

Green Chemistry

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Conversion of Biomass Derived Valerolactone into High Octane Number Gasoline with Ionic Liquid

Jiayu Xin, Dongxia Yan, Olubunmi Ayodele, Zhan Zhang, Xingmei Lu, Suojiang Zhang*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

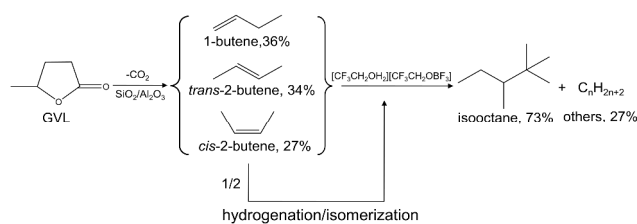
DOI: 10.1039/b000000x

Conversion of biomass into gasoline with high octane number is challenging. In this study, conversion of biomass-derived γ -valerolactone into gasoline was achieved by decarboxylation of valerolactone to produce butenes and alkylation of produced butenes with butane using $[\text{CF}_3\text{CH}_2\text{OH}_2][\text{CF}_3\text{CH}_2\text{OBF}_3]$ as an efficient catalyst. The obtained gasoline was rich in trimethylpentane with a high research octane number of 95.4.

Conversion of biomass into hydrocarbons is one of the most possible alternatives to alleviate the environmental, political, and economic burdens associating with the depletion and consumption of fossil-based resources.^{1,2} In the past several years, much effort was devoted to the research on producing hydrocarbons with extended carbon chains by hydrogenation of carbohydrate derivatives.³⁻⁵ One of the earliest efforts was the aqueous phase reforming (APR) process,⁶ by which, sugars were converted to alkanes by hydrogenation with noble metals as catalysts.⁷ Later, some important approaches were developed by Dumesic *et al.*,^{8,9,10} Corma *et al.*¹¹ and others.¹²⁻¹⁴ In these approaches, the indispensable intermediates employed were 5-hydroxymethyl furfural and furfural derived from C₆ and C₅ sugars. The production costs of these intermediates are high due to high energy consumption in separation and relative low availability.¹⁵ Recently, Dumesic *et al.*¹⁶ reported an approach for the production of alkenes by polymerization of butenes from decarboxylation of γ -valerolactone by solid acid catalyst. However, the products of above processes are alkanes/alkenes without branch or with single branch, which only can be used as substitute for diesel fuel or additives of jet fuels.¹⁷ In addition, the produced fuels contains significant amount of olefin, particularly for the fuels produced by dimerization of butenes. In order to ensure the stability of the fuel, olefin content is strictly required to be lower than 18%.¹⁸ The research on the production of bio-based alkanes for the purpose of gasoline, the biggest consumed transportation fuel, is very rare. The main obstacles may be concluded as: 1) it is difficult to control the carbon numbers of alkanes from 6-12, especially to control the C₈ content with the highest portion;¹⁹ 2) it is difficult to control the antiknock index to satisfy the requirement of gasoline motors.

The carbon numbers of alkanes is crucial for the density, fluidity, viscosity, ignition, distillation and vapor pressure parameters of gasoline, while antiknock index indicates the resistance to autoignition. As one of the most important fuel properties of gasoline, antiknock index is indicated by Research

Octane Number (RON) or Motor Octane Number (MON). Linear alkanes always have very low RON and MON. For example, the RON of *n*-heptane is 0, while that of isooctane (2,2,4-trimethylpentane) is 100. Gasoline with a higher octane number is less prone to auto-ignition and can withstand a greater rise in temperature during the compression stroke of an internal combustion engine without auto-igniting, thus allowing more power to be discharged by higher compression ratio. In order to meet the requirement of antiknock properties, additives including MTBE, ETBE, isooctane and toluene tetraethyllead or oxygenated compounds are usually added into gasoline.^{20,21} However, these additives have many confirmed or non-confirmed drawbacks. The best choice is to produce the gasoline with more C₈ alkanes and more branches.^{22,23}



Scheme 1. Production of high octane number gasoline from GVL

Therefore, we developed a process for the production of highly branched alkanes rich in trimethylpentane as gasoline with high octane number. Scheme 1 shows the process for the production of high octane number gasoline from γ -valerolactone (GVL), which can be produced by hydrogenation of biomass-derived levulinic acid²⁴⁻²⁹ or directly from fructose.³⁰ The first step of the process is decarboxylation of GVL to give butenes including 1-butene, *trans*-2-butene and *cis*-2-butene with $\text{SiO}_2/\text{Al}_2\text{O}_3$ as the catalyst. A part of butenes are hydrogenated and isomerized to produce isobutane. Isobutane also can be produced via bioethanol in a high yield.³¹ Then, remained butenes react with isobutane to give iso-octane as the gasoline fuel. The use of acidic ionic liquid $[\text{CF}_3\text{CH}_2\text{OH}_2][\text{CF}_3\text{CH}_2\text{OBF}_3]$ provides a high yield of highly branched alkanes and thus ensures a high octane number of the products.^{32,33}

