversion and yield were found to be also dependent on operating parameters such as temperature, microwave irradiation power, time and amount of catalysts. Preliminary studies on combined reaction and separation process inside the cavity showed promising results but need further investigation for control and optimization of its operation.

The application of microwave irradiation to the synthesis of this promising biofuel offer benefits including energy efficiency, development of a compact process, rapid heating and instant on-off process (instant heating-cooling process), among others. Unlike the conventional heating, the heat is generated within the material, thus rapid heating occurs. Besides, microwave effects on reaction also likely occur, thus obtaining dramatic increase in the yield even at low bulk temperatures.

The benefits have been indicated by the above mentioned results. However, there are some drawbacks including the problems with non-homogeneous heating that would require thor-

ough 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.

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 ETBE. To overcome the limitations for scaling up microwave-assisted technology for ETBE production, development of a compact 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 multi-layered compact reactors operating under microwave irradiation can be developed instead.

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