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Research paper

Equilibrium and thermodynamic parameters for heterogeneous esterification of butyric acid with methanol under microwave irradiation

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Abstract

Synthesis of methyl butyrate was investigated in a microwave irradiated batch reactor in presence of acid ion-exchange resin catalyst, amberlyst-15. Methyl ester was heterogeneously produced by the reaction between butyric acid and methanol. Effect of reaction parameters of temperature (323–343 K), catalyst loading (0–10.5% w/w), alcohol to acid ratio, M (1–5), and amount of molecular sieves added (0–13.5% w/w) on conversion were studied. Equilibrium conversion of 92.6% was achieved in 60 minutes under microwave irradiation. Equilibrium constants at varied temperatures and dependency of equilibrium constant on temperature were studied. Equilibrium constant and equilibrium conversion showed increase with the increase in temperature as expected as per le-Chatelier principle. Van't Hoff plot for esterification of butyric acid was linear with negative slope indicating that reaction was endothermic. Comparative study showed that microwave irradiated method for methyl butyrate synthesis to be very efficient and fast compared with conventional and ultrasound assisted routes under optimized reaction conditions.

Keywords: Microwave; Esterification; Butyric acid; Methanol; Amberlyst-15; Equilibrium constant

1. Introduction

Esterification is a reversible reaction between carboxylic acid and organic alcohol producing ester and water. The desired product, ester, is a useful product which has applications in chemical industry as solvents, emulsifiers, plasticizers, medicinal agents, flavors, fragrances, and polymerization monomers [1–3]. Methyl butyrate, the methyl ester of butyric acid has a fruity odor largely resembling apples or pineapples. It is produced by distillation of essential oils of vegetable origin, but is also synthesized for the use in perfumes and as a flavoring agent in food industry [4]. Methyl butyrate is produced by the liquid-phase reaction of butyric acid and methanol catalyzed by sulfuric acid or sulfonic acid ion-exchange resins. Use of sulfuric acid generally shows weak catalytic activity, requires high reaction temperatures and long reaction time. In addition, homogeneous catalyst is corrosive, difficult to separate from reaction mixture and requires special energy-inefficient processes for the treatment of the waste acid [5]. The ion-exchange resin is a promising substitute material for homogeneous acid catalysts owing to its advantages. The solid material has desirable physical and chemical properties, and exhibits excellent performance as a heterogeneous catalyst in ester synthesis reaction [6–8]. Despite advantages of heterogeneous method for the synthesis of organic esters, the reaction time and alcohol to acid mole ratio is a concern which can be substantially reduced by using novel techniques such as ultrasound and microwave irradiation. Ultrasound assisted esterification has been studied by several researchers [9–12]. The use of ultrasound waves demonstrated that the reactions are fast and take considerably less time in comparison with conventional heterogeneous route. The studies show that ultrasound irradiated esterification demands excess of alcohol to prevent hydrolysis of ester produced and there is scope for further reduction of reaction time [13]. Therefore, investigations for alternative synthesis method for the esterification are required to ascertain reduced processing time, lower alcohol to acid ratio and enhanced mass transfer rates. The use of microwaves for assisting esterification is still an evolving area and detailed studies are needed to find out its applicability in heterogeneous catalysis.

Studies on microwave-irradiated reactions begun in the year 1986, when pioneering investigations were reported [14]. Microwaves are electromagnetic waves having frequency range

