Production of gasohol from isobutanol

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Abstract. Butanol is a four carbon chain alcohol compound of a non-polar used as a solvent and as an intermediate in several consumer products. It can be produced from petrochemical process route as well as biochemical process. A common petrochemical route to produce butanol is hydroformylation of propylene as primary feedstock followed by hydrogenation. The increasing demand for butanol and the scarcity of petrochemical basestock has put the urgent need for a renewable resource of butanol production. Biobutanol is butanol produced from renewable, biological feedstock through fermentation of plant materials types of food, non-food and biomass. One isomer of butanol which is more similar with gasoline property is isobutanol. The use of isobutanol is commonly as solvent in coatings industry, as lacquers, melamine or phenolic resin. Isobutanol can be potentially used as a gasoline blending component, and it is better than ethanol due to its higher heating value, lower volatility and less corrosive. A brief review of process technology for butanol production is outlined in this paper. The benefit of isobutanol over ethanol was also overviewed. In order to prove the compatibility on fuel application, the production of gasohol was carried out by mixing isobutanol and base gasoline, then evaluated according to commercial fuel specification. From the research work, it has been shown that the addition of isobutanol in base gasoline by certain volum fraction has met the typical fuel specifications used for spark-ignition engine. The physical and chemical properties of the mixture was quite similar to gasoline 88 and gasoline 92 specifications.

1. Introduction

Gasoline or petrol is petroleum derived liquid mixture having 5 to 12 carbon atoms per molecule, and it is primarily used as a fuel in spark-ignition engines. It is an aromatic, flammable liquid that mainly consist of hydrocarbon mixture of alkanes, cycloalkanes and alkenes, with their actual ratio depends on the oil refinery especially crude oil type and grade of gasoline product.

The increasing demand of gasoline fuel and the scarcity of crude oil source, it is an urgent need to produce biofuel from renewable resources to overcome the energy scarcity as well as improving the environment and global economy. Biofuel has been an alternative substitution for current petroleum fuels because it is
renewable and can be produced continuously. Indonesia energy policy has set the target for new and renewable energy development by 2025 is 23% minimum of the total energy mix, wherein bioenergy shares about 10%, hydro 3%, geothermal 7% and other NRE of 3% [1].

Biogasoline is gasoline fuel produced by biochemical process using renewable feedstock. Gasohol is a blend of petroleum gasoline with ethanol or butanol. Indonesia has experienced to produce gasohol from bioethanol in 2006 until 2010, but it was stopped due to inconsistent supply and price volatility, frequently resulting in a purchase price below cost of production. The portion of ethanol in gasoline strictly limited and not more than 10% because of its lower energy content, higher volatility and hygroscopicity. To overcome the lack of ethanol quality, butanol will be an alternative solution to replace ethanol and it will be the next generation fuel. Butanol is a higher member of straight chain of alcohol series with each molecule of butanol (C₄H₁₀O) containing four carbon atoms. Butanol is commonly used industrially as a solvent which is largely produced petrochemically. The global butanol market has steadily increased in recent years and is projected to continue increasing at an annual rate of 3.2% [2].

Basically, there are two alternative process routes to produce butanol, one is petrochemical process and other is biochemical process relied on renewable resources. Oxo synthesis, reppe synthesis and crotonaldehyde hydrogenation are some of petrochemical process route to produce butanol. Most of commercially butanol is produced petrochemically by low pressure oxo process by hydroformylation of propylene as primary feedstock using rhodium-based catalyst according to reaction (1) and (2) [3].

\[
2\text{CH}_3\text{CH}=\text{CH}_2 + 2\text{CO} + 2\text{H}_{2} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} + (\text{CH}_3)\text{2C}(\text{H})\text{CHO} \quad (1)
\]

Propylene \hspace{1cm} \text{Syngas} \hspace{1cm} \text{normal butyraldehyde} \hspace{1cm} \text{iso-butyraldehyde}

\[
n + \text{iso} - \text{Butyraldehyde} \rightarrow \text{Hydrogenation} \rightarrow \text{Product refining} \rightarrow \text{n-Butanol} \hspace{1cm} \text{n-Isobutanol}
\]

\[
\text{CH}_3\text{CH}=\text{CH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} + \text{CH}_3\text{CHCHO} \quad (2)
\]

\[
\text{Catalyst} \hspace{1cm} \text{CO/H}_{2} \hspace{1cm} \text{Catalytic} \hspace{1cm} \text{Hydrogenation}
\]

Butanol is mainly comprised of four isomeric structures, i.e. n-butanol (n-C₄H₉OH), sec-butanol (sec-C₄H₉OH), iso-butanol (iso- C₄H₉OH) and tert-butanol (tert-C₄H₉OH)
Isobutanol or 2-methyl-1-propanol is one of butanol isomers that’s more similar to gasoline and can be used as a fuel on internal combustion engine without any modification. Butanol can be transported in existing gasoline pipelines and produces more power than ethanol and providing potential cost savings, flexible and efficient access to end-user markets.

