



Significant influence of microwave dielectric heating on ionic liquid catalyzed transesterification of ethylene carbonate with methanol

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ABSTRACT

This paper reports an energy efficient route for the transesterification of ethylene carbonate (EC) with methanol using ionic liquid (IL) as catalyst through microwave heating. The influence of the reaction parameters such as the microwave irradiation time, power, EC/methanol ratio, and the cation and anion of both 1-alkyl-3-methyl imidazolium and tetraalkyl ammonium salts, was examined under these conditions. Also the heating characteristics of this reaction mixture were examined at various intervals. The coproduction of an equimolar amount of dimethyl carbonate (DMC) and ethylene glycol (EG) were obtained in high yield and better selectivity. Comparative studies were carried out under different reaction conditions with classical heating modes. An induction period observed during conventional reaction can be avoided by microwave dielectric heating. Overall, this study highlights an environmentally benign technology for the production of DMC, a “green reagent”, through microwave irradiation.

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1. Introduction

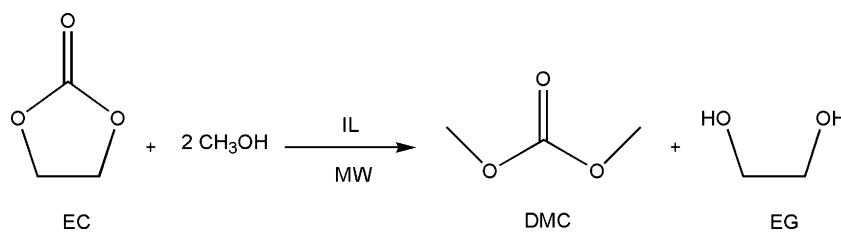
Microwave induced chemical reactions have become a popular technique for promoting faster organic synthesis to heat reaction mixtures, which is evidenced by the increasing number of publications and reviews [1–7]. This rapid and direct heating methods can reduce the reaction times from hours to minutes with high yield and purity of the product [8–11]. Ionic liquid (IL) represent a unique class of reaction media in catalytic processes, and their application in catalysis has entered a period of exploding growth. The use of room temperature IL as environmentally benign media for catalytic processes or chemical extraction is widely recognized and accepted on account of its unique properties, such as negligible vapor pressure, excellent thermal stability, tunable polarity, high coordinating ability, etc. [12–14]. Room temperature IL catalyzed chemical reactions provide excellent results with higher selectivity for the required product. Due to their ionic structure, ILs heat to high temperatures upon microwave irradiation. ILs are also ideal for use in microwave-promoted synthesis chemistry on account of their negligible vapor pressure and high thermal stability [15–17].

Dimethyl carbonate (DMC) a unique chemical compound with versatile reactivity that has found a diversified application in the chemical industry [18–20]. Due to its very high oxygen content, good blending octane values, freedom from phase separation, low

toxicity and rapid biodegradability DMC has established its use as a possible gasoline-blending component. This “green reagent” has attracted considerable attention as a nontoxic substitute for dimethyl sulfate and phosgene which are both toxic and corrosive methylating and carbonylating agents [21,22]. In addition, it has the properties of solvents, reagents and the components needed for specialty materials. DMC is generally synthesized by a reaction between methanol and phosgene [23]. Considerable research has been carried out to establish an eco-friendly route for DMC production. A number of non-phosgene processes for preparing DMC have been developed but few of them are used commercially. In the mid-1980s, Enichem Synthesis patented a procedure for the production of DMC by the cuprous chloride catalyzed oxidative carbonylation of methanol in a slurry reaction system [24,25]. Recently, Ube Industry developed a novel DMC synthesis process that involves a Pd catalyzed reaction between methyl nitrile and carbon monoxide [26]. The above two processes used methanol, carbon monoxide and oxygen as raw materials. In contrast, the utilization of carbon dioxide as a raw material has been attempted, and some catalysts have been reported to be effective for the synthesis of DMC from methanol and carbon dioxide or from epoxide, carbon dioxide and methanol [27–33]. DMC can also be synthesized by a transesterification reaction between ethylene or propylene carbonate and methanol along with ethylene or propylene glycol. For this ester exchange reaction various catalysts, both homogeneous and heterogeneous have been reported to be efficient [34–38].

