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One-step continuous process for the production of 1-butanol and 1-hexanol by catalytic conversion of bio-ethanol at its sub-/supercritical state

Hassan S. Ghaziaskar[ab] and Chunbao (Charles) Xu*[a]

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A one-step, easy to scale-up, continuous process was developed to catalytically convert bio-ethanol into 1-butanol and 1-hexanol as chemicals or fuels, as well as some other compounds that are also useful as biogasoline. The process is novel as it employs ethanol at its sub- and supercritical states. The reactions were performed in a continuous-flow fixed-bed tubular reactor with γ-alumina supported Ni catalysts at 135–300 °C at a weight hourly space velocity of 6.4–15.6 h^{-1} using neat ethanol. The process at 250 °C and 176 bar with an 8% Ni/γ-alumina catalyst led to ethanol conversion of 35%, with the highest selectivity of approximately 62% and 21% towards 1-butanol and 1-hexanol, respectively. In addition to 1-butanol and 1-hexanol, other minor biogasoline components such as butanal, and 2-pentanone, *etc.* were also synthesized from this process. The catalyst was found active for 18 h on stream in this study, and the regenerated catalysts retained their activities for the reactions.

1. Introduction

Due to the increasing concern over greenhouse gas emissions, diminishing crude oil reserves, and the rise of crude oil prices, there is substantially increased need for alternative green sources for fuels and chemicals. Butanol is an important chemical and fuel and potentially a better fuel extender than ethanol, and it has a worldwide market of 370 million gallons per year. The market demand is expected to increase dramatically if green butanol can be produced economically from bio-ethanol. Butanol over ethanol as a fuel has several advantages, including tolerance to water contamination, which makes it more suitable for transportation *via* pipelines. The U.S. fuel market has been constrained by the fact that ethanol, which absorbs water and therefore tends to corrode pipelines, must be transported on trucks, trains and barges in relatively small batches to storage terminals where it is blended with gasoline. Another advantage of butanol is that it can be blended into gasoline at higher concentrations than ethanol without the need to modify the existing vehicle engine system, and it offers better fuel economy than gasoline–ethanol blends (as butanol has ~25% more heating value than ethanol). n-Butanol is being viewed as the next oxygenate to replace ethanol in fuel applications. It behaves similarly as gasoline although it is an oxygenate. It does not create phase separation as the ethanol/gasoline blend. Butanol has characteristics similar to gasoline in terms of energy density (29.2 *vs.* 32 MJ L^{-1}), stoichiometric air–fuel ratio (11.1 *vs.* 14.6), heat of vaporization (0.43 *vs.* 0.36 MJ L^{-1}), research octane number (96 *vs.* 91–99), and motor octane number (78 *vs.* 81–89), so it has attracted considerable attention as a substitute for gasoline recently.[1–4]

A newer butanol synthesis pathway through Guerbet chemistry was demonstrated possible to produce butanol from ethanol through bimolecular ethanol condensation.[5] Guerbet alcohols have been known for over 100 years since Marcel Guerbet pioneered the basic chemistry in the 1890s.[6] In the Guerbet process, bi-functional catalyst (metal/metal oxide catalysts) are needed to convert one alcohol into aldehyde to activate the β-hydrogen and to combine with another ethanol through aldol condensation after proton extraction by dehydration, followed by hydrogenation of the allylic aldehyde to produce butanol. The Guerbet reaction requires one of the alcohols to have at least two carbons because when a metal catalyst converts one of the alcohols into aldehyde, the β-hydrogen becomes acidic and is ready to be removed by a dehydration metal oxide catalyst to chemically combine the acidic hydrogen with a hydroxyl group from another alcohol to produce a heavier alcohol or aldehyde and water (through aldol condensation). The aldehyde can either leave the catalyst surface in the form of a higher molecular weight aldehyde or it can be hydrogenated back to a higher molecular weight alcohol over the metal catalysts.

For ethanol conversion, choice of the elements for both the metal and the support is a key factor for developing supported

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[a] *Institute for Chemicals and Fuels from Alternative Resources (ICFAR), Faculty of Engineering, Western University, London, ON, Canada, N6A 5B9. E-mail: cxu6@uwo.ca; Fax: +1-519-661-4016; Tel: +1-519-661-2111 ext. 86414*

[b] *Department of Chemistry, Isfahan University of Technology, Isfahan, 84156-83111, I. R. Iran*

catalysts with characteristics that can fulfill the requirements.[7] Different catalyst compositions have been proposed by various researchers. Tsuchida *et al.* examined hydroxyapatite catalysts with various Ca/P ratios for bimolecular conversion of ethanol to butanol.[8] They obtained 20% conversion and about 70% selectivity towards butanol at the optimum Ca/P ratio of 1.67 and 298 °C while ethanol gas was diluted to 16.4 vol% with helium. Ndou *et al.* investigated the effect of several solid-base catalysts for ethanol to butanol conversion,[9] including MgO, CaO, BaO, γ-Al_2O_3, Na, K, and Cs on alumina as well as Mg on silica. They found that MgO was the best basic oxide catalyst, and Zn could be an additional electron-density donor to promote ethanol conversion but it could not increase the butanol selectivity. The MgO catalyst offered 56% ethanol conversion with 18.4% butanol selectivity at 450 °C, while the Zn-promoted MgO offered much higher ethanol conversion (95.6%) but with much lower butanol selectivity (2.95%). Yang *et al.* investigated the performance of 8% Fe, Co, and Ni on γ-Al_2O_3 as the catalysts for conversion of ethanol in vapor phase to butanol *via* Guerbet chemistry at 200 °C,[10] where the nickel catalyst produced 19.1% ethanol conversion and 64.3% selectivity to butanol.

A mixture of ethanol : 1-propanol (4 : 1) with helium as the carrier gas (>80 vol%) was converted to 1-butanol, 2-methyl-1-butanol, 1-pentanol, and 2-methyl-1-pentanol elsewhere.[11] Conversion of ethanol : 1-propanol (4 : 1) to butanol through Guerbet chemistry demonstrated by Sangi Co., Ltd. using hydroxyapatite catalyst in a patent application (claiming a n-butanol yield of ∼21% at a relatively high temperature of 411 °C). In this patent, quantification of the conversion and product yields were qualitative as they used peak area to quantify the amount of each component assuming same response factors for all compounds. As the response factor of GC-FID is different for each compound, measurements using only peak area can introduce a large error in the results.

