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Self-Etherification Process for Cleaner Fuel Production

Worapon Kiatkittipong · Khamron Yoothongkham · Choowong Chaisuk · Piyasan Praserthdam · Shigeo Goto · Suttichai Assabumrungrat

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Abstract The process of fluidized catalytic cracking (FCC) gasoline self-etherification with ethanol has several benefits. Firstly, the gasoline volume is effectively increased by adding ethers produced from ethanol which is renewable. Secondly, the etherified gasoline product has higher octane number with lower blending Reid vapor pressure (bRvp) and amount of olefins content. Two catalysts; i.e., Amberlyst 16 and Beta-zeolite are used for etherification in this study. The bRvp of etherified FCC gasoline is lower than that of ethanol direct blend gasoline (called gasohol) and also could be lower than that of original FCC gasoline with moderate ethanol conversion. However, the octane number of etherified FCC gasoline catalyzed by Amberlyst 16 is slightly lower than that of gasohol. Beta-zeolite is a more suitable catalyst than Amberlyst 16 for the etherification of FCC gasoline with ethanol because not only a better catalytic activity for etherification, but some isomerization also occurs without aromatization. Therefore it offers improved gasoline products with higher research octane number and gasoline renewability with lower bRvp than that of gasohol. Olefins and ethanol conversions increase with increasing ethanol ratio in feed. Nevertheless, ethanol feed ratio is limited specification of distillation temperatures which are dependent on the evaporation of ethanol and its amount. The cold start problem might not be occurred even in low bRvp as proven by satisfied drivability index.

Keywords Fluidized catalytic cracking gasoline · Olefin reduction · Octane enhancement · Self-etherification · Beta-zeolite · Amberlyst 16

1 Introduction

At the moment, transport fuel is mainly derived from fossil and the attention has been focused on biomass derived fuel production. Ethanol is one of the most widely-used renewable liquid fuel and may be among the most suitable choices for use with the existing infrastructure i.e. road, gas station and automobile engine. CO_2 produced from ethanol combustion is not considered as a global warming contributor because it is a part of the carbon cycle and therefore is carbon neutral. Since the CO_2 is recycled to the tissue during plant growth, with modern agriculture, soil organic matter can be built up and therefore net CO_2 can be removed from the atmosphere [1].However, some researchers have severely questioned the claim of its renewability. Pimental [2] claimed that ethanol might not be a renewable energy source. Its overall production system is uneconomic and causes environmental burden. In addition, the important concept of life cycle assessment was illustrated for ethanol production [3, 4]. CO_2 emissions over the life cycle of ethanol production are such that the net greenhouse benefit of low ethanol blends is marginal [5]. Although the advantages of using ethanol for fossil fuel

W. Kiatkittipong (✉) · C. Chaisuk
Department of Chemical Engineering, Faculty of Engineering
and Industrial Technology, Silpakorn University,
Nakhon Pathom 73000, Thailand
e-mail: kworapon@su.ac.th

K. Yoothongkham · P. Praserthdam · S. Assabumrungrat
Center of Excellence in Catalysis and Catalytic Reaction
Engineering, Department of Chemical Engineering,
Faculty of Engineering, Chulalongkorn University,
Bangkok 10330, Thailand

S. Goto
Department of Chemical Engineering, Nagoya University,
Chikusa, Nagoya 464-8603, Japan

substitution are controversy, ethanol consumption still extends over the world.

Ethanol can be blended directly into gasoline which is called as gasohol. Flexible-fuel cars can be run on up to 85 vol% (E85) or pure ethanol. However, most of present cars can be run on gasoline blended with lower concentration of ethanol i.e., 10–20 vol%. Therefore the chance of using ethanol as a fuel extender is limited. Furthermore, many recent researches reported disadvantages of the gasohol [6]. With a present standard of engine and the use of catalytic converter, the emissions at the end pipe are relatively small while evaporative emissions have become significant. Evaporative emissions are considered as a loss of fuel which can be occurred from diurnal, running loss, hot soak and refueling [7, 8]. Therefore, some researchers found that the overall air pollutant emissions (exhaust and evaporative emissions) by the use of gasoline-ethanol blend appear to be higher than those posed by conventional gasoline because of its high blending Reid vapor pressure (bRvp) [6]. An ethanol-gasoline mixture also undergoes a phase separation on contact with water which increases the corrosion of steel underground storage tanks, increasing the risk of leakage to surrounding soil. Even though ethanol/gasoline (gasohol) can tolerate significantly higher water content than conventional gasoline before phase separation, the problem on the engine is more serious. Ethanol partitions preferentially into an aqueous phase and therefore causes an off-spec gasoline. Combustion of this partition causes the lean burn effects [8]. Refiners and auto-makers prefer to use ethers to meet the octane number and oxygenate requirement for technical reasons because ethers can overcome the drawbacks of gasoline with direct ethanol blend.