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Nomenclature

A	butyric acid
B	methanol
C	methyl butyrate
C_{A0}	initial concentration of butyric acid [mol.lit^{-1}]
C_A, C_B, C_C and C_D	concentration of butyric acid, methanol, methyl butyrate and water respectively at any time, t [mol.lit^{-1}]
D	water
f	frequency [Hz]
ΔG	change in Gibbs free energy of reaction [kJ.mol^{-1}]
ΔH	change in enthalpy of reaction [kJ.mol^{-1}]
k_f	forward rate constant [lit.mol^{-1}.min^{-1}]
k_r	reverse rate constant [lit.mol^{-1}.min^{-1}]
K_{eq}	equilibrium rate constant (dimensionless)
M	methanol to butyric acid ratio [C_{B0}/C_{A0}] (dimensionless)
P_D	dissipated power [W.m^{-3}]
$(-r_A)$	reaction rate obtained based on butyric acid consumed [mol.lit^{-1}.min^{-1}]
R	universal gas constant [8.314 kJ.kmol^{-1}.K^{-1}]
ΔS	entropy change in reaction [kJ.mol^{-1}.K^{-1}]
T	temperature [K]
V	electrical field strength in [volt.m^{-1}]
x_A	conversion of butyric acid [$(C_{A0}$-$C_A)/C_{A0}$] (dimensionless)
δ	loss angle (radians)
Є'	relative dielectric constant (dimensionless)
Є"	relative dielectric loss (dimensionless)

of 0.3 to 300 GHz, corresponding to wavelengths of ~1 m to 1 cm, respectively. This region of the electromagnetic spectrum lies between the far infrared and radio frequencies. A frequency of 2.45 GHz is generally used, from among several frequency bands that are present in market for domestic and scientific applications [15]. Basic principle of microwave reactors is based on conversion of electromagnetic (EM) energy into heat efficiently, so that extremely fast heating rates are achieved in a reproducible way. Microwave irradiation results in an instantaneous localized superheating owing to induced dipole rotation. The energy transfer takes place within 10^{-9} s with each cycle of electromagnetic energy resulting in non-equilibrium state and instantaneous high temperatures. An increase in temperature causes greater movement of molecules leading to increased number of energetic collisions [16]. Initial studies of several reactions revealed an enhancement of reaction rates in presence of microwave irradiation, as compared to identical reactions heated by conventional methods. Microwave activation of a large number of organic synthesis and metal catalyzed reactions has been reported amply in the past investigations [17–19]. The effects usually were rate enhancements, abnormal increase in boiling temperature of organic solvents, modified reaction path in organic synthesis, yield or selectivity improvements, and less polluting processes [20–22].

The objectives of this experimental study were to test intensification of the process and efficacy of heterogeneous catalyst in presence of microwave irradiation for the synthesis of methyl butyrate. Effects of temperature, catalyst loading, alcohol to acid ratio and amount of molecular sieves added for the ester synthesis were also undertaken.

2. Experimental

2.1. Materials

Methyl alcohol and butyric acid of 99.98% purity (w/w) were supplied by Merck. Both these chemicals were used as supplied. The acidic ion exchange resin (Amberlyst-15) was imported from by Alfa Aesar, USA. Amberlyst-15 is a micro porous polystyrene based ion exchange styrene-DVB (20%) resin with attached sulfonic groups on its polymer matrix. Sulfonated cation exchange resins are formed by the treatment of strong acids like sulfuric acid and subsequent deposition of acid sites on the polymer matrix. A resin catalyst is insoluble polymer matrix which exchanges ions with the adjacent reacting mixture. The resin catalysts are excellent source of strong acids that can exchange ions with the surrounding reaction mixture. This solid catalyst can be separated after completion of reaction and can also be reused several times.

2.2. Batch experiments

Esterification reactions were performed in a Multiwave PRO microwave reactor having dimensions of height, width, diameter as 760, 600, and 720 mm respectively. The reactor was equipped with a rotor mechanism to hold 16 reaction vessels (vials) of 100 mL capacity each and could be operated in batch mode. Reaction vessels were made up of a PTFE-TFM liner, supported by a ceramic vessel jacket and closed with a self-sealing lip-type seal. Microwave reactor was supplied by Anton Paar GmbH, Graz, Austria. Two standard magnetrons of 850 W delivered up to 1500 W microwave power in an un-pulsed mode over the full power range. Its integrated software prevented thermal overshoots and the design of microwave applicator provided maximum field density with enhanced degree of homogeneity, which paved the way for efficient heating. The sensor mechanism ensured actual temperature of the reaction mixture during the course of reaction.