Experimental

Catalyst preparation

Preparation of $\text{SiO}_2/\text{Al}_2\text{O}_3$

SiO₂/Al₂O₃ solid catalyst was prepared by a sol-gel method. A known amount Si(OC₂H₅)₄ (99%, Xilong Chemical Industry) was dissolved in ethanol, and its pH value was adjusted at 3.0 by glacial acetic acid. The solution was maintained at 50 °C under vigorous stirring to obtain a homogenous silica sol. A known amount of aluminum precursor Al(NO₃)₃·9H₂O (99%, Xilong Chemical Industry) was dissolved in distilled water. Si(OC₂H₅)₄ and Al(NO₃)₃·9H₂O solutions were then mixed and stirred for 2 h at 50 °C. Ammonium hydroxide solution (NH₄OH, Sigma-Aldrich) was slowly added into the mixed solution to form a hydrogel at pH of 8.0, after aged for 24 h at 25 °C, the liquid was removed by filtration. The remained solid was washed with distilled water for several times to remove ammonium nitrate and subsequently washed with ethanol to form porous structure of hydrogel. The resulted gel was dried in a convection oven at 100°C for 24 h, and then calcinated at 500 °C for 4 h to get SiO₂/Al₂O₃ catalyst.

Preparation of [CF₃CH₂OH][CF₃CH₂OBF₃]

100 g 2,2,2-trifluoroethanol (CF₃CH₂OH, 99%, J&K Scientific Ltd.) was placed in a 500 ml polytetrafluoroethylene bottle with a rubber cap, an inlet and a safety outlet. BF₃ (99%, Heli Chemical Industry Co.) contained in a high pressure steel cylinder was slowly released to the bottle through a 3 mm diameter polytetrafluoroethylene tube. In order to remove the heat generated during the reaction, the bottle was surrounded by dry ice and the reactants were stirred continuously. The weight of the bottle with reactants was recorded periodically. BF₃ was stopped to pass when no weight increase was observed, which means the reaction between BF₃ and CF₃CH₂OH was finished. The obtained product was found to be [CF₃CH₂OH][CF₃CH₂OBF₃].

Experimental procedure

Decarboxylation

Decarboxylation of GVL (2 g, 99%, purchased from J&K Scientific Ltd.) was carried out in a 50 ml batch-type reactor with continuous stirring from 250-350 °C with 10% SiO₂/Al₂O₃ catalyst mentioned above.

Alkylation

Alkylation of isobutane and butenes (1-butene: 2-butene=3:7, supplied by Changlin Senmao Chemical Ltd Co., >99.9 % purity) was performed in a 100 ml stirred stainless steel reactor. Reaction temperature was maintained by placing the reactor in a cooling bath filled with cycling ethanol. Even though, a temperature increase of 3-8 °C inside of the reactor was observed. [CF₃CH₂OH][CF₃CH₂OBF₃] catalyst was firstly placed in the reactor and then the isobutane and butane mixture was pumped into the reactor by a syringe pump to carry out the reaction.

Analytical method

The gas and liquid products were analyzed by a GC (Agilent GC 7890) equipped with a flame ionization detector and a DB-Petro column (0.25 mm*100 m, Agilent Co.). The analysis conditions were: nitrogen as carrier gas, split ratio=26:1, injector temperature=250 °C, detector temperature=300 °C. The

temperature program for GC analysis were: initial column temperature 40 °C, hold for 10 min, 0.5 °C/min to 80 °C, then 5 °C/min to 300 °C hold for 15 min.

Results and discussion

Conversion of GVL into butenes

The products of decarboxylation of GVL was a mixture of butenes including 1-butene, 2-butene (*cis*-2-butene and *trans*-2-butene) and CO₂. For a reaction time of 4 h, low temperature gave a low yield (Table 1). A good yield of 97 % was achieved at a temperature of 350 °C (entry 3, Table 1). However, a temperature higher than 350 °C decreased the yield of butenes possibility due to the coke formation, likely by polymerization of pentenoic acid produced by ring open reaction of GVL,³⁴ which further decreased the activity of SiO₂/Al₂O₃ catalyst. The side reactions were also noticed at high temperature, some cracking products including methane and propane were found at 400 °C. Reaction time also affected the yields of butenes, 1 h reaction only gave a yield of 50 %, while increases the reaction time to 4 h increased the yield to 97 % and further prolonged the reaction time longer than 4 h had minimal effect on the decarboxylation (Table 1).