Most of ethers are derived from methanol and ethanol [9–25] and some from butanol [26] and glycerol [27–29]. Although methanol can also be produced from biomass, the production is cost-intensive and therefore it is currently made from natural gas which is more cost-competitive [30]. As a result, ethers derived from ethanol could be the most suitable additives for gasoline extender and octane modifier. The most well-known ethanol-derived ethers are ethyl tertiary butyl ether (ETBE) and tertiary amyl ethyl ether (TAEE). Commercially, ETBE and TAEE can be produced by etherification of ethanol with isobutene (IB) and isoamylene (IA), olefinic compounds, respectively. Several researchers investigated the liquid phase reaction of ETBE synthesis. The kinetic expressions [31–33] and thermodynamic equilibrium were reported [34]. It still has drawn the attention from some researchers [35–39]. For TAEE synthesis, the major isomer of IA is 2-methyl-2-butene (2M2B) which is usually assumed to be in isomerization equilibrium with 2-methyl-1-butene (2M1B). Rihko and Krause [40] found that 2M1B was more reactive than 2M2B which is in good agreement with other researches [41, 42]. There are a number of studies focusing on etherification of 2M1B and 2M2B with ethanol in both kinetics [43, 44] and the reaction equilibrium [45, 46].

Unconventional routes for ethers synthesis were also previously investigated. *tert*-Butyl alcohol (TBA), a major by-product of propylene oxide production, and *tert*-amyl alcohol (TAA), a major component of fusel oil which is a by-product obtained from biomass fermentation were employed as a reactant with ethanol for ETBE and TAEE synthesis, respectively [47–53]. However, unfortunately, the productions of ETBE and TAEE via these olefinic compounds i.e., IB, IA or alcohols i.e., TBA, TAA are unlikely to meet demands of oxygenate ethers. Heavier reactive olefins should be considered as additional reactants for ether production. 3-Methoxy-3-methylheptane was firstly investigated by etherified 2-Ethyl-1-hexene with methanol [54]. Consequently, etherification of C5- and C8-alkenes i.e., 2-methyl-1-butene and C8–2,4,4-trimethyl-1-pentene, respectively, with different C1- to C4-alcohols was studied [55].

FCC light gasoline is a potential valuable feedstock of reactive olefins for production of oxygenated ethers. On the contrary, these olefinic compounds are among the most photochemical reaction components of hydrocarbon emissions from automotive engines which strongly affect on ground ozone level. Therefore they should be diminished also in order to meet the new mandatory of gasoline composition which allows the olefin content not to exceed 20 or 18 vol% as regulated by the International charter on clean fuels and Euro 4 standard, respectively. Pescarollo et al. [56] studied the etherification of the entire light FCC gasoline with methanol. IA conversion was 68.8% close to thermodynamic equilibrium while conversions of C_6 and C_7 reactive olefins were 42.9% and 23.2%, respectively. Simultaneous improvements in octane number and gasoline volume with reductions in olefinicity, atmospheric reactivity and bRvp of gasoline were obtained. Similar reaction was also studied by using Amberlyst 16, a cation-exchange resin, as a catalyst in a temperature range of 50–80 °C [57]. They reported the initial etherification rates and thermodynamic limitations for the reaction of methanol with the C_5 and C_6 olefinic compounds. The equilibrium constants of C_6 olefins etherified with ethanol were lower than those of IA, C_5 olefins. Various zeolites were investigated on FCC light gasoline etherified by methanol. The activities were ordered as: $H\beta > HMOR > HZSM\text{-}5$. $H\beta$ also showed higher catalytic stability than other catalysts for the production of TAME [58].

Conversions of olefins in FCC gasoline by hydroisomerization and aromatization have been recently investigated by many researchers [59–63]. The loss of octane number from olefin reduction was compensated by the formation of iso-paraffins and aromatics. This process is beneficial in the viewpoint of olefin reduction; though aromatic compounds which have a greater tendency to emit unburned hydrocarbons [64] might be produced.