Metals like Ni can act as the hydrogen autotransfer catalysts[12] responsible for the ethanol dehydrogenation to aldehydes and hydrogenation of the heavier aldehydes to heavier alcohols, while the metal oxides are dehydration catalysts, as was also reported by a US patent.[13] The mechanism of hydrogen autotransfer in metal ($M \leftrightarrow MH_2$) has been well known, and the aldehyde can be reduced to form heavier alcohols by the H_2-adsorbed on a metal catalyst. Also Alonso *et al.*[14] examined the efficiency of hydrogen auto-transfer catalysts and found that Ru worked better for homogeneous catalysis, while Ni was good for heterogeneous catalysis. In O'Lenick's literature review on Guerbet chemistry, a number of metal oxides such as copper, manganese, chromium, cobalt, and molybdenum oxides were suggested for the dehydration reaction, while nickel, platinum, and palladium metals were suggested as active dehydrogenation/hydrogenation catalysts.[6]

Sub-/supercritical fluids are in a special phase achieved when the pressure and temperature of a compound are increased to near or above their respective critical points (240.7 °C, 61.4 bar for ethanol). A sub-/supercritical fluid can be an ideal reaction medium as it has higher diffusivity, lower viscosity and better solubility for organic compounds.[15] In this work, we intended to develop a novel one-step continuous process for the production of 1-butanol and 1-hexanol by catalytic conversion of bio-ethanol at its sub-/supercritical state.

2. Material and methods

2.1. Materials

Corn-derived anhydrous ethanol (purity >99%) was purchased from Commercial Alcohols Inc. Methanol (purity >99%) was used as solvent obtained from J.T. Baker, USA. γ-Alumina (Catalox® SCCa-5/150, purity 97.6 w/w% with <1.0% α-Alumina, surface area 152 $m^2 g^{-1}$, pore volume 0.49 mL g^{-1}, and with a mean particle size of 85 μm) were supplied by Sasol North America Inc. Mn_2O_3 (purity >98%, density 4.5 g mL^{-1}, mesh >325) was obtained from Alfa Aesar®, MA, USA. Manganese(II) nitrate, hydrate (purity >98 w/w% and degree of hydration of 4–6), nickel(II) nitrate hexahydrate, ammonium molybdate tetra hydrate, and 1-butanol (purity >99.8%) were all purchased from Sigma-Aldrich Co., USA. Pyrex glass beads (20–50 mesh) were used for diluting some of the catalysts.

2.2. Catalyst preparation

The catalysts of Ni/γ-Al_2O_3 (or simply denoted as NiAl in this paper) with varying nickel contents (8–27 wt%) were prepared by the wet impregnation method using water soluble metal nitrate salt and γ-alumina support. Briefly, a pre-calculated amount of γ-alumina and $Ni(NO_3)_2 \cdot 6H_2O$ dissolved in distilled water were mixed in a flask. The mixture was shaken in a warm bath at 40 °C for 12 h, followed by vacuum drying at −0.9 bar and 80 °C in a rotary evaporator (150–200 rpm) for ∼2 h and oven dried at 120 °C overnight. The dried solids were then subject to calcination and reduction in a continuous-flow tubular reactor (3/8-inch OD, 11-inch length) heated in an electric furnace at 500 °C. High purity hydrogen with a flow rate of 100 mL min^{-1} controlled by a mass flow controller (model FMA 5510, OMEGA, U.S.A) was passed over the dried Ni(II) impregnated alumina for 8 h at 500 °C to reduce nickel ions to metallic nickel. In most cases when a nickel loaded γ-alumina catalyst was only used, the reduction was performed *in situ*, right prior to the reaction. In case of mixed catalysts, after the calcination/reduction of nickel ions was completed the catalyst was passivated by passing nitrogen gas over it for 2 h during the cooling time of the reactor, and then it was mixed at a specific amount with metal oxide catalyst and packed into the reactor.

For the comparison purpose, the mixture of 27% Ni/γ-alumina (2.48 g) and neat commercial Mn_2O_3 powder (0.50 g) was used, corresponding to a Ni/Mn_2O_3 ratio of 1 : 1 (w/w). Mn_2O_3 (98 wt%, -325 mesh powder) was calcined at 550 °C in a muffle furnace for 6 h before use. In addition, we prepared 20 wt% Mn_2O_3/γ-Al_2O_3 catalyst with a similar wet impregnation method as described previously. The only difference was that in the preparation of 20 wt% Mn_2O_3/γ-Al_2O_3, no reduction is needed, while the calcination was performed in a muffle

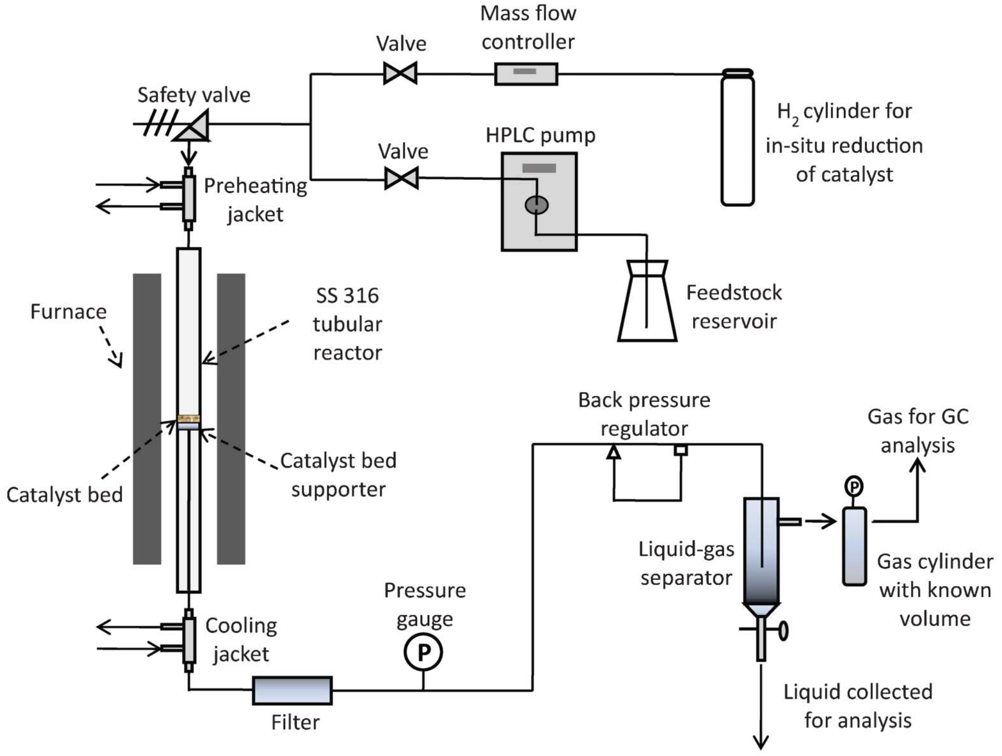

Fig. 1 Schematic diagram of the set-up used for sub- and supercritical ethanol conversion.

furnace for 6 h in air. In the reaction tests, 2.38 g of 20 wt% $Mn_2O_3/\gamma\text{-}Al_2O_3$ catalyst was used, equivalent to 0.5 g neat Mn_2O_3.