In a typical experiment, measured quantity of methanol, catalyst (amberlyst-15) and molecular sieves were charged into the reaction vials (vessels). The set of vials with contents were then placed in the vessel holders on rotor assembly. Rotor with reaction vials was placed inside the microwave reactor. All the reaction vials were magnetically stirred to ensure complete homogeneity. The reactor was sealed and microwave irradiation started with set temperature and power required in an automatic mode. Microwave reactor was set to have ramp time of two minutes followed by hold time. Once the desired temperature was reached, the rotor with reaction vessels were taken out. Required amount of butyric acid was then injected into the heated contents in each of the batch vials via syringe. The rotor assembly with batch vessels containing reaction mixture was mounted back in the casing of Multiwave PRO immediately and microwave irradiation initiated. The instant was marked as zero reaction time.

Experimental runs were carried out uninterruptedly for the time interval of 10, 20, 30, 40, 50 and 60 minutes for different batches. Small amount of samples (0.5 mL) were withdrawn at the end of reaction since. The samples were analyzed to quantify the ester formation.

2.3. Mechanism of energy dissipation

Polar solvents are suited for microwave heating. Some solvents are capable of absorbing incident microwave energy and convert it into heat. The absorbed microwave energy by solvent and its conversion into heat is related with the loss angle, δ. Loss angle, is commonly expressed in the form of a tangent given by following equation:

$$\tan\delta = \epsilon'/\epsilon'' \qquad (1)$$

The dielectric constant (ϵ') represents the ability of a dielectric material to store electrical potential energy in presence of electric field. The loss factor quantifies the extent of the conversion of absorbed energy into heat. Polar solvents with moderate to high loss tangents couple with microwave radiation which induces dipolar movement as a result of dipole–dipole interactions of polar molecules with the electromagnetic field. In a microwave field, the polarity alternatively changes very rapidly (e.g., at the microwave frequency of 2.450 GHz, the polarity changes 2.45 billion cycles per second). This rotation of molecules results in friction with the medium surrounded by micro waves. This phenomenon results in a rapid heating giving rise to effective collisions. These collisions lead to efficient intermolecular mixing, thus enhancing reaction rate compared to conventional heating.

The microwave energy in itself is not thermal energy. Microwave resulted heating is a consequence of microwave energy interactions with a dielectric material. Dissipated amount of microwave energy into heat can be approximated by

$$P_D = 55.61\times10^{-14}\ V^2 f\,\varepsilon' \tan\delta \qquad (2)$$

Where, P_D is the power dissipation, watt/m^3; V is the electrical field strength in volt/m; f is the frequency in Hz. This dissipated power is equal to the product of enthalpy changes due to rise in temperature of reaction contents and the reaction volume.

2.4. Analysis

2.4.1. Titrimetric analysis

An acid value method was used to quantify the conversion of butyric acid for the esterification reaction to synthesize methyl butyrate. The mass of potassium hydroxide (KOH) in milligrams required to neutralize one gram of carboxylic acid is called acid value. Two milliliters of reaction samples were collected at regular time intervals and stored in refrigerator. At the end of each experimental run, the samples were analyzed by standard titrimetric method. Samples from the reaction mixture were subjected to titration for the residual acid content using 0.1 N KOH with phenolphthalein as indicator. The acid values (KOH mg/g) were then calculated for the residual butyric acid in the reaction mixture. Use of methanol was made as a quenching agent. Alcoholic KOH was standardized by 0.1 N oxalic acid. Methyl butyrate obtained was expressed in terms of percent (%) conversion based on consumption of butyric acid.