However, the previous processes for upgrading FCC gasoline are still based on non-renewable energy. To enhance the renewability of gasoline, ethanol could be more partly substituted into gasoline with quality improvement aspects as illustrated in our preliminary work [65]. In this study, the entire FCC gasoline was fed with ethanol in a molar ratio of 80:20 and 70:30. The gasoline composition, olefin and ethanol conversion, and the amount of ethers production were clarified. The gasoline properties i.e., RON, bRvp, distillation temperature (IBP, T10, T50, T90 and FBP), estimated minimum cold start temperature and drivability index were compared between original FCC gasoline, commercial E10 gasohol, FCC with direct blend of ethanol and etherified FCC gasoline. Aspect of catalyst characterization on catalytic activity was also discussed.

2 Experimental

2.1 Chemicals

FCC gasoline is cut off from a catalytic cracking unit of an oil refinery. Ethanol (99 vol%) and other chemicals needed in the experiment were analytic grade. All chemicals were used without further purification.

2.2 Catalysts

The ion exchange resin catalyst, Amberlyst 16 and the strong acid solid catalyst, Beta-zeolite with Si/Al = 40 (H^+ form) were selected for this study. Amberlyst 16 and Beta-zeolite were purchased from Fluka and Tosoh (Japan), respectively. The catalysts were dried overnight in an oven at 110 °C before use. The properties of the catalysts are shown in Table 1. The acidity of the catalysts and pore size were reported by the producer. BET surface area of the catalysts was measured by Micromeritics ASAP 2020. A sample of 0.3 g was degassed at 300 °C for 3 h and the amount of N_2 adsorption was recorded. The thermogravimetric analysis (TGA) curves were obtained in flowing air on SDT Q600 (TA instruments) with a temperature increasing rate of 5 °C/min in the range of 30–1,000 °C.

Table 1 Properties of catalysts

Catalysts	Surface area (m^2/g)	Pore diameter (nm)	Acidity (mmol H^+/g)
Amberlyst 16	45	20	5.0
Beta-zeolite	625	0.58	1.03

2.3 Apparatus

The reaction was carried out in a cylindrical shape autoclave reactor as shown in Fig. 1. The 100 cm^3 reactor was maintained at a constant temperature by circulating hot water in jackets. The turbine was used to stir the mixture at the maximum speed of 1163 rpm by a speed controller in all experiments to minimize the external mass transfer resistance [52]. A valve for liquid sampling and a port for the thermocouple were installed at the top.

2.4 Analysis

In gasoline investigations, the compounds called "PIANO" consisting of paraffins, isoparaffins, aromatics, naphthenes and olefins were determined with the amount of the oxygenates. They were analyzed by an FID gas chromatograph with a Supelco capillary column. The analysis was done by injecting 1 μL of sample in the column. It should be noted that a sample must be centrifuged before the injection in order to separate residue catalyst which can damage the GC column. The injector and detector temperature were 250 °C. The column was heated with three ramps. Firstly, the column was heated from 5 to 65 °C with a ramp rate of 6 °C min^{-1} and holding at 65 °C for 45 min. Afterward, heated to 180 °C, with a ramp rate of 3 °C min^{-1} and holding for 5 min. Finally, the temperature was increased at a ramp rate of 10 °C min^{-1}–200 °C where it was held for 0.5 min. The amount of ethanol was further analyzed

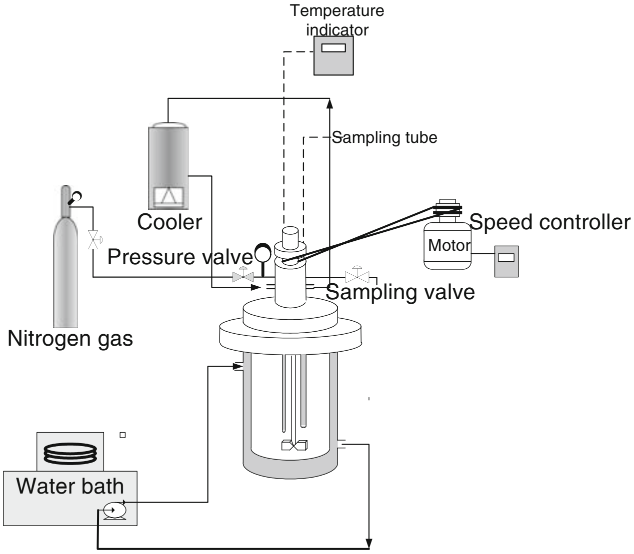

Fig. 1 Experimental apparatus

by Shimadzu GC 14B with hydrogen flame ionization detector. The separation column was a DB-1 capillary column and He was used as a carrier gas. The standard test methods of ASTM D-2699, ASTM D-5191 and ASTM D-86 were employed to determine Research Octane Number (RON), blending Reid vapor pressure (bRvp) and distillation temperature, respectively.