In this study, we monitored the microwave heating characteristics of EC–methanol reaction mixture in the presence of various ILs.

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Scheme 1. Transesterification of ethylene carbonate with methanol.

Through this flash heating technique the transesterification for the coproduction of DMC and EG was established in a relatively short reaction time with high selectivity (Scheme 1) under mild reaction conditions. In our previous studies, different types of ILs were utilized as catalyst for transesterification reaction of EC or Propylene carbonate with methanol using conventional heating methods but high pressure of CO₂ is needed to stabilize EC from decomposition under these conditions [39,40].

2. Experimental

2.1. Materials

Anhydrous ethylene carbonate (99%) and anhydrous methanol (99.8%) were purchased from Aldrich and used without further purification. All types of ILs were kept in glove box under argon atmosphere and used without further purification. 1-*n*-butyl-3-methyl imidazolium chloride (BMImCl, ≥90.0%), 1-*n*-hexyl-3-methyl imidazolium chloride (HMImCl, ≥97.0%), 1-*n*-octyl-3-methyl imidazolium chloride (OMImCl, ≥97.0%), 1-ethyl-3-methyl imidazolium nitrate (EMImNO₃, ≥99.0%), 1-ethyl-3-methyl imidazolium trifluoro methane sulfonate (EMImOTf, ≥98%), tetrabutyl ammonium chloride (TBAC, ≥97%), tetraoctyl ammonium chloride (TOAC, ≥97%), tetradodecyl ammonium chloride (TDAC, ≥99%) and tetrabutyl ammonium bromide (TBAB, ≥99%) were purchased from Fluka chemicals. 1-Ethyl-3-methyl imidazolium chloride (EMImCl, 98%), tetrapropyl ammonium chloride (TPAC, 98%), tetrahexyl ammonium chloride (THAC, 96%), and tetrabutyl ammonium iodide (TBAI, 98%) were obtained from Aldrich. 1-Ethyl-3-methyl imidazolium hexafluoro phosphate (EMImPF₆, EP) was supplied by TCI laboratory chemicals.

2.2. Microwave equipment

Microwave irradiation was carried out in a multimode microwave reactor (Korea Microwave Instrument Corporation, KMIC 2000) with a continuously adjustable power from 0 to 2 kW using a 3-stub tuner operating at a frequency of 2.45 GHz. The surface temperature of the reactor was measured using an IR temperature detector. The reaction mixture was stirred with magnetic stirrer fixed under the microwave cavity.

2.3. Microwave induced transesterification of EC with methanol

All reactions were carried out in a 100 ml Pyrex glass reactor. A typical procedure is as follows: EC (2.2 g, 25 mmol), and the required amount of methanol (50–200 mmol) and IL (2 mmol) were placed in a reactor and capped inside the microwave cavity. The required microwave power was set and irradiated for the set time. The pressure inside the reactor was monitored using a pressure gauge, and for safety purpose a cracking pressure valve was set to 21 bar. After irradiation, the reactor was allowed to cool to room temperature and the products were analyzed by gas chromatography (Agilent6890, HP-5 column; 30 m, 0.320 mm, 0.25 μm, 60 to 325/350 °C) through comparison with authentic samples. EC con-

version and DMC yield were obtained from the GC results. The products were identified by GC–MS (Agilent6890 GC (DB-5 column) fitted with a TOF-MS Pegasus III mass spectrometer). The yield of each product was calculated as the number of mol of the product formed per mol of the ethylene carbonate. For comparison, the reactions were carried out using a conventional process in a 50 ml stainless steel autoclave.

3. Results and discussion

In order to take the advantage of the microwave heating effect, it is preferable to carry out the reaction in the presence of a compound with high dielectric properties. Equimolar amounts of DMC and EG were produced in relatively good yield with high selectivity from the transesterification of EC with methanol in the presence of various ILs as catalysts. The temperature profile for the representative reaction mixtures as a function of irradiation time was probed and its significance on reaction is discussed in detail. Optimization of reaction condition was carried out by varying the reaction parameters such as the microwave irradiation time, microwave power, EC/methanol ratio and various types of ILs. For comparison, a series of conventional reactions were implemented at various reaction conditions. The detailed experimental results are reported in the following discussions.