2.4.2. Gas chromatography

Butyric acid was further analyzed from the liquid samples taken in regular time intervals to confirm the conversion values obtained by titrimetic method. Chemito Gas chromatograph (Model 6890) was used to quantify liquid samples to determine methyl butyrate formed in the reaction. Gas Chromatograph was equipped with two detectors, a thermal conductivity detector (TCD) and a flame ionization (FID) detector, connected in series. HP-Innowax column (made up of polyethylene glycol with diameter of 320 µm and thickness of 0.5 µm) and length of 30 m was used. The GC was fitted with a controller to give temperature programmed analysis. Hydrogen gas was used as burner gas whereas nitrogen was used as the carrier gas. Operation of FID is based on the sensing of ions formed during combustion of organic samples in a hydrogen flame. Concentration of organic substances in the sample gas stream is directly proportional to the generation of the ions. Both analysis methods yielded conversion with only 2% deviation.

3. Results and discussions

3.1. Effect of reaction temperature

The reaction temperature is a crucial parameter in heterogeneous esterification as it controls the reaction kinetics as well as diffusion rates [23,24]. In this study, ester synthesis was carried out at increasing temperatures in the range of 323–343 K for the synthesis of methyl butyrate. The reactions were conducted at M = 1, catalyst loading 8.1% (w/w), added molecular sieves 9.5% (w/w).The effect of temperature on conversion is shown in Fig. 1 which shows that equilibrium conversion increased from 75 % to 92.6% as the reaction temperature varied from 323 K to 343 K. This increase in the conversion with temperature rise could be reasoned that an elevated temperature would help the reactant molecules to obtain adequate energy to cross over the energy barrier thus enhancing reaction rate and conversion [25].

It is observed that the maximum equilibrium conversion was achieved in record time of less than 60 minutes in comparison with conventional heating for the same temperature range

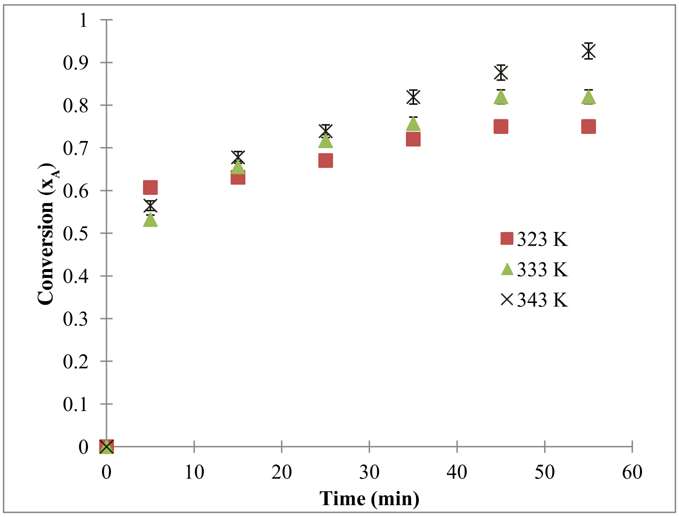

Fig. 1. Effect of temperature on conversion of butyric acid at alcohol to acid ratio 1, catalyst loading 8.1% and molecular sieves added 10.8%.

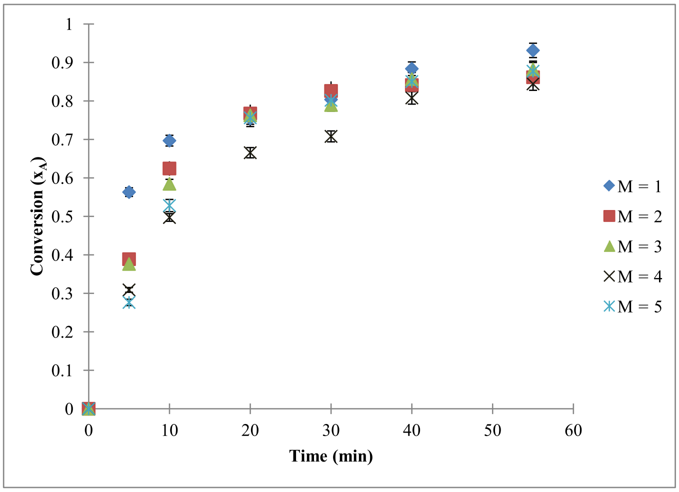

Fig. 2. Effect of alcohol to acid ratio (M) on conversion of butyric acid at temperature 343 K, catalyst loading 8.1% and molecular sieves added 10.8%.