2.5 Operation Procedure

The experiments were carried out at 70 °C for 10 h in the batch reactor. The system was pressurized by N_2 at 0.8 MPa to ensure that all reaction components were in the liquid phase. The reaction system consisted of FCC gasoline and ethanol with a volume ratio of 80:20 and 70:30 with 10 g of catalyst. The samples of feed and product were collected at the initial and final of the experiment. It should be noted that for collecting the final product after run for 10 h, the reactor was cooled down to room temperature before opening the reactor and collecting the sample in order to minimize the evaporation loss.

3 Results and Discussion

3.1 Gasoline Composition and Reaction Activities

The distributions of the hydrocarbon groups present in the FCC gasoline feed are shown in Table 2. Most olefins were in a range of C_5 through C_7 hydrocarbons. The fraction of total olefins was about 25 vol%. Table 3 provides the gasoline composition, olefins conversion and ethanol

Table 2 Compositions of FCC gasoline in volume percent

Carbon number	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	Total
n-Paraffins	0.435	1.054	0.816	0.766	0.932	0.28	0.249	0.133	0.046	0.014	4.726
i- Paraffins	0.268	8.109	7.759	0.18	4.805	3.991	3.214	1.33	0.135	0	35.79
Olefins	1.976	8.739	6.856	6.097	1.129	0.655	0.218	0	0	0	25.67
Naphthenes	0	0.112	1.821	3.023	3.737	2.522	0.564	0.21	0.049	0	12.038
Aromatics	0	0	0.333	2.373	4.979	4.944	2.782	1.26	0.31	0	16.98
Total	2.679	18.014	17.584	18.439	15.582	12.391	7.026	2.933	0.54	0.014	95.204

Table 3 Gasoline composition, olefins conversion and ethanol conversion of FCC gasoline with different treatments (FCC: ethanol volumetric ratio = 80:20)

Component	FCC gasoline (g)	Ethanol (g)	20 vol% Ethanol		
			Direct blend (g)	Etherified gasoline	
				Amberlyst 16 (g)	Beta-zeolite (g)
Olefins					
-C4	1.76	–	1.76	0.92	0.86
-C5	8.85	–	8.85	6.15	5.1
-C6	5.69	–	5.69	4.42	3.54
-C7	4.54	–	4.54	3.56	2.73
-C8	1.09	–	1.09	0.29	0.28
-C9	0.44	–	0.44	0.29	0.29
-C10	0.35	–	0.35	0	0.15
Other hydrocarbon	54.84	–	54.84	55.79	55.08
Oxygenates					
-Ethanol	0	22.44	22.44	15.87	14.29
-Ether	0	–	–	12.71	17.68
Total	77.56	22.44	100	100	100
C4 Olefins conversion (−)	–	–	0	0.48	0.51
C5 Olefins conversion (−)	–	–	0	0.31	0.42
C6 Olefins conversion (−)	–	–	0	0.22	0.38
C7 Olefins conversion (−)	–	–	0	0.22	0.40
Ethanol conversion (−)	–	–	0	0.29	0.36

conversion of FCC gasolines directly blended and etherified with ethanol with a volume ratio of 80:20. Since pure ethanol was supplemented into the FCC gasoline with 20 vol% (~22.4 wt%) for both cases, the amount of final gasoline product was increased. In the case of ethanol direct blend, the amount of each component is constant because the reaction cannot occur without the catalyst. In the cases of etherified gasoline, Amberlyst 16 and Beta-zeolite were used as catalysts. Olefins and ethanol were mainly converted to ethers. Comparing between two catalysts, it was found that Beta-zeolite gives higher ethanol and olefins conversions, resulting in higher ether products. It is worthy to note that olefins conversions are lower with larger atomic number of olefins in both catalysts because large molecular of olefins hardly enters to pores of catalyst [58]. The tendency of these results was similar to that of the etherified FCC gasoline with methanol experimented by Pescarollo et al. [56]. They reported that the conversions of C4, C5, C6, and C7 olefins were 0.84, 0.64, 0.43, and 0.23, respectively. Even though the FCC feed composition and the ratio of alcohol to FCC were different, a simple comparison between the performance of methanol [56] and ethanol (as shown in Tables 3 and 4) for etherification could be noticed. Higher conversion of isobutene (C4) and isoamylene (C5) in FCC with methanol than with ethanol were observed. These results are similar to the individual study of C4 and C5 olefins with alcohol in the literature [40, 45, 66–68]. The activity of ethanol was less than that of methanol as a result of the decrease of dielectric constant or polarity. The value of dielectric constants decreased with increasing of molecular weights of alcohols which were 32.6 and 24.3 for methanol and ethanol, respectively. The more polar component could be preferably adsorbed over the actives sites than the less polar component [55].