3.1. Effect of reaction time and microwave power

The effect of the microwave irradiation time was studied using BMImCl as catalyst at 100 W microwave power. The results are shown in Fig. 1. It was demonstrated from the figure that EC conversion increased steadily with increasing reaction time until 30 min, subsequently the conversion of EC showed slight improvement. On the other hand, although the DMC yield increased in accordance with the EC conversion, the yield curve showed a plateau

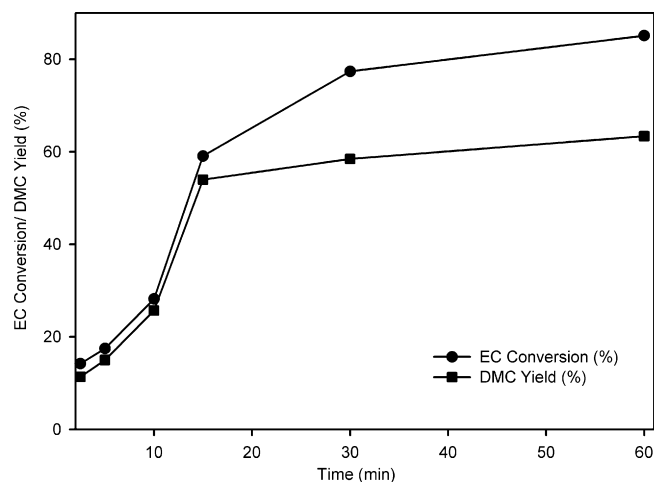


Fig. 1. Effect of reaction time (reaction conditions: EC/methanol/IL = 12.5/100/1, IL = BMImCl, MW power = 100 W).

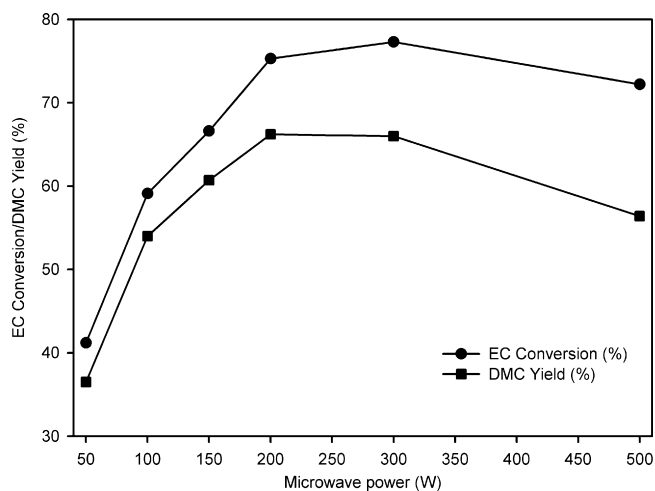


Fig. 2. Effect of microwave power (reaction conditions: EC/methanol/IL = 12.5/50/1, IL = BMImCl, time = 15 min).

after 30 min. This might be because at prolonged irradiation time, dielectric heating may promote the decomposition of EC instead of converting it into the transesterified products. Hence shorter reaction time is more suitable for better catalytic activity. Fig. 2 shows the effects of microwave power on the EC conversion and DMC yield. Higher conversion with high DMC yield was obtained at 300 W microwave power in a short time of 15 min irradiation. Thereafter the conversion of EC showed a steady increase with no appreciable improvement in yield. At 500 W DMC yield was significantly lower. A higher power or a longer irradiation time may be expected to promote rapid heating of the reaction mixture which in turn catalyzed the decomposition of EC to ethylene oxide and CO₂ as indicated by the pressure increase after the completion of reaction. This suggests that a lower microwave power and shorter reaction time is ideal for transesterification under microwave irradiation.