2.3. Experimental apparatus and methods

Experiments were carried out in a continuous fixed-bed tubular reactor (3/8-inch OD, 11-inch length) mounted vertically in an electric furnace (model 21100, Barnstead Thermolyne with Euroterm 2116 temperature controller), as schematically shown in Fig. 1. The bottom of the reactor was connected to a cooling jacket, a 2 μm stainless steel filter (Swagelok Co., UK), pressure gauge, a back-pressure regulator (KPB Swagelok series, 0–276 bar, UK), and a liquid–gas separator. A piston pump (series III, Lab Alliance Co., Canada) was used to feed liquid ethanol continuously into the reactor at 150–300 °C and pressure of up to 180 bar. Gasification of ethanol was observed at the temperatures of 250 and 300 °C. The gases were collected in a gas bag and analyzed using a micro GC and found that they were mostly hydrogen, methane, carbon dioxide, ethane, and small amount of propane.

The experiments were performed at different temperatures and pressure by pumping ethanol as the only reactant with a flow rate of 0.5–1.0 mL min^{-1} over 3.0–3.5 g of solid catalyst throughout the work, corresponding to a WHSV of 6.4–15.6 h^{-1}. WHSV stands for weight hourly space velocity and calculated as feed room temperature mass flow/catalyst mass. The feedstock reservoir was put on a top loaded balance (AND Co.) to accurately measure the weight of ethanol fed to calculate the actual mass flow (g min^{-1}) during the course of the reaction. Herein the weight of nickel loaded on the support was taken as the catalyst mass to calculate the WHSV.

In some tests the catalyst particles are mixed with 20–50 mesh Pyrex glass beads (at 1 : 1 w/w), in order to increase the residence time of ethanol in the catalyst bed. However, it was observed that diluting 8% $Ni/\gamma\text{-}Al_2O_3$ or 27% $Ni/\gamma\text{-}Al_2O_3$ catalyst with the Pyrex glass beads resulted in lower catalyst efficiency. Therefore, in most of the experiments the catalysts were not diluted with Pyrex glass beads.

For the continuous reaction system, the conversion was calculated as percent moles of ethanol reacted to the moles of ethanol fed to the reactor and the yield of each product was calculated as percent moles of carbon in the product to the moles of carbon in the fed ethanol. The selectivity of each product was also calculated as the percent moles of carbon in the target product divided to the total moles of carbon in the ethanol reacted. These calculations can be given simply by the following eqns (1)–(3):

$$Conversion(\%) = \frac{\text{Moles of ethanol reacted}}{\text{Moles of ethanol fed to the reactor}} \times 100 \quad (1)$$

$$Yield(\%) = \frac{\text{Moles of carbon in the product}}{\text{Moles of carbon in ethanol fed to the reactor}} \times 100 \quad (2)$$

$$Selectivity(\%) = \frac{\text{Moles of carbon in the target product}}{\text{Moles of carbon in ethanol reacted}} \times 100 \quad (3)$$

2.4. Products analysis

The liquid reaction products collected at different time intervals were analyzed with a Shimadzu GC-MS (model QP2010 series, Kyoto, Japan), with ionization achieved by electron impact at 70 eV, equipped with a capillary column: SHRXI-5MS equivalent of DB-5 and HP-5 (30 m length, 0.25 mm i.d., and 0.25 μm film thickness). The operating conditions of the GC-MS analysis were: injection port temperature, 260 °C; interface temperature, 270 °C; column oven temperature program: 40 °C for 2 min, ramped at 80 °C min^{-1} to 240 °C with 1 min hold; helium carrier gas (flow rate of 1.04 mL min^{-1} at 40 °C); 0.1 μL injection volume. The injector was operated in the split mode with a split ratio of 200. At a higher split ratio higher volumes of the samples can be injected to have better analytical precision.

To prevent the interference of methanol as the solvent, the *m*/*z* scan was started from 40 amu. The total ion current *versus* time was recorded to obtain the chromatogram for quantitative work by GC-MS, and the components mass spectrum within a mass range of 40 to 400 were used for qualitative identification purposes. Identification of compounds was achieved using the 8th edition of Wiley mass spectra database, and then by comparing the mass spectra and retention times of the chromatographic peaks with those of authentic samples. The physical properties of eight major products of ethanol conversion over different catalysts are given in Table 1. Some other minor compounds were also formed in the reactions that make the composition of the liquid product similar to a biogasoline as reported elsewhere.[5]

Quantification analyses were performed by injections of standard solutions of various concentration, containing ethanol, 1-butanol, tetrahydrofuran, ethyl acetate, acetaldehyde, 1,1-diethoxyethane, and 1-hexanol and toluene as an internal standard. Multiple point internal standard method with six analyses was used for the quantitative analyses. The internal standard method accounts for any variances in gas chromatograph performance. Toluene was chosen as an internal standard since it has a predictable retention time and area. Moreover, it had a unique retention time that was not overlapping with other components. Each analysis contains the internal standard whose concentration was kept constant and the analyte of interest whose concentration covers the range of the expected concentrations. The standard sample solutions up to 5 mL were prepared using the authentic standards with methanol as the solvent, and 0.1 μL of them was injected into the GC-MS and the total ion chromatogram were obtained. The results were plotted with the ratio of the peak area of the analytes to the peak area of the internal standard on the X-axis and the ratio of the concentration of the analytes to the concentration of internal standard on the Y-axis. The calibration curves were constructed using linear regression line fitted into the calibration data. With this, the relative concentration of the analyte in an unknown sample to that of the internal standard was calculated based on the corresponding ratio of peak area of the analyte to that of the internal standard and the calibration factor. GC-MS analyses of mixtures of known compositions of ethanol, 1-butanol, tetrahydrofuran, ethyl acetate, acetaldehyde, 1,1-diethoxyethane and 1-hexanol and toluene as an internal standard sample (<0.5 v/v% each) showed that the measurement accuracy by % relative standard deviation (%RSD) was acceptably low (6.6–15.5%).