However, the comparable or some higher conversions of C6 and C7 olefins with ethanol compared to those with methanol were unexpected. The higher conversion of C6 olefins with ethanol over that with methanol also has been previously observed by Rihko and Krause [57]. These contrasting results might be explained by the study of Cruz et al. [69]. They declared that ethanol can react with alkenes easier than methanol due to the higher acidity of ethanol. The complexity of the system might be related to the complicated mechanism of adsorption over active site. Many components; i.e., alcohol, ether and hydrocarbon having significantly different polarity should play a role; therefore, this issue should be further investigated.

The ratio of FCC gasoline and ethanol was changed to 70:30 and the reaction was carried out at the same operating condition described earlier. The results are summarized in Table 4. Beta-zeolite still shows a better catalyst

Table 4 Gasoline composition, olefins conversion and ethanol conversion of FCC gasoline with different treatments (FCC: ethanol volumetric ratio = 70:30)

Component	FCC gasoline (g)	Ethanol (g)	30 vol% ethanol		
			Direct blend (g)	Etherified gasoline	
				Amberlyst 16 (g)	Beta-zeolite (g)
Olefins					
-C4	1.72	–	1.72	0.78	0.67
-C5	7.72	–	7.72	3.39	3.19
-C6	5.12	–	5.12	3.79	2.28
-C7	3.86	–	3.86	2.07	1.88
-C8	0.94	–	0.94	0.51	0.58
-C9	0.39	–	0.39	0.12	0.17
-C10	0.29	–	0.29	0.22	0.06
Other hydrocarbon	46.81	–	46.81	48.32	47.82
Oxygenates					
-Ethanol	–	33.15	33.15	18.69	16.06
-Ether	–	–	–	22.11	27.29
Total	66.85	33.15	100	100	100
C4 Olefins conversion (–)	–	–	0	0.55	0.61
C5 Olefins conversion (–)	–	–	0	0.56	0.59
C6 Olefins conversion (–)	–	–	0	0.26	0.55
C7 Olefins conversion (–)	–	–	0	0.46	0.51
Ethanol conversion (–)	–	–	0	0.44	0.52

performance than Amberlyst 16. Compared with Table 3, the ethanol conversion and all C4–C7 olefins conversions increased with increasing ethanol fraction in feed. The remaining unreacted ethanol from the case with the feed ratio of 70:30 did not exceed the ethanol content of 15 vol% in the case of Beta-zeolite. Therefore it is not over the gasoline specification of i.e., E15 and E20 which are limited by ethanol content of 15 and 20 vol%, respectively. The effect of gasoline composition in both Tables 3 and 4 are further discussed with the gasoline properties shown in Table 5.

3.2 Gasoline Properties and Their Quality Improvement

Table 5 summarizes the gasoline properties comparison. FCCs with direct ethanol blend at 20 and 30 vol% increased RON from original of 88 up to 94.8 and 97.9, respectively. However, unfortunately their bRvp also increased dramatically. As shown experimentally, FCCs etherified with ethanol by using both Amberlyst 16 and Beta-zeolite catalysts can effectively decrease the values of bRvp because the reactive olefins in FCC gasoline and ethanol are converted to ethers which have lower bRvp. FCCs etherified with 30 vol% ethanol both catalyzed by Beta-zeolite and Amberlyst 16 give lower bRvp than FCC with direct ethanol blend at 20 vol%. These results also confirm the increase of ethanol substitution ability into gasoline. Comparing with original FCC gasoline, the bRvp value of etherified gasoline catalyzed by Beta-zeolite is lower or similar in the cases of using 20 and 30 vol%, respectively. These results may strongly depend on the decrease of olefins content and the amount of unreacted ethanol remaining in the solution. Therefore, it is worthy to note that the difference of bRvp between original FCC gasoline and etherified gasoline may not be as significant as that of bRvp between FCC with direct ethanol blend and etherified gasoline. The decrease in bRvp reduces the evaporative loss of fuel hence preventing vapor lock in summer. As known that too low bRvp might cause a cold start problem, however, it might not be in this case as it was proven by minimum cold start temperature and drivability index (DI) which will be discussed later.