3.2. Effect of EC/methanol ratio

The effectiveness of microwave heating depends greatly on the concentration of the reaction mixture. In order to utilize this property, the reactions were performed at various EC/methanol ratios and the results are shown in Fig. 3. EC conversion as well as the DMC yield increased with decreasing EC/methanol ratio. Transesterification is an equilibrium reaction, stoichiometrically 2 mol

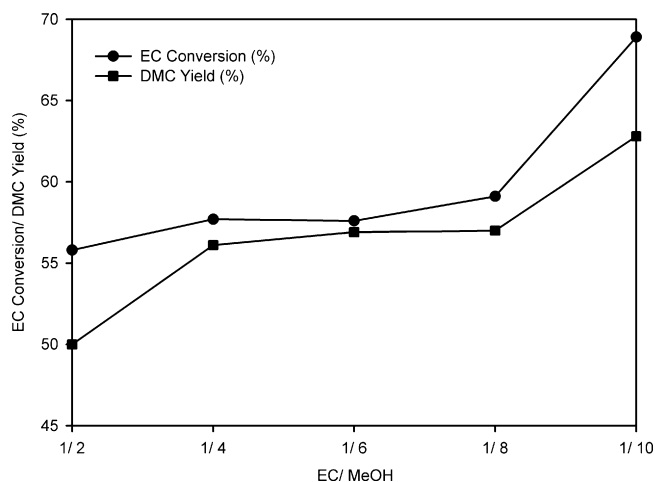


Fig. 3. Effect of EC/methanol ratio (reaction conditions: IL = BMImCl 0.08 mmol, MW power = 100 W, time = 15 min).

Table 1
Effect of imidazolium based IL: variation of cations and anions.

Entry	Catalyst	EC conversion (%)	DMC yield (%)
1	EMImCl	47.5	45.6
2	BMImCl	59.1	57.0
3	HMImCl	60.0	55.6
4	OMImCl	56.2	54.1
5	EMImPF ₆	26.4	15.1
6	EMImNO ₃	38.0	36.7
7	EMImOTf	6.2	1.7

Reaction conditions. EC/methanol/IL: 12.5/100/1; MW power: 100 W; time: 15 min.

of methanol is required for complete transesterification of 1 mol of EC. In classical heating methods an excess of alcohol, lower EC/methanol ratio drives the reaction toward the transesterified product. Better results were observed at higher EC/methanol ratio under the influence of microwave irradiation. However, for a very high ratio of 1/2 the selectivity was found to be lower. Considering the higher conversion and selectivity, EC/methanol ratio of 1/8 has been taken as the optimum ratio for further studies.

3.3. Effect of cations and anions of imidazolium/quaternary ammonium based IL

Conventionally, the activity of the IL catalyst depends greatly on the bulkiness of the cation as well as the nucleophilicity of the anion. A longer chain length of alkyl substituent on the cation and a higher nucleophilicity of the anion of IL generally results in better catalytic performance. Therefore, different types of ILs with different alkyl substituents and anions on the imidazolium moiety were used to examine the effect on the catalytic properties under the influence of microwaves. Table 1 gives the summary of the results. The first four entries explain the effect of the alkyl substituents on catalytic activity. Although the EC conversion showed the order of EMImCl < BMImCl < HMImCl > OMImCl, the difference in activity was very narrow compared with conventional results [40]. The order of catalytic activity was proved to be similar to the previous reports. But the narrowness of these results could be explained on the basis of temperature generated during microwave irradiation, which will be discussed in the following section. Apart from this dielectric constant (ϵ_r) of IL depends markedly on the nature of the anion, therefore the EMIm cation with the OTf⁻, PF₆⁻, NO₃⁻, Cl⁻ anion was selected. Despite having a higher dielectric constant and thermal stability of IL bearing OTf⁻ and PF₆⁻, the catalytic activity of these ILs were lower than those with Cl⁻ (entries 1, 5–7). The conversion of EC increased in the order of OTf⁻ < PF₆⁻ < NO₃⁻ < Cl⁻, which is consistent with the order of anion nucleophilicity. An imidazolium salt with a more nucleophilic anion might be more active in the production of DMC. From these observations, it is suggested that the nature of the anion is a decisive factor in determining the catalytic activity of ILs.