which needed about 4 h to reach equilibrium. The possibility could be that the acceleration of reaction rate by MW exposure resulted from wave–material interactions leading to thermal effects linked to the generation of localized high temperatures leading to high conversions. Since conventional and microwave heated reactions were carried out at same bulk temperatures, there must be increased temperature at the local reaction sites; i.e. at the surface of catalyst. This is possible since the heat transfer by microwaves depends on the specific loss factor in different materials, the solid catalyst, and the liquid reactants [26]. Further, the rate enhancement could be due to a combined effect of the microwave absorption properties of reaction mixture and due to polar nature of methanol. Specific MW effects appeared to be owing to enhancement of polarity of the system during the reaction progress, which might have been provided by ionic dissociation of methanol ion pairs from the ground state of the reaction toward the transition state [27,28].

3.2. Effect of alcohol to acid mole ratio

Methanol to acid molar ratio is one of the most important aspects affecting conversion and usually excess of methanol is needed particularly in the conventional approach, to drive the reaction in the desired direction [29]. In order to study the effect of methanol/butyric acid initial quantities on esterification, different experiments were carried out using varying alcohol to acid mole ratios. The mole ratio of methanol to butyric acid, M was varied between 1 and 5. Theoretically, methyl butyrate synthesis reaction requires one mole of methanol for each mole of butyric acid. However, in conventional ester synthesis, alcohol is used in excess (M greater than 1) to drive the reaction toward completion as the esterification is reversible [30]. Water formed during the reaction, if not removed immediately causes the reverse reaction and limits conversion. Water produced in the reaction was removed by the adsorption of molecular sieves added thus keeping forward reaction in progress.

Fig. 2 shows the effect of alcohol to acid mole ratio on the conversion of butyric acid. The maximum conversion of 92.6% was obtained for an alcohol to acid molar ratio of 1 with a catalyst loading of 8.1% (w/w), temperature of 343 K and added molecular sieves 10.8% (w/w). As the alcohol to acid mole ratio is increased, the conversion shows the decreasing trend. Analysis of power-temperature profile of microwave reactor shows drop in the incident energy density (microwave irradiation energy for unit reaction volume per unit time) with an increase in alcohol to acid ratio owing to increased volume of methanol. This resulted into less absorption of MW energy by reaction mixture and reduced local superheating on the surface of catalyst resulting into decrease in equilibrium conversion [31].

3.3. Effect of catalyst loading

Catalyst loading was varied in the range of 0–10.5% (w/w) maintaining all other parameters at the optimized values to study its effect on equilibrium conversion. Some studies show a higher loading of catalyst results in increased conversion and reduction of the time required to reach the reaction equilibrium [32,33]. The effect of catalyst loading on the conversion of the butyric acid is shown in Fig. 3. It is noted that each new run was performed using fresh resin catalyst. As expected, the conversion increased with an increase in the catalyst loading from 0 to 8.1% (w/w) due to more available active sites, resulting in higher reaction rate and equilibrium conversion. Reaction rate and equilibrium conversion both found to be increasing with increasing catalyst loading in the stated range.

It is also observed that the conversion curve is steep in the first ten minutes indicating that rate of reaction is steep initially as the more catalytic sites are available for the unconsumed reactants.Further, it appears that increase in viscosity of the reaction mixture by varying catalyst amount up to 8.1% is insignificant and does not obstruct absorption of microwave energy resulting into subsequent increase in equilibrium