Table 1. GVL conversion and butane yield under different reaction condition with 10% SiO₂/Al₂O₃ as the catalyst in batch type reactor

Entry	Time (h)	Temp.(°C)	Yield of butene ^a (mol%)		
			1-butene	2-butene	Total
1	4	250	2	5	7
2	4	300	18	41	59
3	4	350	39	58	97
4	4	400	33	57	90
5	1	350	19	41	50
6	2	350	33	54	87
7	6	350	37	60	97
8	10	350	36	61	97

^a moles of actual butene/moles of theoretic butene

Preparation of high octane number gasoline

CO₂ produced can be easily separated from butenes by increasing the pressure above ambient pressure to liquefy butenes.³⁵ The remained butenes can be hydrogenated and isomerized to produce isobutane, which were also extensively studied and reported.³⁶⁻⁴⁰ Some proving experiments were carried and supported in ESI. In this study, Pd/C was used and almost completely conversions and near 100% yields were achieved at relatively mild conditions (Table S2). By using Pd/ZSM-8, n-butane was also isomerized to isobutane with a moderate yield (Table S3).

The production of gasoline-ranged alkanes from butenes and isobutane can be performed by alkylation catalyzed by superacid catalyst. BF₃ is a widely used Lewis acid catalyst for high acidity catalytic reactions directly or by supported on mesoporous materials. It also can form coordination of compositions 1:1 or 1:2 with organic compounds containing oxygen atoms. Commonly available adduct, BF₃·2Ethanol is a conveniently handled liquid and has catalytic effects for many organic reaction. But these adducts cannot be used for alkylation reaction due to high solubility of ethanol in produced alkanes. In our study, it

was found that if the hydrogen atoms of methyl group are replaced by fluorine, its solubility in alkanes is neglectable ($\approx 0.5\%$). We considered liquefying BF_3 with $\text{CF}_3\text{CH}_2\text{OH}$ to form an ionic liquid as a good catalyst for alkylation reaction of isobutane and butenes produced from GVL.

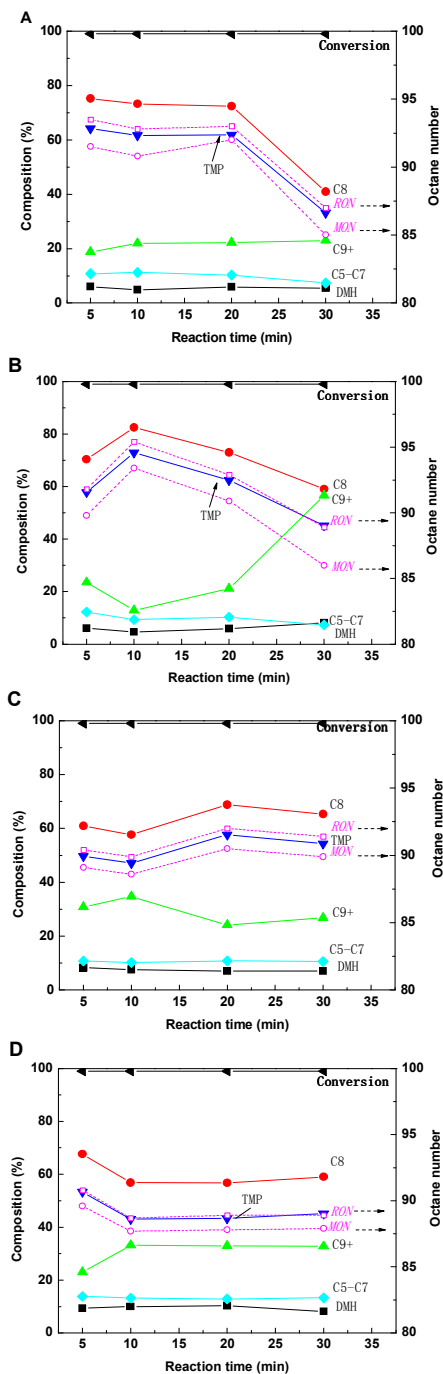


Figure 1. Effect of reaction time on the alkylation of isobutane and butenes catalyzed by $[\text{CF}_3\text{CH}_2\text{OH}_2][\text{CF}_3\text{CH}_2\text{OBF}_3]$ at (A) 0 °C; (B) 10 °C; (C) 20 °C; (D) 30 °C