Considering the superior catalytic activity of tetraalkyl ammonium halides over 1-alkyl-3-methyl imidazolium halides under conventional heating mode, its influence under microwave irradiation was also investigated (Table 2). The higher activity of the tetraalkyl ammonium salt arises from the bulkiness of the tetrahedral ammonium ion, which forces the halide ion away from the cation, resulting in less electrostatic interaction between the cation and anion [41]. Consistent with the classical heating methods EC conversion increased with increasing the bulkiness of the tetrahedral ammonium ion up to a hexyl substituent (entry 3), after which the activity decreased. The presence of longer alkyl chain substituent on the ammonium ion causes steric hindrance on the active site, which impedes access of reactants. On the other hand, changing the anion from Cl⁻ to Br⁻, did not show any significant influence on the catalytic activity under microwave field (entries 2

Table 2
Effect of quaternary ammonium based IL: variation of cations and anions.

Entry	Catalyst	EC conversion (%)	DMC yield (%)
1	TPAC	74.8	71.4
2	TBAC	78.8	75.9
3	THAC	85.6	79.4
4	TOAC	72.4	69.7
5	TDAC	61.6	60.2
6	TBAB	78.4	66.0
7	TBAI	85.3	81.7

Reaction conditions. EC/methanol/IL: 12.5/100/1; MW power: 100 W; time: 15 min.

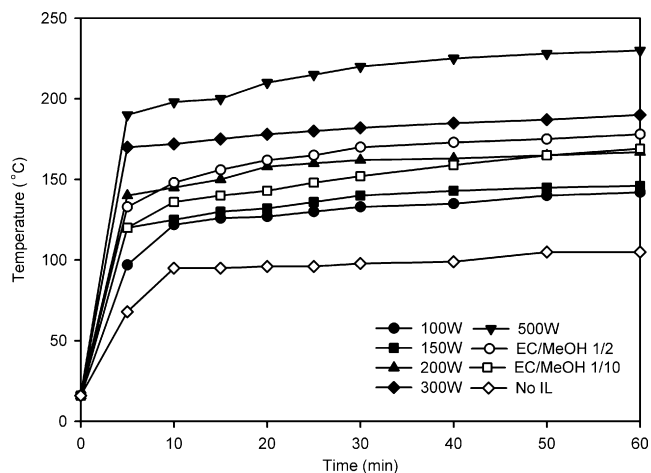


Fig. 4. Heating profile for EC/methanol/IL reaction mixtures at different microwave power and EC/methanol ratio.

and 6). However, the TBA cation bearing I^- showed a higher activity than the other quaternary ammonium salts.

3.4. Heating profile of microwave energy on transesterification reaction mixtures

Since the temperature produced during microwave irradiation significantly affect the reaction kinetics, we examined the heating characteristics of reaction mixtures under a variety of reaction conditions and are presented in Figs. 4 and 5. It was observed that in all cases an equilibrium state was established after a rapid increase in temperature within the initial 15 min of the irradiation time. In the absence of IL, the increase in

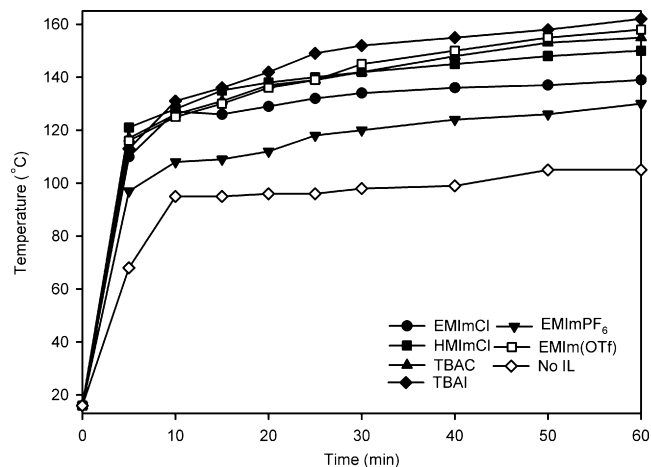


Fig. 5. Heating profile for EC/methanol/IL reaction mixtures in the presence of various IL catalysts at 100 W.

temperature was quite low and no reaction was observed. The temperature acquired in this case might be due to the dielectric heating of EC and excess methanol in the reaction mixture. It could be assumed from this observation that IL acts as a catalyst for the transesterification reaction, microwaves alone did not catalyze the reaction. Whereas the heat generated was exceptionally high by the presence of catalytic amount of IL. In the presence of IL catalyst the transesterification reaction leads to the formation of EG with high dielectric loss ($\tan \delta = 1.35$, $\epsilon_r = 37.0$), which might maintain a higher temperature for a longer irradiation time.