Comparing the RON between ethanol directly blended and etherified gasolines, the gasoline etherified by Amberlyst 16 shows slightly lower octane number than ethanol directly blended gasoline because ethanol has higher value of octane number (RON = 118) than ethers, e.g., ETBE, TAEE and *tert*-hexyl-ethyl-ether (THEE) whose RON are 118, 105, and 110, respectively. However, the gasoline etherified using Beta-zeolite as catalyst shows similar RON to that of ethanol direct blended gasoline and slightly higher than that of etherified gasoline catalyzed by Amberlyst 16.

Table 5 Comparison of gasoline properties

Properties	ASTM standard	FCC gasoline	Gasohol E10	20 vol% ethanol			30 vol% ethanol		
				Direct blend	Etherified gasoline		Direct blend	Etherified gasoline	
					Amberlyst 16	Beta-zeolite		Amberlyst 16	Beta-zeolite
RON	D-2699	88.0	95.0	94.8	93.0	94.1	97.9	96.9	98.2
bRvP (psi)	D-5191	6.5	<9.0	7.441	7.05	5.657	8.0	7.24	6.58
Density (g/cm^3)		0.683	0.749	0.735	0.739	0.745	0.735	0.739	0.745
Viscosity × 10^6 (g_f.s/cm^2)		6.213		6.325	5.374	6.310	6.152	6.035	5.160
Distillation	D-86								
Temperature °C (°F)									
IBP		35.5(95.9)		41.9(107.4)	43.3(109.9)	47.7(117.9)			
T 10		57.1(134.8)	<70(158)	55.2(131.4)	56.9(134.4)	59.7(139.5)			
T 50		99.0(210.2)	70–110(158–338)	70.2(158.4)	75.0(167)	73.8(164.9)	N.D	N.D	N.D
T 90		168.7(335.7)	<170(338)	165.9(330.6)	167.1(332.8)	170.2(338.4)			
FBP		196.0(384.8)	<200(392)	194.7(382.5)	193.1(379.6)	198.2(388.8)			
Driveability index, DI °C (°F)		631(1168)	<677(1250)	617(1143)	635(1175)	638(1182)			
Estimated minimum cold start temperature °C (°F)		−6.7(19.9)	–	−8.1(17.42)	−6.9(19.58)	−5.1(22.82)			

Fan et al. [59] found that Beta-zeolite was an effective catalyst for upgrading FCC gasoline via isomerization and some aromatizations. However, fortunately the amounts of aromatic are not increased in the case of FCC gasoline etherified with Beta-zeolite (not shown here). As the amounts of aromatic are not increased, there is no greater tendency in damage to elastomers and increased of toxic aromatic emissions as unburned hydrocarbons. Therefore, the enhancement of octane number in the case of FCC etherified by Beta-zeolite is not from etherification reaction only but also from isomerization. In addition, Corma et al. [70] studied various zeolites as catalysts for the cracking of *n*-heptane, a model molecule of gasoline range. When using Beta-zeolite as a catalyst, the ratio of isobutene to *n*-butene and isopentene to *n*-pentene products were 1.27 and 2.0, respectively. Therefore, ether products may not be possibly limited by the amount of reactive olefins originally present in gasoline, the reactive olefins could be further obtained via cracking by Beta-zeolite.

In the case of Amberlyst 16, Slomkiewicz et al. [71] reported that Amberlyst showed high catalytic activity for double bond isomerization or the *cis-/trans*-transformation. However, the isomerization from linear olefin to branched olefin is much more difficult because the reaction normally required significantly higher temperature at which Amberlyst could not resist [72].

Apart from bRvp which represents the volatility property of gasoline, T10, T50, and T90 (D-86 temperature at 10, 50 and 90 vol%, respectively) and drivability index are key motor gasoline specifications in the US. The distillation temperature (IBP, T10, T50, T90, and FBP) and drivability index are also provided in Table 5. Initial boiling point (IBP) increased with the presence of ethanol both in gasoline with direct ethanol blend and etherified gasoline with some unreacted ethanol. Comparing with unmodified FCC gasoline, T10, T50, T90, and FBP decrease in the case of gasoline with direct ethanol blend and etherified with Amberlyst 16. While in the case of etherified with Beta-zeolite, the distillation temperature decreases only for T10 and T50. IBP and T10 effects cold starting ability and inversely vapor lock problem. Increase these front end distillation temperature may increase minimum cold start temperature while decrease the possibility of vapor lock. The minimum cold start temperature could be estimated by the empirical relation as [73] Minimum cold start temperature (°C) $= 5.62\sqrt{\mathrm{T10} - 40} - 30$.