Gases produced in the runs at temperatures of 250 °C and 300 °C were collected in gas sampling bags and analyzed with an Agilent micro GC 3000A (model G2801A). The micro GC-TCD consists of two channels and two columns: Molecular Sieve 5A PLOT (10 m, 0.32 mm, 30 μm) and Plot Q (3 m, 0.32 mm, 30 μm) with argon and helium carrier gas, respectively.

2.5. Catalyst characterization

A surface area analyzer (Nova 2200e/TO, Quantachrome Instruments, USA) was used to measure the surface areas of the fresh and spent catalysts. In the measurements, the samples were degassed at 250 °C for 2 h and the weight of the sample was exactly measured *via* an analytical balance, prior to N_2 isothermal adsorption at 77 K. Powder X-ray diffraction (XRD) patterns of fresh and spent catalysts were recorded on a PANalytical XRD instrument with Cu-Kα1 radiation. XRD patterns were recorded with 0.02 (2θ) steps over 2θ of 6–97° angular range and a vscan rate of 0.16° s^{-1}. Thermogravimetric analysis (TGA) of fresh and spent catalysts were carried out using TGAi 1000 (Instruments specialists Inc.), where the catalyst samples were heated in 30 mL min^{-1} air, 25 °C to 900 °C at 20 °C min^{-1}.

3. Results and discussions

A one-step continuous process was developed for the production of 1-butanol and 1-hexanol by catalytic conversion of bioethanol at its sub-/supercritical state. The experimental work

Table 1 Specification of compounds used for standard solution preparation

No.	Compound name	Retention time (min)	Molecular weight (g mol^{-1})	Density (g mL^{-1})	Boiling point (°C)
1	Acetaldehyde	1.39	44.05	0.785	21
2	Ethanol	1.44	46.07	0.789	78
3	Butanal	1.79	72.11	0.800	75
4	Ethyl acetate	1.89	88.11	0.902	77
5	Tetrahydrofuran	2.01	72.11	0.889	66
6	1-Butanol	2.23	74.12	0.810	117
7	2-Pentanone	2.45	86.13	0.809	103
8	1,1-Diethoxyethane	2.85	118.17	0.831	102
9	1-Hexanol	4.12	102.17	0.814	157

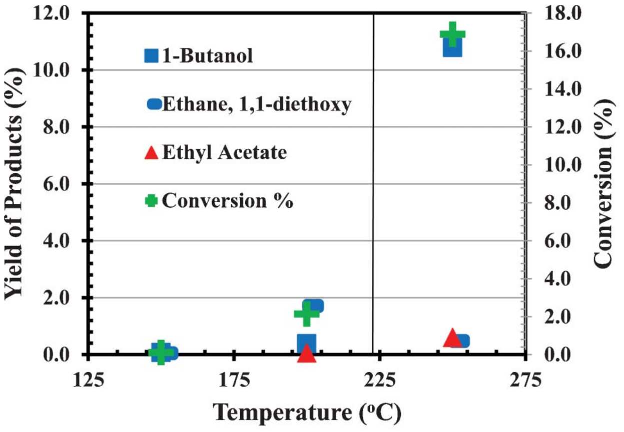

Fig. 2 The % conversion of ethanol and the % yield of main products formed over the solid bi-functional catalyst $Mn_2O_3/\gamma\text{-}Al_2O_3$ mixed with $Ni/\gamma\text{-}Al_2O_3$ (1 : 1 w/w) at 141 bar at different temperatures.

was started with conversion of ethanol over a solid catalyst including $Mn_2O_3/\gamma\text{-}Al_2O_3$ mixed with $Ni/\gamma\text{-}Al_2O_3$, and $Ni/\gamma\text{-}Al_2O_3$ with different nickel loadings of 8, 17, and 27 wt% at various temperatures and pressure. Among various transition metals, the high C–C bond-breaking activity of nickel, and its relatively low price make it a promising active metal for ethanol conversion. The performance of the above catalysts in direct conversion of sub-/supercritical ethanol to higher alcohols is detailed below.

3.1. Effects of temperature

The reactions were performed in the above described fixed-bed tubular reactor at 150–300 °C using neat ethanol at a flow rate of 1.0 mL min^{-1} ethanol. After a constant temperature and pressure was achieved, five samples were collected in increments of 14 mL and the last sample was analysed for quantification. The percent yield (%Y) of products formed and the percent conversion (%C) during the continuous conversion of ethanol over the solid bi-functional catalyst $Mn_2O_3/\gamma\text{-}Al_2O_3$ with $Ni/\gamma\text{-}Al_2O_3$ (1 : 1 w/w) at different temperatures at pressure of 141 bar are shown in Fig. 2. At 150 °C extremely low ethanol conversion was obtained, while at a higher temperature of 200 °C three major compounds of 1-butanol, ethane 1,1-diethoxy (*i.e.* acetal) and ethyl acetate were formed. At 250 °C, seven compounds of 1-butanol, 1-hexanol, acetal, ethyl acetate, acetaldehyde, butanal, and 2-pentanone were detected. The %Y of 1-butanol and %C of ethanol were increased drastically with increasing temperature. While the %Y of the acetal increased with increasing temperature up to 200 °C and then reduced after that. As is well known, the density of hot-compressed ethanol decreases smoothly with increasing temperature up to 200 °C, while it suddenly drops when it is close to its critical point (240.7 °C, 6.1 MPa).[15,16] This drop in ethanol density at sub- and supercritical conditions may govern the product selectivity towards the compounds which have a higher solubility in sub- and supercritical ethanol. This might be the reason that the formation of acetal (more polar and highly soluble in ethanol) was observed more at low temperatures or at subcritical conditions, while 1-butanol is promoted as the major product at supercritical conditions. Formation of acetal could occur when the hydroxyl group of a hemiacetal molecule becomes protonated to lose a water molecule.[17] The carbocation that is produced can then be rapidly be attacked by another molecule of alcohol.

Loss of the proton from the attached alcohol gives the acetal. Acetals are stable compared to hemiacetals but their formation is reversible as with esters. As a reaction to create an acetal proceeds, water must be removed from the reaction mixture or it will hydrolyse the product. The formation of acetals reduces the total number of molecules present and therefore entropy-wise is not favourable. Minor change *vs.* temperature was observed for the ethyl acetate yields. At temperatures of 300 °C and higher, more unwanted products and mostly gases were produced. Therefore, in this work 250 °C was used in investigating the effects of pressure on ethanol conversion.