We carried out the alkylation reaction of butenes (1-butene:2-butene=3:7) and isobutane (butenes:isobutane=1:10) at 10 °C to produce saturated hydrocarbons. As expected, the high octane number gasoline was produced in complete conversion of butenes. The effect of reaction time can be elucidated by the changes in the product distributions and calculated RON.⁴¹ Figure 1 shows the effect of reaction time on the alkylation of isobutane with butenes catalyzed by $[\text{CF}_3\text{CH}_2\text{OH}_2][\text{CF}_3\text{CH}_2\text{OBF}_3]$ at various temperatures. At 0 °C, a higher C8 fraction and octane number were achieved with a reaction time of 5 min. However, the highest C8 fraction and octane number were achieved at 10 °C, indicating the most suitable reaction temperature was 10 °C. At 10 °C, the highest RON increased from 5 to 10 min and decreased from 10 to 30 min, the highest RON was obtained at a reaction time of 10 min. Meanwhile, the most valuable C8 fraction also showed the same trend. A reaction time longer than 10 min led to the decreases of the RON and C9 content (Figure 1A). The decrease is due to the oligomerization reactions responsible for higher C9+ fractions with longer reaction time. For all reaction times at 10 °C, more than half of alkanes obtained were C8 fractions. Under optimum condition, more than 80% alkanes obtained were C8 fraction. In the pioneer work of Dumesic *et al.*,¹⁶ the highest C8 fraction produced by dimerization of butenes was only 43%, which was greatly lower than the result here. The main products obtained in their study are olefins, as unsaturated hydrocarbons, they have relative lower stability and strong tendencies to react with butene to form higher molecular olefins including C 12 and C16. Furthermore, the products from our approach are saturated hydrocarbons having better stability at lower reaction temperature. Although the C8 fraction is the most suitable components for gasoline fuel,^{42, 43} the trimethylpentanes (TMPs) are the most favored ones because TMPs have an octane number of 100 while that of dimethylhexanes (DMH) is 44. It is seen that the highest C8 and TMP selectivities, lowest DMH and C9+ fraction were obtained at a reaction time of 10 min, which ensured the highest TMP contents and corresponding highest RON and MON, while prolonged the reaction time decreased the C8 content. The highest RON of 95.4 of the products was achieved at the optimum conditions without any additives. When the reaction time was increased to 30 min, the C9+ fraction also increased greatly from 23% to 57% possibly because oligomerization reactions predominated under these conditions.

Effect of reaction temperature on the reaction catalyzed with $[\text{CF}_3\text{CH}_2\text{OH}_2][\text{CF}_3\text{CH}_2\text{OBF}_3]$ and with a reaction time of 10 min is shown in Figure 2. It is seen that both valuable TMP and C8 fractions achieved high values at 10 °C, while the increase of the temperature to 20 and 30 °C lowered the TMP content. For all temperatures, complete conversions of butenes were achieved. At temperatures higher than 10 °C, the increases of C9+ and C5-C7 fractions became significant. Considering the decrease of C8 fraction, it is certain that some produced C8 hydrocarbons added to isobutylene to form higher homologues, a part of which further cleaved to lower molecular alkanes including C5, C6 and C7 at higher temperature.

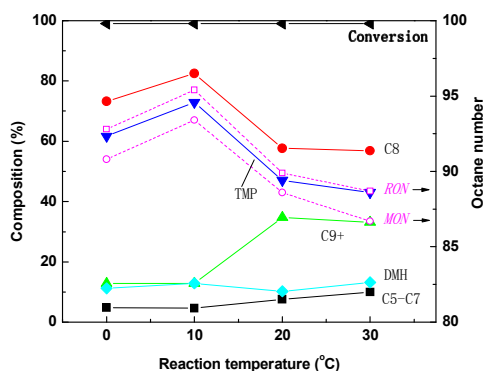


Figure 2. Effect of reaction temperature on the alkylation of isobutane and butenes catalyzed by $[\text{CF}_3\text{CH}_2\text{OH}_2][\text{CF}_3\text{CH}_2\text{OBF}_3]$ with a reaction time of 10 min

Table 2. Reusability of $[\text{CF}_3\text{CH}_2\text{OH}_2][\text{CF}_3\text{CH}_2\text{OBF}_3]^a$

Exp. Cycles	1	3	5	7	9	11
C5 [%]	1	1	2	2	1	1
C6 [%]	2	2	3	3	3	2
C7 [%]	2	3	4	4	3	3
C8 [%]	82	73	63	50	46	41
TMP [%]	73	64	54	41	39	35
DMH [%]	9	9	9	9	7	5
TMP/DMH	8	7	6	5	6	7
C9+ [%]	13	20	28	42	47	54
RON	95.4	93.5	91.6	88.9	88.8	88.0

^a Reaction conditions: 50 ml butenes and isobutane (1:10), 30 ml $[\text{CF}_3\text{CH}_2\text{OH}_2][\text{CF}_3\text{CH}_2\text{OBF}_3]$, 10 min, 10 °C. Full table is available in Table S4.

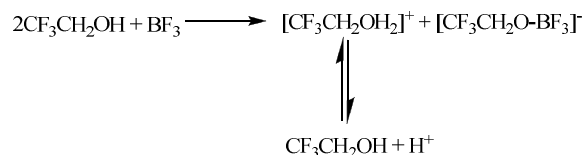
The reusability and regeneration of the ionic liquid catalyst are important factors for the application. The reusability of $[\text{CF}_3\text{CH}_2\text{OH}_2][\text{CF}_3\text{CH}_2\text{OBF}_3]$ on product distribution, TMP/DMH, RON were examined with isobutane/(1-butene+2-butene) of 10, reaction time of 10 min at 10 °C. The isobutane/butenes mixtures reacted in the reactor with catalyst and then the reactant/product phase was removed by phase separation. Fresh reactants were then added for the next experimental cycle. Totally 12 cycles were examined. From Table 2, it is shown that the catalyst showed similar performance in the first 6 reactions, noticeable changes in product quality with higher ratio of C9+ fraction were observed in the following reactions, which also caused the gradual decrease of RON. This is most likely due to the acidity decrease by separation of catalyst with reactant/product phases. If the catalyst is used in the continuous process, it may show better performance.