As shown in Table 5, the estimated minimum cold start temperature of etherified gasoline did not pose a cold start problem comparing to original FCC gasoline. However, the appropriate values strongly depend on the regional and seasonal of their used.

From the above results, these may imply that distillation temperatures of ethanol containing fuels are dependent on the evaporation of ethanol and its amount. These results can also be confirmed with the decrease of the bRvp as shown in the Table 5, i.e., with higher ethanol converted, the distillation temperatures in the case of Beta-zeolite seem to be higher than those of Amberlyst 16 and ethanol directly blended, respectively. It is worthy to note that T50 of FCC-ethanol blend is marginal with the specification value of gasohol E10, it is possibly that blending with higher amount of ethanol i.e., 30 vol% may make the T50 off specs. Therefore, the distillation temperature test of ethanol 30 vol% was not performed but the available results are enough for discussion.

A drivability index (DI) has been developed to predict cold-start and warm-up drivability. The drivability index, DI is defined as follows [8, 74].

$$\mathrm{DI} = (1.5 \times \mathrm{T10}) + (3 \times \mathrm{T50}) + \mathrm{T90} \qquad (1)$$

When oxygenate are present in the gasoline, the DI could be corrected as follows [75]

$$\mathrm{DI} = (1.5 \times \mathrm{T10}) + (3 \times \mathrm{T50}) + \mathrm{T90} + 20 \times \mathrm{wt\%\ oxygen} \qquad (2)$$

Drivability index provides the relationship between drivability and distillation properties. T10 represents the gasoline ability to vaporize rapidly and enable cold starting. T50 and T90 represent the heavier gasoline components' ability to vaporize as the engine warms up and be burnt during combustion. Therefore, lower values of DI generally result in better cold-start and warm-up performance; however, low DI can indicate poor drivability in that the combustion is too rich of stoichiometry [75]. Therefore once good drivability is achieved, there is no benefit to further lowering the DI [76].

As shown in Table 5, DI values of FCC gasoline and those of etherified FCC gasoline do not show considerable difference, however, the values of DI of the gasoline products are in the satisfied range of the gasoline specification.

3.3 Aspect of Catalyst Characterization on Catalytic Activity

Linnekoski et al. [44] investigated the etherification and hydration of isoamylene catalyzed by ion exchange resin. Addition of only small amount of water resulted in significantly dropped in ethanol and olefins conversion [44]. Karinen et al. [55] reported that water reacted to tertiary alcohol at an early stage relative to the other reactions. This is because the higher acidity of water compared to that of ethanol resulted in the increasing of basic solvated proton which lowers activity as previously mentioned in the literature [77–79]. In our experiments, although both catalysts were dried at 110 °C overnight, the remaining water adsorbed in the pore of catalyst might be examined by thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTGA).

TGA and DTGA of Amberlyst 16 were investigated as shown in Figs. 2 and 3, respectively. The weight loss of Amberlyst 16 at the temperature lower than 200 °C are almost 10 wt% which should be corresponding to the amount of water desorption [80, 81]. The consecutive mass loss step of Amberlyst 16 might be the thermal desulfonation [80]. The final peak at 470 °C of DTGA (Fig. 3) might be the thermooxidative decompositions of a polymers matrix [80] which corresponds well with high intensity exothermic as shown in Fig. 2.

On the contrary, insignificant weight loss at the temperature lower than 200 °C can be observed in the case of Beta-zeolite as shown in Fig. 4, indicating traces of water desorption. Thermal analysis also revealed desorption of precursor component such as organic template [81] i.e., at the temperature of 420 and 560 °C. The DTGA in Fig. 5 showed corresponding well of intense exothermic heat. However, it should be noted that weight loss and exothermic heat were much more pronounced in the case of Amberlyst 16. This TGA results also confirm the higher thermal stability of Beta-zeolite than that of Amberlyst 16.