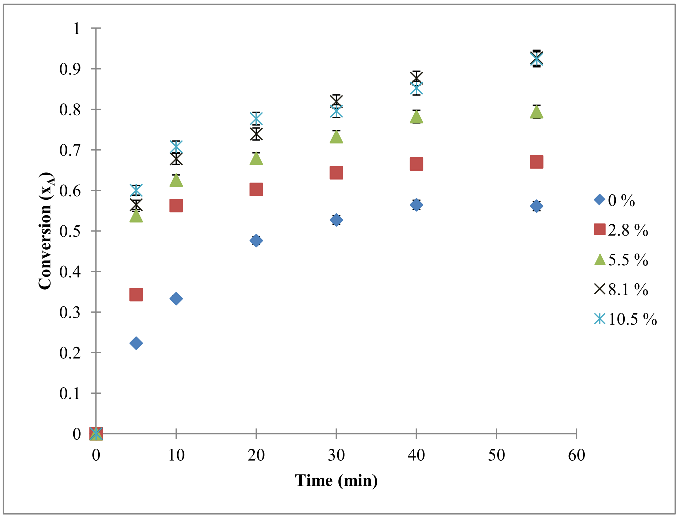

Fig. 3. Effect of catalyst loading on the conversion of butyric acid at temperature 343 K, alcohol to acid ratio 1 and molecular sieves added 10.8%.

conversion. It appears that the energy density of microwave induced irradiation does not change much irrespective of changes in solid content owing to addition of catalyst. Increase in catalyst amount beyond 8.1% showed no significant gains in terms of equilibrium conversion indicating non availability of substrate molecules. The added amount of catalyst was more than the required and most sites would remain vacant. In this condition external mass transfer limits the reaction rate [34]. Hence the optimum catalyst loading was taken as 8.1% and further esterification runs were carried out using this value.

3.4. Effect of addition of molecular sieves

Esterification of butyric acid with methanol produces water as one of the products of the reaction. As the reaction progresses, the amount of water formed as by-product during reaction increases. Reaction may proceed in the reverse direction if the water formed is not removed forthwith. Addition of molecular sieves or silica gel removes water formed favoring forward reaction [35,36].

Molecular sieves (3 Å type) were added in the range of 0–13.5% (w/w) to study its effect on esterification of butyric acid and methanol. The experiments were carried out at catalyst loading of 8.1%, alcohol to acid ratio of 1, and a temperature of 343 K. Fig. 4 shows the effect of molecular sieves on conversion of methyl butyrate. As seen in the figure, conversion increased with increasing amount of molecular sieves from 0 to 10.8%.This could be because of the adsorption of produced water by the molecular sieves prohibiting reverse reaction [13]. The optimum value of molecular sieves added to reaction of methyl butyrate synthesis was 10.8% beyond which there was no significant increase in equilibrium conversion. This shows that amount of molecular sieves was adequate for adsorbing water produced during esterification at other optimized reaction conditions. When reaction was carried out without addition of molecular sieves, the conversion obtained was close to 70 % indicating the presence of reverse reaction.

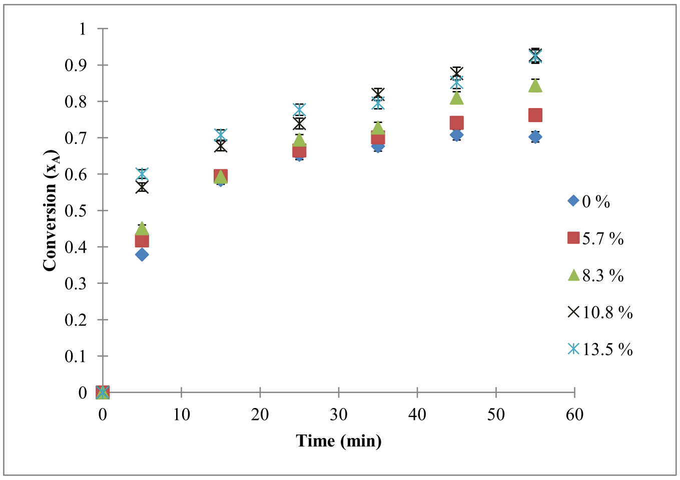

Fig. 4. Effect of molecular sieves on the conversion of butyric acid at temperature 343 K, alcohol to acid ratio 1 and catalyst loading 8.1%.