3.2. Effects of pressure

Interestingly, our preliminary tests demonstrated that $Ni/\gamma\text{-}Al_2O_3$ alone is more active than the mixed catalyst of $Mn_2O_3/\gamma\text{-}Al_2O_3$ and $Ni/\gamma\text{-}Al_2O_3$ for the one-step conversion of ethanol to higher alcohols. As such, effects of reaction pressures on product yields were examined at 250 °C under different pressure (3.8–183 bar) using $Ni/\gamma\text{-}Al_2O_3$ catalyst with nickel loading of 8 wt% and 27 wt%, diluted with Pyrex glass beads (1 : 1 w/w) in sub- and supercritical conditions. The results are presented in Fig. 3. The typical qualitative composition of the products in the tests at different pressure levels are displayed in Table 2. As is shown previously in Table 2, the composition of products at different pressures is similar. However, when the pressure increases, the amount of 1-hexanol and 1-butanol derivatives increases. In the tests at 250 °C, 183 bar, and 8% $Ni/\gamma\text{-}Al_2O_3$ catalyst, the %Y of the typical components is listed

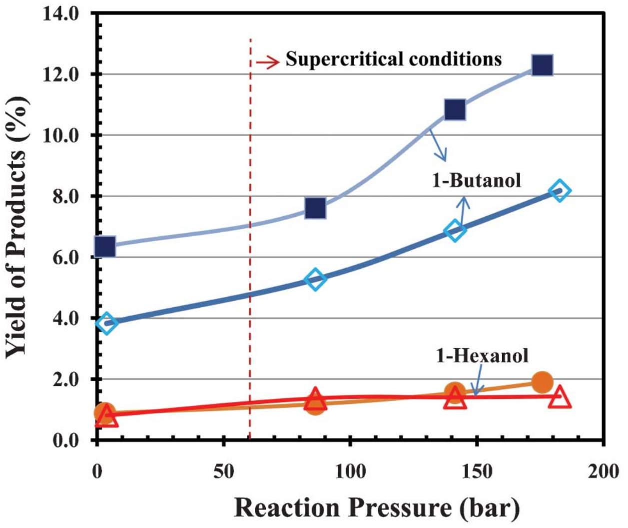

Fig. 3 The % yield of 1-butanol and 1-hexanol products *versus* pressure at 250 °C using 8% $Ni/\gamma\text{-}Al_2O_3$ (solid symbols) and 27% $Ni/\gamma\text{-}Al_2O_3$ (open symbols) diluted with Pyrex glass beads (1 : 1 w/w).

Table 2 Product composition at 250 °C and different sub- and supercritical pressure using 27% Ni/γ-Al_2O_3 catalyst, diluted with Pyrex glass beads (1 : 1 w/w)

	Pressure of reaction (bar)			
No.	3.8	86	141	183
1	Acetaldehyde	Acetaldehyde	Acetaldehyde	Acetaldehyde
2	Acetone	Acetone	Acetone	Acetone
3	Diethyl ether	Diethyl ether	Diethyl ether	Diethyl ether
4	Butanal	Butanal	Butanal	Butanal
5	Ethyl acetate	Ethyl acetate	Ethyl acetate	Ethyl acetate
6	1-Butanol	1-Butanol	1-Butanol	1-Butanol
7	2-Pentanone	2-Pentanone	2-Pentanone	2-Pentanone
8		Ethane, 1,1-diethoxy	Ethane, 1,1-diethoxy	1-Butanol, 2-methyl
9	1-Ethoxy, butane	1-Butanal, 2-ethyl	1-Butanal, 2-ethyl	Ethane, 1,1-diethoxy
10	1-Butanal, 2-ethyl	1-Butanol, 2-ethyl	1-Butanol, 2-ethyl	1-Butanal, 2-ethyl
11	1-Hexanol	1-Hexanol	1-Hexanol	1-Butanol, 2-ethyl
12	Butanoic acid ethyl ester		Butane, 1,1-diethoxy	1-Hexanol

in Table 2, *i.e.*, acetaldehyde, butanal, ethyl acetate, 1-butanol, 2-pentanone, and 1-hexanol were 0.93, 4.11, 0.74, 20.16, 1.26, and 5.8, respectively.

Fig. 3 illustrates the %yield of 1-butanol and 1-hexanol products *versus* pressure at 250 °C using 8% Ni/γ-Al_2O_3 and 27% Ni/γ-Al_2O_3 diluted with Pyrex glass beads (1 : 1 w/w). As shown in the Figure, with increasing the reaction pressure, the %Y of 1-butanol is increased drastically and it is almost doubled from 3.8 bar to 176–183 bar. The highest 1-butanol %Y was 12.8% at 183 bar with 27% Ni/γ-Al_2O_3. The selectivity at pressure of 176–183 bar was better than 70% for 1-butanol. While the 1-butanol yield with 8% Ni/γ-Al_2O_3 is almost double that of 27% Ni/γ-Al_2O_3, the yields of 1-hexanol with both catalysts remained almost the same (<2%), while the 1-hexanol yield slightly increases with increasing pressure.

Comparing the results displayed in Fig. 2 and 3, the use of 8% or 27% nickel loaded on γ-alumina as the catalyst showed higher catalytic activity toward 1-butanol synthesis at sub- and supercritical conditions than the bi-functional catalysts (*i.e.*, mixed catalyst of Mn_2O_3/γ-Al_2O_3 and Ni/γ-Al_2O_3). While, the yield of all other products excluding acetaldehyde was found below 2%. It shall be emphasized that, in these tests the catalysts are mixed with Pyrex glass beads (1 : 1 w/w), which may be advantageous for a longer ethanol residence time in the catalyst bed. However, it was also observed that when 8% Ni/γ-Al_2O_3 or 27% Ni/γ-Al_2O_3 catalyst was diluted with the Pyrex glass beads a lower catalyst efficiency was achieved. Therefore, in other experiments the catalysts were not diluted with the Pyrex glass beads.

The variations in temperature and pressure could significantly change the density of the reaction mixture and hence the residence time. As expected a longer residence time would lead to a higher conversion. Thus, at higher pressure, the density of the reaction mixture increases, so does the residence time, and as a result the conversion. The other reason for the positive effects of pressure on conversion may be simply that higher pressure promotes the reaction kinetics by the increase in the reactant concentration.