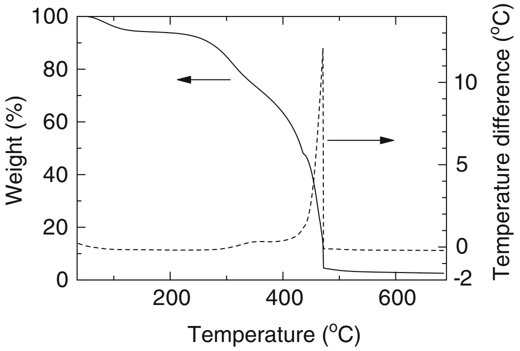

Fig. 2 Thermogravimetric analysis (TGA) of Amberlyst 16

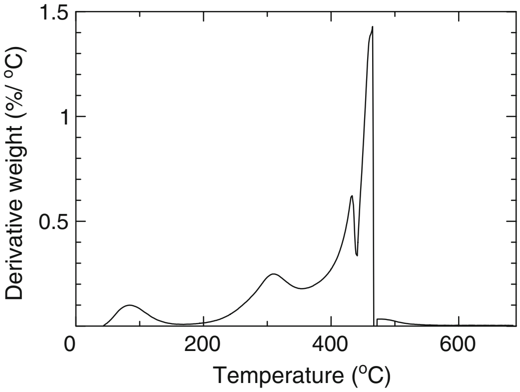

Fig. 3 Differential thermogravimetric analysis (DTGA) of Amberlyst 16

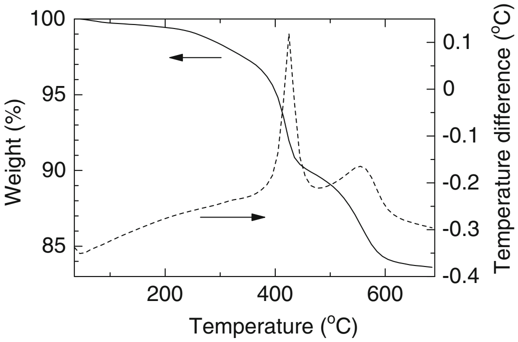

Fig. 4 Thermogravimetric analysis (TGA) of Beta-zeolite

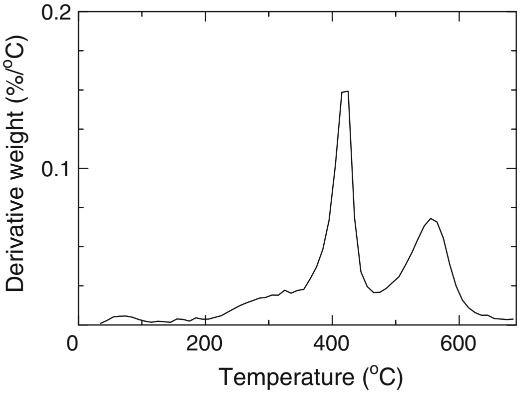

Fig. 5 Differential thermogravimetric analysis (DTGA) of Beta-zeolite

Therefore, it can be concluded here that Beta-zeolite is a more suitable catalyst for upgrading FCC gasoline with ethanol compared to Amberlyst 16. For other gasoline properties, the density and the viscosity of the etherified gasoline are close to those of the commercial gasohol.

In summary, etherification of FCC gasoline enhances the possibility of ethanol substitution and therefore its renewability without increasing gasoline volatility. Olefinic compound was consumed in the reaction process which lessens cost for the refining industry to limit total gasoline olefins following the regulations without octane loss.

It is recommended that additional works such as development of an industrial-scale process for the self-etherification reaction, studies of the nature of the catalytic reaction, and studies of the process economics should be further investigated.

4 Conclusion

Although ethanol direct blend increased RON of FCC gasoline, the value of bRvp became also significantly higher. Etherification of FCC gasoline with ethanol decreased the bRvp significantly and could be possibly lower than that of original FCC gasoline. Beta-zeolite was a more suitable catalyst than Amberlyst 16 for upgrading FCC gasoline. This was due to the higher of catalytic activity for etherification, ethanol could be converted more and therefore increased the renewability of the gasoline while olefinic compounds could be decreased to meet the Euro 4 standard. Normally, the FCC etherified gasoline might give slightly lower of RON compared to ethanol direct blend because RON of ethers were usually lower than that of ethanol. However, Beta-zeolite also showed a catalytic activity of isomerization reaction, RON of the gasoline product was enhanced. The etherified gasoline also showed satisfactions in term of minimum cold start temperature and driveability index. Therefore, the process allows the use of ethanol to substitute in gasoline at higher content than conventional method with direct blending and more suitable gasoline properties can be obtained.

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