Table 3. Key properties of produced gasoline and the specifications of EN 228¹⁸

Properties	Requirements	Gasoline	Test methods
Research octane number (RON)	>95	95.4	Ref. ⁴⁴
Lead content [mg/kg]	5	Not detected	EN 237
Sulfur content [mg/kg]	50	Not detected	EN ISO 3675
Density [kg/m ³]	720-775	748	EN ISO 20846
Appearance	Clear and bright	Clear and bright	Visual inspection
Olefins [% (V/V)]	<18	0.5	ASTM D 1319
Aromatics [% (V/V)]	35	Not detected	ASTM D 1319
Benzene content [% (V/V)]	1	Not detected	EN 238
Oxygen content [% (m/m)]	<2.7	0	EN 1601

Since the products produced by this method should be acceptable for transportation fuel, the properties were determined and the requirements were shown in Table 3. From Table 3, it is seen that key properties can meet the specifications of EN 228.¹⁸ Some values, lead, sulfur, olefins, aromatics, benzene contents are better than the requirement. Especially, the RON can also meet the specification without adding any additives commonly used in petroleum-based gasoline.

Elucidation of the activity of $[\text{CF}_3\text{CH}_2\text{OH}_2][\text{CF}_3\text{CH}_2\text{OBF}_3]$



Scheme 2. Formation of $[\text{CF}_3\text{CH}_2\text{OH}_2][\text{CF}_3\text{CH}_2\text{OBF}_3]$ and its acidity

$[\text{CF}_3\text{CH}_2\text{OH}_2][\text{CF}_3\text{CH}_2\text{OBF}_3]$ showed a very good performance for the conversion of bio-based butenes and isobutane into high octane number gasoline. After completely saturated $\text{CF}_3\text{CH}_2\text{OH}$ with BF_3 , it was found the obtained complex has a molecular formula of $[\text{CF}_3\text{CH}_2\text{OH}_2][\text{CF}_3\text{CH}_2\text{OBF}_3]$. Figure 3 shows the ¹H NMR of $\text{CF}_3\text{CH}_2\text{OH}$ and $[\text{CF}_3\text{CH}_2\text{OH}_2][\text{CF}_3\text{CH}_2\text{OBF}_3]$. CH_2 proton can be easily assigned to around 4.1 ppm and OH proton assigned to 5.4 ppm without BF_3 . After saturated with BF_3 , the chemical shift of hydroxyl in $\text{CF}_3\text{CH}_2\text{OH}$ of 5.4 ppm shifted to 8.8 ppm due to the high electron withdrawing ability of BF_3 . BF_3 may form a bond with oxygen atom of $\text{CF}_3\text{CH}_2\text{OH}$ and lead to complete transfer of the proton to $\text{CF}_3\text{CH}_2\text{OH}$ as following equilibrium (Scheme 2) to form $[\text{CF}_3\text{CH}_2\text{OH}_2]^+$ cation and $[\text{CF}_3\text{CH}_2\text{OBF}_3]^-$ anion as shown in Scheme 2. From this, it can be proposed that adduct of BF_3 and $\text{CF}_3\text{CH}_2\text{OH}$ is ionic liquids in its nature.

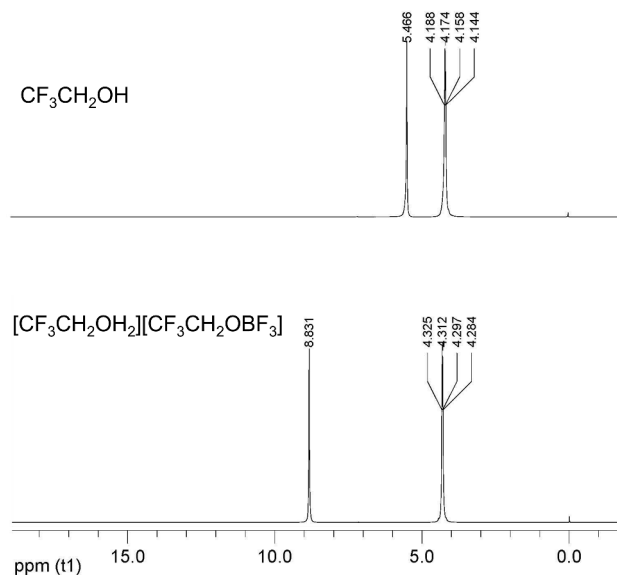
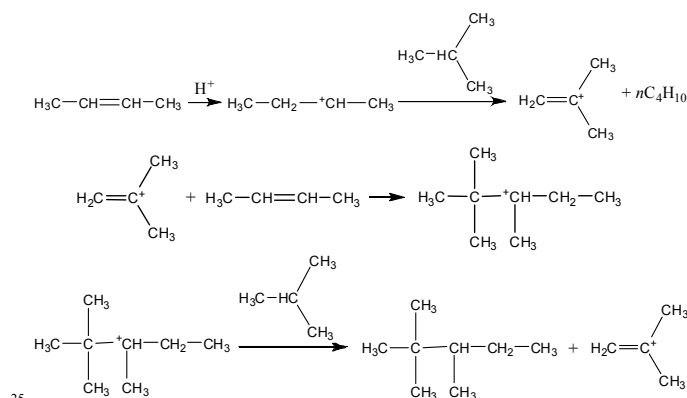