3.3. Effects of catalyst types and nickel loading

Effects of type of catalysts and nickel loading on the product yields and selectivity as well as the ethanol conversion were studied at 176 bar, 250 °C, and a flow rate of 0.5 mL min^{-1} (corresponding to a WHSV of 6.4 h^{-1}). The results are comparatively shown in Table 3. As shown in Table 3, the highest product yield (21.6%, molar basis or 17%, weight basis), selectivity (61.7%), and ethanol conversion (35%) were obtained with the 8% Ni/γ-Al_2O_3 catalyst. At the same conditions, the highest selectivity of 20% and yield of ∼5% were also achieved for 1-hexanol. This work is thus superior to the recently published patent on conversion of ethanol in vapor phase at 200–350 °C and normal pressure using a

Table 3 Performances of different catalysts in conversion of ethanol to 1-butanol at supercritical conditions (250 °C and 176 bar)

Catalyst	1-Butanol yield (%)	Ethanol conversion (%)	1-Butanol selectivity (%)
8% Ni/γ-Al_2O_3	21.6	35.0	61.7
Reg. 8% Ni/γ-Al_2O_3[a]	20.3	33.9	59.9
Reg. 8% Ni/γ-Al_2O_3[a]	19.0	33.4	56.8
Reg. 8% Ni/γ-Al_2O_3[a]	18.3	28.8	63.6
8% Ni/γ-Al_2O_3[b]	10.35	15.9	65.0
17% Ni/γ-Al_2O_3	18.5	29.3	63.2
27% Ni/γ-Al_2O_3		Full gasification of ethanol	
27% Ni/γ-Al_2O_3[b]	9.2	16.7	55.2
Mn_2O_3/γ-Al_2O_3 + 27% Ni/γ-Al_2O_3[b]	12.0	18.7	64.0
Neat Mn_2O_3 + 27% Ni/γ-Al_2O_3[b]	4.0	9.8	40.8

[a] Regenerated catalysts at flow rate of 100 mL min^{-1} H_2 and 500 °C for 4, 6, and 8 h, respectively. [b] Dispersed with Pyrex glass beads of a particle size of 20–50 mesh (1 : 1 w/w).

catalyst comprising strontium phosphate apatite having an Sr/P atomic ratio of 1.5–2.0[18] where the n-butanol yield (*i.e.* 14.8%) and ethanol conversion (*i.e.* 21.1%) were reported. The reason for the superior performance of our catalytic reaction system might be owing to our reaction conditions involving a different catalyst and sub-/supercritical ethanol under pressure. Sub-/supercritical ethanol could be a superior reaction medium as it has higher diffusivity, lower viscosity and better solubility for organic compounds.[15] It was observed that when 27% Ni/γ-alumina was used as a catalyst, all fed ethanol was gasified to form CH_4, H_2 and C_2H_6 gaseous products. In contrast, when the 27% Ni/γ-alumina catalyst was diluted with Pyrex glass beads gasification was not severe but the product yields and conversion of the reaction were lower compared to the 8% Ni/γ-Al_2O_3 or 17% Ni/γ-Al_2O_3 with or without dilution of Pyrex glass beads.

The number of compounds produced with Ni/γ-Al_2O_3 catalysts was found to be much less compared to the 1 : 1 mixture catalyst of (Mn_2O_3/γ-Al_2O_3 + Ni/γ-Al_2O_3). More importantly, the selectivity of the reaction using 8% Ni/γ-Al_2O_3 catalyst is much higher than what was reported previously for the Guerbet reactions.[10] The superior performance of the Ni/γ-Al_2O_3 over the bi-functional catalyst suggests different mechanism involved in the reaction system of this work than the Guerbet mechanism. Direct condensation of two ethanol molecules into 1-butanol might be involved in this process (*i.e.*, $2C_2H_5OH \rightarrow C_4H_9OH + H_2O$). However, the formation of some side products as shown in Table 2, suggests oxidation of ethanol and butanol to aldehydes, aldol condensation after proton extraction, dehydration of the aldol products, and hydrogenation of the allylic aldehydes, typical of the Guerbet reactions. Therefore, the Guerbet mechanism

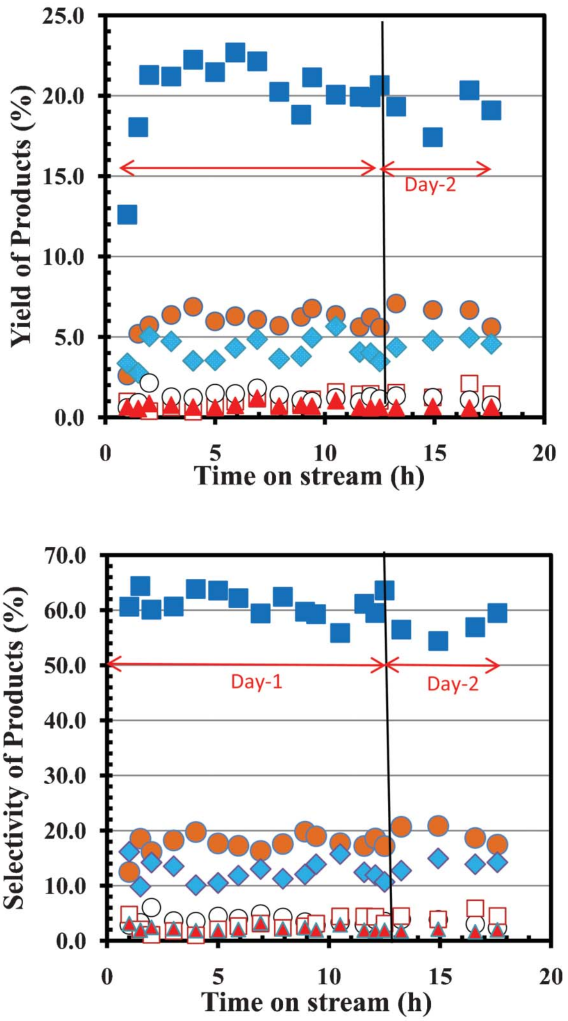

Fig. 4 Product yields and selectivity *versus* time at supercritical condition of 176 bar and 250 °C using 8% Ni/γ-Al_2O_3 catalyst. The reaction was carried out for 13 h on Day 1 and then was continued for another 5 h on Day 2. The symbols in the figure represent 1-butanol (■), 1-hexanol (●), butanal (♦), acetaldehyde (□), 2-pentanone (○), and ethyl acetate (▲).