3.5. Determination of equilibrium constant and thermodynamic parameters

Butyric acid undergoes a reversible reaction with methanol to form ester and water in presence of solid ion exchange catalyst. The equilibrium reaction between butyric acid and methanol is as shown below:

$$\underset{A}{CH_3OH(l)} + \underset{B}{C_3H_7CO_2H(l)} \underset{k_r}{\overset{k_f}{\longleftrightarrow}} \underset{C}{C_3H_7CO_2CH_3\ (l)} + \underset{D}{H_2O(l)} \tag{3}$$

And equilibrium constant is expressed by equation (4)

$$K_{eq} = \frac{[C_C]_{eq}[C_D]_{eq}}{[C_A]_{eq}[C_B]_{eq}} = \frac{k_f}{k_r} \tag{4}$$

The effects of temperature on the equilibrium constant are usually expressed using the classical Van't Hoff relation. This equation gives information about the dependency of equilibrium constant on temperature. The Van't Hoff equation can be derived from the Gibbs–Helmholtz equation. For the standard Gibbs free energy, the Gibbs–Helmholtz equation is:

$$\frac{d\ln K_{eq}}{dT} = \frac{\Delta H^0}{RT^2} \tag{5}$$

Standard free energy change of the esterification reaction is given by:

$$\Delta G^0 = -RT\ln K_{eq} \tag{6}$$

ΔH is the standard enthalpy change of a reaction and ΔS is the change in entropy of the reaction system. ΔH is the amount of heat absorbed or released in a reaction an it indicates whether a reaction is endothermic or exothermic depending on if the enthalpy is required or released. Gibb's free energy change by definition is given by the following equation:

$$\Delta G^0 = \Delta H^0 + T\Delta S^0 \tag{7}$$

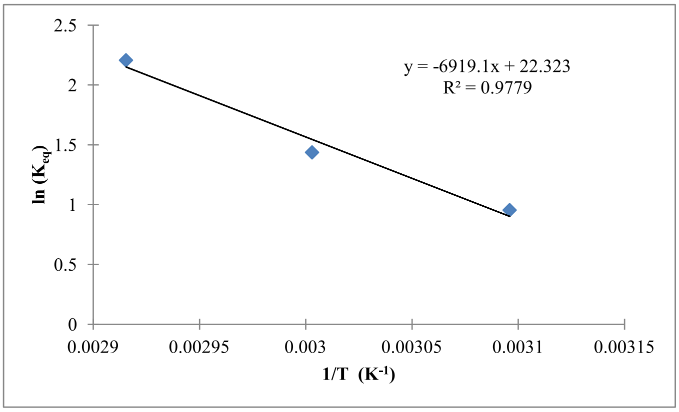

Fig. 5. Van’t Hoff plot for butyric acid esterification with methanol under microwave irradiation.

$$T\Delta S^0 = \Delta G^0 - \Delta H^0 \tag{8}$$

Substituting equation (8) with equation (6), the resulting equation is

$$\ln K_{eq} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{9}$$

Plot between equilibrium constant and temperature for the heterogeneous esterification of butyric acid with methanol is shown in Fig. 5. At constant pressure, with ln (K_{eq}) on the ordinate and $1/T$ on the *abscissa* has a slope of $-\Delta H^0/R$ with y-intercept $\Delta S^0/R$. Fig. 5 shows that natural log, ln (K_{eq}) is linearly dependent on 1/T.

Endothermic reactions show negative slope. As the temperature increases, the equilibrium constant increases, as illustrated in Fig. 5. From the negative slope it is proved that the esterification reaction is endothermic. The ΔH values for catalytic esterification at varied reaction temperatures were estimated from the linear Van’t Hoff plot by fitting the obtained data of ln (K_{eq}) with inverse of temperature. Change in Gibbs energy for the reaction was calculated from equation (6). Change in entropy of the reaction, ΔS for the microwave irradiated synthesis of methyl butyrate was calculated with the obtained ΔH and ΔG values.