Figure 3. ^1H NMR of $\text{CF}_3\text{CH}_2\text{OH}$ and $[\text{CF}_3\text{CH}_2\text{OH}_2][\text{CF}_3\text{CH}_2\text{OBF}_3]$

Olah *et al.*⁴¹ found that the most suitable acid strength for alkylation was about $H_0 = -10.7$. An acid strength too high ($H_0 < -14.1$) leads to produce cracked products, while too low favors oligomerization reaction. The result obtained from this study indicates that $[\text{CF}_3\text{CH}_2\text{OH}_2][\text{CF}_3\text{CH}_2\text{OBF}_3]$ is high acidic contributing by $[\text{CF}_3\text{CH}_2\text{OH}_2]^+$. The reaction catalyzed by H^+ provided by $[\text{CF}_3\text{CH}_2\text{OH}_2][\text{CF}_3\text{CH}_2\text{OBF}_3]$ is mechanistically considered as a chain process as shown by Scheme 3. Butene reacts with H^+ to form $i\text{-C}_4^+$ cation, which further reacts with butene and forms $i\text{-C}_8^+$ cation as the intermediate. In the presence of isobutane, its hydride is abstracted by $i\text{-C}_8^+$ cation and forms $i\text{-C}_4^+$ cation, which keeps the catalytic cycle going. The objective product from this reaction, 2,2,3-trimethylpentane (2,2,3-TMP), which has a research octane number of 100, is the most suitable component for high octane gasoline. At the same time, isomerization of $i\text{-C}_8^+$ cation also proceeds and further reacts with isobutane to produce 2,2,4-TMP, 2,2,3-TMP and 2,3,4-TMP. Conversion of 1-butene is also proceeds via similar reactions.



Scheme 3. Reaction pathways between 2-butene and isobutene catalyzed by acid catalyst

However, a variety of side reactions that leads to produce low octane number hydrocarbons depending on the reaction conditions. The $i\text{-C}_8^+$ cation can undergo isomerization catalyzed by acid catalyst through rearrangements giving various isomeric cations leading to the formation of low octane isomers such as DMH³⁶. The $i\text{-C}_8^+$ cation also can add to isobutylene to form higher homologues such as $i\text{-C}_{12}^+$, $i\text{-C}_{16}^+$, *etc.* These cations lead to the formation of heavier alkanes or alkenes. The larger isomeric carbocations also can cleave into smaller carbocations (C_5^+ , C_6^+ , and C_7^+) and alkenes through β -scission, which can be considered as the reverse process of the addition of carbocations to alkenes⁴⁵. For example, $i\text{-C}_{12}^+$ may cleave into $\text{C}_5\text{H}_{10} + \text{C}_7\text{H}_{15}^+$ or $\text{C}_6\text{H}_{12} + \text{C}_6\text{H}_{13}^+$ or $\text{C}_7\text{H}_{14} + \text{C}_5\text{H}_{11}^+$. The produced smaller carbocations abstracts hydride from isobutane forming the $i\text{-C}_4^+$ cation and corresponding hydrocarbons having lower octane numbers compared with 2,2,4-TMP.

Conclusions

In summary, we describe here a method that a practical feedstock (GVL) is efficiently converted to high octane number gasoline rich in TMP via decarboxylation and alkylation reactions. Decarboxylation of GVL produces butenes including 1-butene, trans-2-butene and cis-2-butene in the highest yield of 97% with $\text{SiO}_2/\text{Al}_2\text{O}_3$. After hydrogenation and isomerization of a part butenes to isobutane, high octane number gasoline can be produced by alkylation between butenes and isobutane with $[\text{CF}_3\text{CH}_2\text{OH}_2][\text{CF}_3\text{CH}_2\text{OBF}_3]$ as the catalyst. The products are mixture of alkanes rich in TMPs, which has a RON of 100 and serve as the most suitable component for high octane gasoline. The highest octane number of the product is 95.4, indicating that high quality gasoline can be produced from biomass derived oxygenated compounds without hydrodeoxygenation and without any additives.