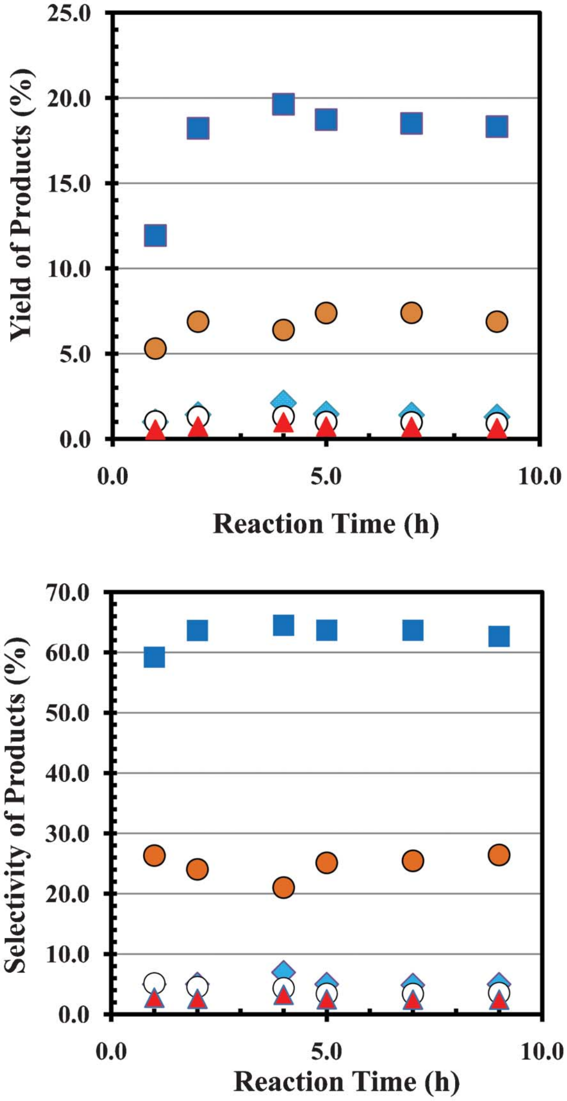

Fig. 5 Product yields and selectivity for the reaction at supercritical condition of 176 bar and 250 °C using 8% Ni/γ-Al_2O_3 catalyst after the third time of regeneration. The symbols in the figure represent 1-butanol (■), 1-hexanol (●), butanal (♦), 2-pentanone (○), and ethyl acetate (▲).

could also be involved in the process, mostly in the formation of the minor side products.

Control tests using no nickel catalyst but fresh γ-alumina were also performed. Negligibly small conversion of ethanol to diethyl ether, acetaldehyde, and tetrahydrofuran was observed. While the γ-alumina used was white at the start of the test, it was fully dark brown when the reaction was finished after about 6 h on stream, implying some coke deposition occurred during the course of the control tests.

3.4. Stability of the catalysts

To study the stability of the catalyst, the product yields in the reaction were monitored for 13 h on stream at 176 bar and 250 °C using 8% Ni/γ-Al_2O_3 catalyst. As shown in Fig. 4, all yields remained almost constant up to 13 h on stream after the reaction was started on Day 1. The catalyst was kept in ethanol in the reactor system and the reaction was resumed on Day 2 for another 5 h before completion. As shown in Fig. 4, the catalyst maintains its activity with similar yields and selectivity as those obtained in the Day 1 test. Therefore, the catalyst in this study demonstrated good stability, remaining active for 18 h on stream. The fluctuation of the results as shown in the graph was mostly due to the fluctuation in the flow rate of the ethanol fed.

The same catalyst was *in situ* regenerated at 500 °C with 100 mL min^{-1} hydrogen for 4 h. After the *in situ* regeneration, the reaction was performed and negligible changes in the products yields and selectivity were observed. After regeneration of the catalyst for the 3rd time at 500 °C with 100 mL min^{-1} hydrogen for 8 h, the catalyst could still retain its activity up to 9 h on stream in the reaction, as displayed in Fig. 5, which shows its promise in future applications.

3.5. Catalyst characterizations

Powder XRD analyses were performed on the γ-alumina support and the fresh/spent γ-alumina supported Ni catalysts. The obtained XRD patterns are displayed in Fig. 6. Compared with the XRD spectra for the γ-alumina support, all NiAl catalysts showed common XRD lines corresponding to metallic nickel (Ni) as well as γ-Al_2O_3. This evidenced that the reduction temperature of 500 °C used for the catalyst reduction with H_2 was sufficient to reduce the nickel species to its metallic form. Moreover, the XRD patterns of spent catalysts show that Ni metal was not converted to its oxide forms within the course of reaction likely due to the presence of reducing atmosphere during the reaction (H_2, CH_4 and C_2H_6, *etc.*).

TGA of the spent catalysts were carried out by temperature-programmed oxidation under an air flow of 30 mL min^{-1}, from 25 °C to 900 °C at a ramp rate of 20 °C min^{-1}. The TGA plots of the spent Ni/γ-alumina catalysts with various Ni loadings as well as the spent γ-alumina used in ethanol conversion reactions at 250 °C and 176 bar are displayed in Fig. 7. The weight loss of all different spent catalysts after being on-stream for about 10–18 h were found less than 8.2 wt%. Since, the carbon adsorbed on the surface of the catalyst can be oxidized at the air flow, these data suggest that the degree of coking (carbon deposition) on the NiAl catalysts