The calculated values of ΔH, ΔG and ΔS for the heterogeneous esterification of butyric acid are presented in Table 1. As seen in Table 1, the reaction enthalpy decreased and entropy increased as the reaction temperature increased. As expected for endothermic reactions, equilibrium conversion and equilibrium constant found to be increased with temperature. Rise in entropy of the reaction with temperature increase is evident from the table. This increase is caused by the randomness of reacting molecules at the elevated temperatures.

Table 1
Thermodynamic parameters calculated at various temperatures.

Sr. no.	Temp. (K)	% conv. (x_A)	K_{eq}	ΔG^0 (kJ.mol^{-1})	ΔH^0 (kJ.mol^{-1})	ΔS^0 (J.mol^{-1}.K^{-1})
1	323	75.00	9	−2.19	$6.23*10^{-2}$	6.95
2	333	81.94	27.3	−3.30	$5.71*10^{-2}$	10.1
3	343	92.6	165.9	−5.08	$5.02*10^{-2}$	14.9

3.6. Comparison of microwave irradiated synthesis of methyl butyrate with conventional and ultrasound assisted method

The results obtained by microwave induced synthesis of methyl butyrate were compared with those obtained by conventional heterogeneous method as well as that carried out in presence of ultrasound waves. In conventional method, the heterogeneous reaction was carried out in a stirred batch reactor of 250 mL volume under optimized reaction conditions [8]. The reaction took 240 minutes to reach equilibrium conversion (93.5%). The optimum molar ratio of alcohol to acid was 3. In ultrasound assisted method, the reaction was carried out in a batch reactor in presence of ultrasound horn as reported earlier [13]. In this method, reaction time of 150 minutes was needed to achieve equilibrium conversion (91.6%). In both the former cases, excess of alcohol (M = 3) was used to prevent reverse reaction. In third method, assisted by microwave, equilibrium conversion of 92.6 % was achieved in 60 minutes under optimum condition. The corresponding conversion values reported in the first hour of reaction were 68% and 85% respectively for earlier two synthesis methods. Stoichiometric values of alcohol to acids were used in MW synthesis route. Comparative conversion of butyric acid in synthesizing methyl butyrate is shown in Table 2.

It can be inferred that microwave irradiated synthesis of methyl ester is more efficient and takes record less time to reach equilibrium conversion exceeding 90%. Further, it needs no excess of alcohol to progress reaction to a forward direction unlike in the two earlier synthesis methods where excess alcohol was needed to forbid reverse reaction. It could possibly be due to the fact that microwave irradiation produces efficient internal heating by direct coupling of the microwave energy with reactants and catalyst molecules in the reaction mixture, and the reaction is very efficient. Wherein, in conventional method, reactants are slowly activated by external heat source. Heat is imparted to material, by transferring first through the vessel wall in order to reach the reactants thus making it a slow and inefficient method for transporting energy into the reacting system.

4. Conclusions

Methyl butyrate was successfully synthesized by the reaction of methanol with butyric acid, heterogeneously catalyzed by amberlyst-15, under microwave irradiation. Maximum

Table 2
Comparison of various routes for heterogeneous synthesis of methyl butyrate.

Sr. no.	Synthesis method	% Conversion	Reaction time (min)	Alcoh./acid mole ratio
1	Batch reactor	93.5	240	3
2	Ultrasound assisted batch reactor	91.6	135	3
3	Microwave irradiated batch reactor	92.6	60	1

equilibrium conversion of 92.6% was obtained at 343 K, alcohol to acid ratio 1, catalyst loading 8.1% (w/w) and molecular sieves 10.8% (w/w). Microwave irradiation not only reduced the reaction time but also alcohol to acid mole ratio needed for methyl ester synthesis for achieving optimum equilibrium conversion as compared to the ratio used in conventional and ultrasound assisted reaction. Acid ion exchange resin catalyst, amberlyst-15 showed high efficacy for the synthesis of methyl butyrate in the presence of microwave irradiation. Calculated values of ΔG, ΔH and ΔS for the heterogeneous esterification of butyric acid show thermodynamic consistency.

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