Notes and references

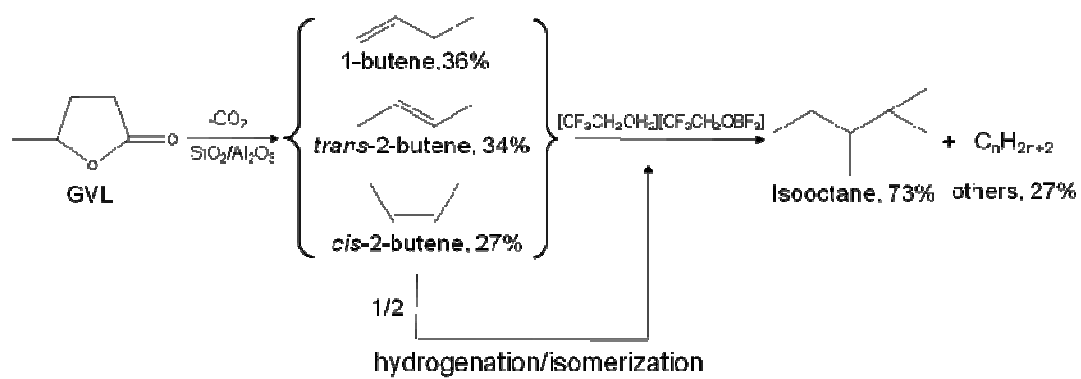
This work was supported by National Basic Research Program of China (2013CB733506), National Natural Science Foundation of China (No. 21210006, 21276260), International S&T Cooperation Program of China (2014DFA61670), External Cooperation Program of BIC, Chinese Academy of Sciences (GJHZ201306) and Key Project of Natural Science Foundation of Beijing of China (No. 2131005).

Beijing Key Laboratory of Ionic Liquids Clean Process, State Key Laboratory of Multiphase Complex System
Institute of Process Engineering, Chinese Academy of Sciences
Zhongguancun, Beiertiao, Haidian, Beijing 100190 (China)
Fax: (+86) 10-8262-7080
E-mail: sjzhang@ipe.ac.cn

† Electronic Supplementary Information (ESI) available: Experimental, supported tables and figures. See DOI: 10.1039/b000000x/

- H. Michel, *Angew. Chem. Int. Ed.*, 2012, 51, 2516-2518.
- R. C. Baliban, J. A. Elia and C. A. Floudas, *Energy Environ. Sci.*, 2013, 6, 267-287.
- U. Biermann, U. Bornscheuer, M. A. R. Meier, J. O. Metzger and H. J. Schäfer, *Angew. Chem. Int. Ed.*, 2011, 50, 3854-3871.
- R. W. Gosselink, D. R. Stellwagen and J. H. Bitter, *Angew. Chem. Int. Ed.*, 2013, 52, 5089-5092.