In order to put an insight on the influence of IL on transesterification reaction together with microwave irradiation, the heating characteristics of microwave irradiation was analyzed in terms of the reaction conditions. Fig. 4 shows the influence of microwave power and the EC/methanol ratio on the heating profile. In all the cases temperature increased rapidly to a high value within 15 min and increased slowly reaching a plateau thereafter. The equilibrium temperature increased with increasing microwave power. In particular, at 500 W microwave power, the temperature reached more than 200 °C within 10 min. From the results of reaction time and microwave power, it can be concluded that longer reaction time and higher microwave power drifted the reaction towards a lower profile. It is clear from the temperature study that the maximum reaction temperature is attained at a shorter irradiation time. This high temperature may promote the decomposition of EC rather than its transesterification with methanol. In a separate experiment without CO_2 pressure, it is proved that IL is capable of catalyzing the decomposition of EC to EO and CO_2 [42]. Thus a higher microwave power and longer reaction time results in a lower selectivity. Taking into consideration of EC/methanol ratio study, the temperature observed for 1/2 is higher than 1/10, higher the EC/methanol ratio higher the equilibrium temperature was. This could be due to higher dielectric properties of EC ($\epsilon_r = 89.6$) than methanol ($\tan \delta = 0.66$, $\epsilon_r = 32.6$). At higher EC/methanol ratio, the reaction mixture has higher concentration of EC, which has the higher ϵ_r than methanol. On the other hand, a decrease in EC/methanol ratio might result in a decrease in temperature due to the dilution by methanol. In addition, the level of EG formation in the reaction mixture during the course of reaction caused the temperature to rise up. Due to this reason there was no significant difference in the heat produced in both cases after starting the microwave irradiation.

Recently, Wakai et al. reported that ϵ_r decreases with increasing chain length of the alkyl residue of the 1-alkyl-3-methyl imidazolium salt. The same trend was observed for anions with the sequence, $OTf^- > PF_6^-$ [43]. In contrast to their observations, the temperature of the reaction mixture increased considerably after changing IL from EMImCl to HMIImCl (Fig. 5), whereas the anionic trend was found to be same as observed previously. As observed from entries 1 and 3 in Table 2, HMIImCl catalyst produced higher yield of DMC and equimolar amount of EG. This might be the reason for the increase in temperature and catalytic activity. Since the temperature remained below 140 °C, a higher selectivity for the products was observed. Even though the temperature produced for OTf^- was higher, the catalytic activity followed a reverse order. Compared with the imidazolium based IL, significant heat generation was observed in the presence of quaternary ammonium salts. In the case of TBAC and TBAI the higher concentration of EG produced in the reaction mixture absorbs the microwave radiations more effectively for the rapid heating. From these observations it is clear that IL is not only acting as a catalyst but also a heat generating additive. Since for each mole of EC conversion corresponding moles of both DMC and EG are produced simultaneously, which showed a significant influence on improving the reaction conditions by promoting the heating rate.

Table 3
Comparison with conventional synthesis.

Entry	Temperature (°C)	Time (min)	EC conversion (%)	DMC yield (%)
1		30	1.4	1.1
2	80	60	27.5	6.8
3		360	44.1	12.0
4	100	30	3.7	3.0
5		60	29.0	6.8
6		360	70.9	32.3
7	120	30	18.5	6.4
8		60	39.9	12.0
9		360	83.1	45.0

Reaction conditions. EC/methanol/IL: 12.5/100/1; IL: BMImCl.