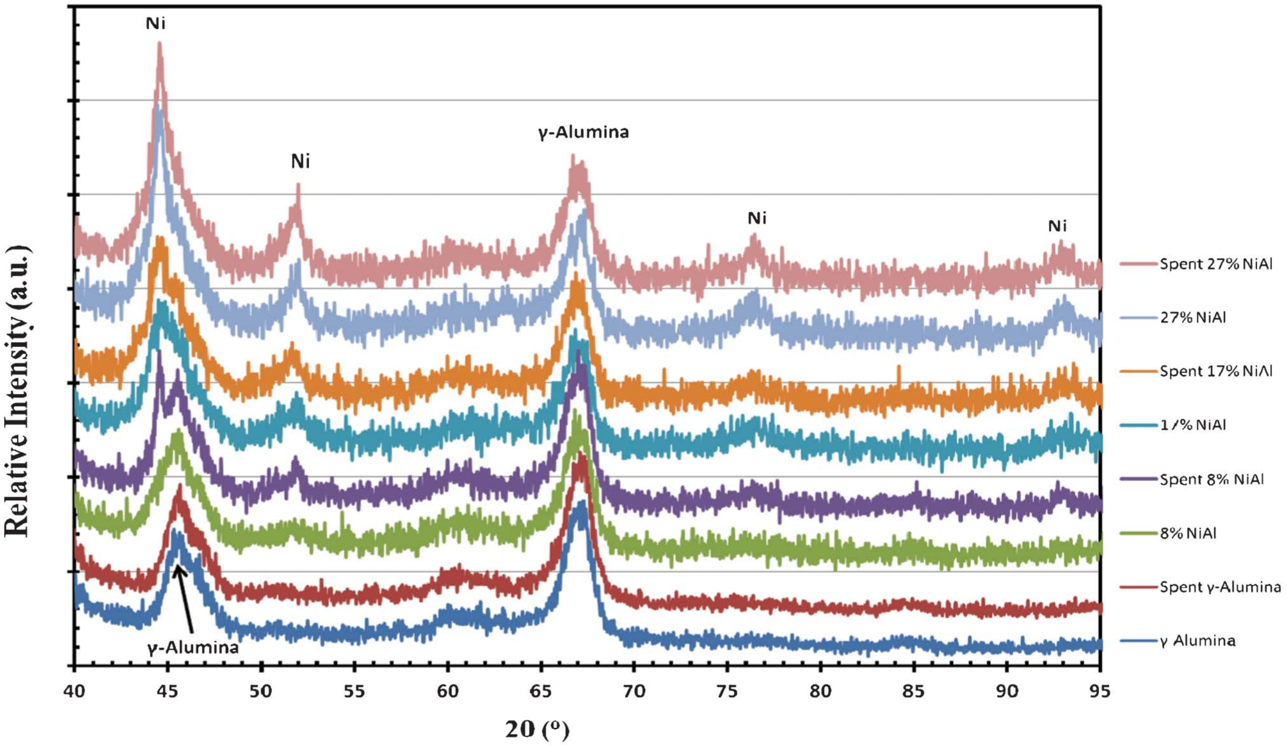

Fig. 6 XRD patterns of the γ-alumina support and the fresh/spent γ-alumina supported Ni catalysts (NiAl).

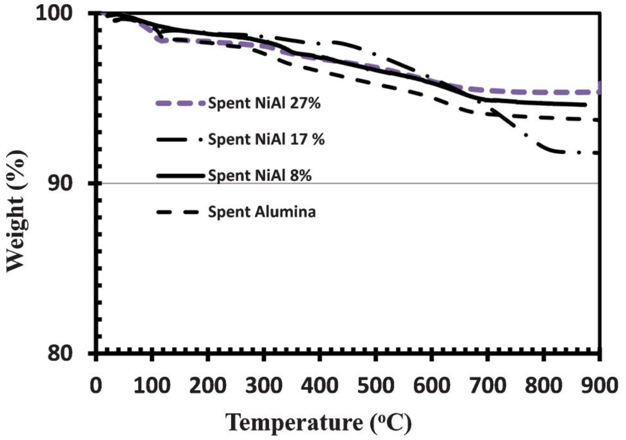

Fig. 7 TGA plots of the spent Ni/γ-alumina catalysts with various Ni loadings as well as the spent γ-alumina used in supercritical ethanol conversion reactions at 250 °C and 176 bar. The catalyst samples were heated in air at 30 mL min^{-1}, from 25 °C to 900 °C at a ramp rate of 20 °C min^{-1}.

from this process was not severe, being in a good agreement with their high stability as described in Fig. 4 and 5.

BET surface area were also measured on the fresh/spent γ-alumina used in the control tests, and the NiAl catalysts with various nickel loadings, as shown in Table 4. The fresh γ-alumina as the support material has the highest surface area and the BET surface areas reduced from 128 to 111 $m^2 g^{-1}$ as expected for the fresh NiAl catalysts as nickel loading increases from 8% to 27%. The BET surface area for the spent γ-alumina used in the control test has the lowest surface area, 76 $m^2 g^{-1}$, which was likely due to collapse of the pore structures of the catalyst during the reaction or the carbon deposition on the catalyst, blocking the micropores of the alumina sample. The carbon deposition/coking on the spent catalysts, not severe though, may be evidenced in Fig. 7. Interestingly, the spent 8% Ni/γ-alumina had an increased BET surface (143 $m^2 g^{-1}$) than the fresh one (128 $m^2 g^{-1}$), which might be due to Ni leaching during the course of the reaction in supercritical condition. The metal leaching is a common challenge for heterogeneous catalysts in liquid phase reaction systems. As such, Ni leaching would occur in the process, while interestingly nickel leaching did not negatively affect the catalyst's activity as the catalyst demonstrated activity for more than 18 h on stream and could be regenerated.

Table 4 BET surface areas of various fresh/spent catalysts

Catalyst samples	BET surface area ($m^2 g^{-1}$)
Fresh γ-Al_2O_3	152
Fresh 8% Ni/γ-Al_2O_3	128
Fresh 17% Ni/γ-Al_2O_3	119
Fresh 27% Ni/γ-Al_2O_3	111
Fresh Mn_2O_3 powder and 27% Ni/γ-Al_2O_3	123
Spent γ-alumina	76
Spent 8% Ni/γ-alumina	143

4. Conclusions

This study developed a one-step continuous process operating at 150–300 °C for conversion of sub-/supercritical ethanol into butanol and 1-hexanol as chemicals or fuels, as well as some other compounds that are also useful as biogasoline. The process distinguishes itself from the ones in the literature as it employs sub- and supercritical bio-ethanol as the reaction medium and γ-alumina supported Ni catalysts at an optimal metal loading. With the continuous flow fixed-bed tubular reactor and 8% Ni/γ-Al_2O_3 catalyst at a WHSV of 6.4 h^{-1} at 250 °C and 176 bar, the highest ethanol conversion of 35%, 1-butanol selectivity of 61.7%, and 1-butanol yield of 21.6%, as well as 1-hexanol yield of ∼5% with a selectivity of 20% were obtained.

The ethanol conversion and products selectivity were strongly dependent on the operating temperature/pressure and the nickel loading in the catalysts. Generally a higher temperature/pressure favoured the conversion and selectivity, while as the temperature was above 300 °C, more unwanted products and mostly gases were produced. It was demonstrated that 8% Ni/γ-Al_2O_3 is the most active catalyst among all catalysts tested including the Ni/γ-Al_2O_3 catalysts with 8–27 wt% Ni loading, and mixed catalysts of (Mn_2O_3/γ-Al_2O_3 + 27% Ni/γ-Al_2O_3) and (neat Mn_2O_3 + 27% Ni/γ-Al_2O_3). The 8% Ni/γ-Al_2O_3 catalyst in this study demonstrated outstanding stability, remaining active for 18 h on stream. After regeneration of the catalyst for multiple times at 500 °C with 100 mL min^{-1} hydrogen for 4–8 h, the catalyst could still maintain its activity for ethanol conversion to 1-butanol and 1-hexanol.

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