5. J. Q. Bond, A. A. Upadhye, H. Olcay, G. A. Tompsett, J. Jae, R. Xing, D. M. Alonso, D. Wang, T. Zhang, R. Kumar, A. Foster, S. M. Sen, C. T. Maravelias, R. Malina, S. R. H. Barrett, R. Lobo, C. E. Wyman, J. A. Dumesic and G. W. Huber, *Energy Environ. Sci.*, 2014, 7, 1500-1523.
6. J. N. Chheda, G. W. Huber and J. A. Dumesic, *Angew. Chem. Int. Ed.*, 2007, 46, 7164-7183.
7. G. W. Huber, R. D. Cortright and J. A. Dumesic, *Angew. Chem. Int. Ed.*, 2004, 43, 1549-1551.
10. G. W. Huber, J. N. Chheda, C. J. Barrett and J. A. Dumesic, *Science*, 2005, 308, 1446-1450.
9. E. L. Kunkes, D. A. Simonetti, R. M. West, J. C. Serrano-Ruiz, C. A. Gartner and J. A. Dumesic, *Science*, 2008, 322, 417-421.
15. D. M. Alonso, J. Q. Bond, J. C. Serrano-Ruiz and J. A. Dumesic, *Green Chem.*, 2010, 12, 992-999.
11. A. Corma, O. de la Torre, M. Renz and N. Vollandier, *Angew. Chem. Int. Ed.*, 2011, 50, 2375-2378.
12. P. Anbarasan, Z. C. Baer, S. Sreekumar, E. Gross, J. B. Binder, H. W. Blanch, D. S. Clark and F. D. Toste, *Nature*, 2012, 491, 235-239.
13. D. Liu and E. Y. X. Chen, *ChemSusChem*, 2013, 6, 2236-2239.
14. G. Li, N. Li, Z. Wang, C. Li, A. Wang, X. Wang, Y. Cong and T. Zhang, *ChemSusChem*, 2012, 5, 1958-1966.
15. H. Zhao, J. E. Holladay, H. Brown and Z. C. Zhang, *Science*, 2007, 316, 1597-1600.
16. J. Q. Bond, D. M. Alonso, D. Wang, R. M. West and J. A. Dumesic, *Science*, 2010, 327, 1110-1114.
17. L. Caspeta, N. A. A. Buijs and J. Nielsen, *Energy Environ. Sci.*, 2013, 6, 1077-1082.
18. DIN EN 228: 2013, Automotive fuels-unleaded petrol-Requirements and test methods.
19. U. V. Mentzel, S. Shunmugavel, S. L. Hruby, C. H. Christensen and M. S. Holm, *J. Am. Chem. Soc.*, 2009, 131, 17009-17013.
20. X. Guo, G. Liu and E. D. Larson, *Ind. Eng. Chem. Res.*, 2011, 50, 9743-9747.
21. J. H. Mack, V. H. Rapp, M. Broeckelmann, T. S. Lee and R. W. Dibble, *Fuel*, 2014, 117, 939-943.
22. L. F. Albright, *Ind. Eng. Chem. Res.*, 2002, 41, 5627-5631.
23. M. Mascal, S. Dutta and I. Gandarias, *Angew. Chem. Int. Ed.*, 2014, 53, 1854-1857.
24. E. I. Gürbüz, J. M. R. Gallo, D. M. Alonso, S. G. Wettstein, W. Y. Lim and J. A. Dumesic, *Angew. Chem. Int. Ed.*, 2013, 52, 1270-1274.
25. L. Bui, H. Luo, W. R. Gunther and Y. Román-Leshkov, *Angew. Chem. Int. Ed.*, 2013, 52, 8022-8025.
26. W. R. H. Wright and R. Palkovits, *Chemsuschem*, 2012, 5, 1657-1667.
27. X. Du, L. He, S. Zhao, Y. Liu, Y. Cao, H. He and K. Fan, *Angew. Chem. Int. Ed.*, 2011, 50, 7815-7819.
28. H. Mehdi, V. Fábos, R. Tuba, A. Bodor, L. Mika and I. Horváth, *Top. Catal.*, 2008, 48, 49-54.
29. D. M. Alonso, S. G. Wettstein, M. A. Mellmer, E. I. Gurbuz and J. A. Dumesic, *Energy Environ. Sci.*, 2013, 6, 76-80.
30. L. Qi and I. T. Horváth, *ACS Catalysis*, 2012, 2, 2247-2249.
31. J. Sun, K. Zhu, F. Gao, C. Wang, J. Liu, C. H. F. Peden and Y. Wang, *J. Am. Chem. Soc.*, 2011, 133, 11096-11099.
32. J. Xin, S. Zhang, D. Yan, O. Ayodele, X. Lu and J. Wang, *Green Chem.*, 2014, 16, 3589-3595.
33. S. Zhang, J. Xin, Z. Zhang, G. Zhao, D. Yan, X. Zhang. China Patent, CN101892071-A, 05, Jul, 2010.
34. J. Q. Bond, D. M. Alonso, R. M. West and J. A. Dumesic, *Langmuir*, 2010, 26, 16291-16298.
35. P. K. Behrens and S. I. Sandler, *J. Chem. Eng. Data*, 1983, 28, 52-56.
36. J. I. Villegas, N. Kumar, T. Heikkilä, V. P. Lehto, T. Salmi and D. Y. Murzin, *Chem. Eng. J.*, 2006, 120, 83-89.
37. T. Echizen, T. Suzuki, Y. Kamiya and T. Okuhara, *J. Mol. Catal. A: Chem.*, 2004, 209, 145-153.
38. F. Donati and P. McMorn, in *Catalysis in Application*, eds. S. D. Jackson, J. S. J. Hargreaves and D. Lennon, The Royal Society of Chemistry, 2003, pp. 260-265.
39. Z. Hong, K. B. Fogash and J. A. Dumesic, *Catal. Today*, 1999, 51, 269-288.
40. H. Liu, G. D. Lei and W. M. H. Sachtler, *App. Catal. A: Gen.*, 1996, 146, 165-180.
41. G. A. Olah, P. Batamack, D. Deffieux, B. Török, Q. Wang, Á. Molnár and G. K. Surya Prakash, *App. Catal. A: Gen.*, 1996, 146, 107-117.
42. X. Ren, J. Meng, A. M. Moore, J. Chang, J. Gou and S. Park, *Bioresour. Technol.*, 2014, 152, 267-274.
43. X. Zhang, Q. Zhang, T. Wang, L. Ma, Y. Yu and L. Chen, *Bioresour. Technol.*, 2013, 134, 73-80.
44. Y. Chauvin, A. Hirschauser and H. Olivier, *J. Mol. Catal.*, 1994, 92, 155-165.
45. J. Weitkamp, P. A. Jacobs and J. A. Martens, *App. Catal.*, 1983, 8, 123-141.



Biomass-derived γ -valerolactone was converted into high octane number gasoline with $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $[\text{CF}_3\text{CH}_2\text{OH}_2][\text{CF}_3\text{CH}_2\text{O-BF}_3]$ as efficient catalysts.