3.5. Comparison with conventional transesterification reaction

A series of reactions were carried out at different temperatures and times in order to establish the competency of microwave heating for transesterification with conventional mode of heating. Generally extreme conditions such as high pressure, high temperature, and longer reaction time is needed for better yield and selectivity under classical heating mode. In our previous work we performed the reaction under CO₂ pressure using ILs as catalyst. Under pressurized condition, the extent of EC decomposition could be reduced to lower level. Unlike classical heating mode, higher yield and better selectivity were achieved in a considerably shorter time of 15 min by microwave heating, moreover the rate of decomposition of EC was lower. Table 3 summarizes the transesterification of EC with methanol using BMImCl as a catalyst. At 80 °C, the reaction gave a lower conversion and yield than microwave heating methods (entry 2, Table 1) even after 6 h of reaction time. A longer reaction time and higher temperature is needed for better catalytic activity under conventional heating mode (entries 2–3, Table 3). Indeed, at higher temperatures, a better performance was observed at a longer reaction time of 6 h, whereas the selectivity for the products is found to be lower than microwave irradiation. Almost similar results for entry 9 at 120 °C for 6 h were obtained at an irradiation time of 60 min with much higher selectivity. These comparative experiments confirms the energy efficiency of microwave irradiation for the coproduction of DMC and EG by the transesterification of EC with methanol. A comparative study has been conducted between microwave and conventional transesterification reaction in terms of EC conversion versus reaction time. The results are shown in Fig. 6. From the first curves at 80 and 100 °C, it is clear that there is an induction period to activate the reaction

by IL towards transesterification reaction. Whereas at 120 °C the induction period is found to decrease. But for microwave assisted reaction, there is no significant induction period observed. The better activity of ionic liquid as a catalyst under microwave irradiation may be due to the rapid polarization of ionic species than classical heating. Hence better performance of IL as catalyst can be achieved by coupling the ionic properties of IL with the microwave dielectric heating.

According to the earlier reports, the base catalyzed ester exchange reaction takes place through the activation of methanol by the catalyst [35]. The microwaves found incapable of converting EC and methanol to DMC and EG without the presence of IL. From these experimental observations, the reaction could be expected to follow through the ring opening of EC by methoxy anion produced by IL induced polarization of methanol. Under microwave dielectric heating, the polarization of EC by IL may also help the ring opening quite instantaneously resulting higher conversion and selectivity. The heating profile of reaction mixture could be expected to put light on this mechanistic point of view in such a way that higher concentration of EC increases the reaction bulk temperature. Besides, the increased generation of heat under these condition might be due to the rapid polarization of EC followed by its ring opening. The rapid formation of equimolar mixture of DMC and EG increased the temperature further. A higher yield of the products was observed under microwave flash heating due to this efficient polarization of EC and methanol in the presence of IL as a catalyst.

4. Conclusion

This study examined the heating characteristics of a polar mixture of EC–methanol in the presence of IL. The superior dielectric properties of the reactants as well as the improved heating characteristics of the IL under microwave irradiation produced favorable conditions for the transesterification reaction. A higher yield of DMC with higher selectivity was observed in a shorter reaction time of 15 min. Compared with conventional transesterification reactions, microwave heating occurred quite rapidly to obtain comparable conversion and yield. Unlike conventional IL catalyzed transesterification, the alkyl chain length of the cation showed less significance on the catalytic activity due to the dielectric heating of microwaves. The nature of anion also played a decisive role in maintaining the activity of IL as catalyst. The appropriate selection of the cation and anion of the IL enhanced the heating characteristics of the reaction mixture, which improved the catalytic activity. Overall, a greener approach for conducting transesterification reaction was established through specific microwave heating.

Acknowledgements

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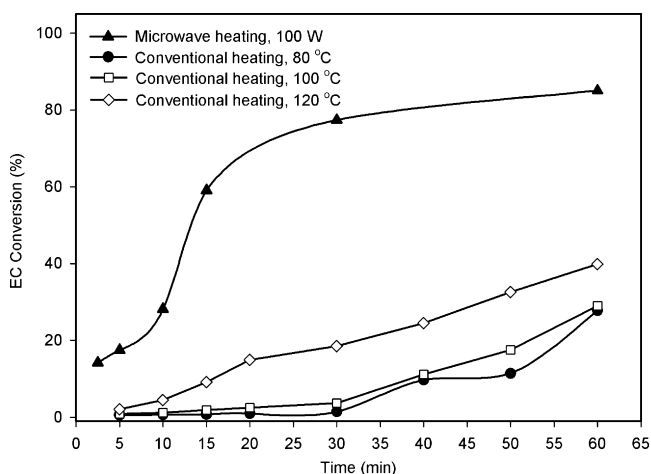


Fig. 6. Conversion versus time under conventional and microwave reaction.

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