Standard specification of butanol blending with gasoline for use as automotive spark-ignition engine fuel [5] has been announced by ASTM D7862 since October 2013.

The specification covers three butanol isomers namely 1-butanol, 2-butanol, and 2-methyl-1-propanol as shown in table 2.

Table 2. Comparison of butanol isomers [6]

| No | Properties                      | 1-Butanol (n-Butanol) | 2-Butanol (sec-Butanol) | 2-Methyl-1-propanol (Isobutanol) |
|----|---------------------------------|-----------------------|-------------------------|----------------------------------|
| 1  | Density (kg/cm³)                | 809.8                 | 806.3                   | 801.8                            |
| 2  | Research Octane Number (RON)    | 96                    | 101                     | 113                              |
| 3  | Motor Octane Number (MON)       | 78                    | 82                      | 94                               |
| 4  | Melting Point, °C               | -89.5                 | -114.7                  | -108                             |
| 5  | Boiling Temperature, °C         | 117.7                 | 99.5                    | 108                              |
| 6  | Enthalpy of Vaporation at T_boil, (kJ/kg) | 584                  | 550                     | 564                              |
| 7  | Flash Point, °C                 | 35                    | 24                      | 28                               |
| 8  | Auto ignition Temperature, °C   | 345                   | 406                     | 415                              |
|    | Flammability Limits:            |                       |                         |                                  |
|    | - Lower Limit (Vol %)           | 1.4                   | 1.7                     | 1.2                              |
|    | - Upper Limit (Vol %)           | 11.2                  | 9.8                     | 10.9                             |
Butanol can also be produced from process of fermentation by means of bacteria of the *Clostridium* *species*. This process occurs under anaerobic conditions, and butanol as one of the products - called biobutanol.

Biobutanol is obtained from biochemical process using renewable or biological feedstock such as molasses, sugar cane, sugar bit, and other carbohydrate substrats, as well as cellulosic raw materials or biomass [4]. As the cost of raw material has a significant influence on price, the main interest has recently been in low-cost substrates such as agricultural residues or industrial by-products and waste materials.

Biobutanol has not been produced commercially yet, but the process technology development has reached to pilot scale stage in several countries. Current activity of research and development are mainly focused on improving and optimizing the process condition to produce biobutanol effectively.

Upstream processing before fermentation includes pretreatment of biomass feedstock, hydrolysis, and in some cases detoxification of inhibitors formed during pretreatment. The common fermentation process is called as Acetone-Butanol-Ethanol (ABE) fermentation. The anaerobic fermentation consists of two stages: first the acidogenic phase where Clostridial bacteria produce acetic and butyric acids, carbon dioxide (CO₂) and hydrogen (H₂) from sugars, followed by the solventogenic phase where acids are converted into acetone, butanol and ethanol, typically in the ratio of 3:6:1 [7].

The final products obtained from fermentation are recovered and purified in downstream processing. Adsorption, gas stripping, liquid-liquid extraction, pervaporation, perstraction and reverse osmosis are the most used separation methods integrated with the ABE fermentation [8]. Butanol obtained from fermentation has toxic to organism so it leads to low production and the concentration in fermenter is about 1-2wt% of butanol. In situ removal of ABE by gas stripping has been reported to be one of the most important techniques of solvent removal which be able to maintain the ABE concentration in the fermentation broth below toxic levels [9]. In order to improve the butanol production from ABE fermentation and to minimize inhibition caused by butanol as well as facilitate product recovery, the use of feedstock comprising of carbohydrate source is fermented in the presence of bacteria to produce butyric acid and hydrogen. Then butanol can be directly produced by hydrogenation of butyric acid in the presence of a catalyst. The Hydrogenation process improves upon the biomass second step of the two-step fermentation process [10].

Biomass can be converted to fermentable carbohydrates with bacteria to butyric acid, and then converts butyric acid and hydrogen to butanol by catalytic hydrogenation. The fermentation-hydrogenation process provides overall butanol yields higher than ABE fermentation yield [11].

An integrated fermentation-separation process, such as extractive fermentation, can be used to reduce product inhibition and increase process productivity and product yield. Extractive fermentation may also allow the process to produce and recover the fermentation product in one continuous step, so it reduce downstream processing load and recovery costs.

The fermentation route generally is not so competitive with petrochemical synthesis but by doing research and development continuously there will be a breakthrough to find out the newest technology overcoming all constraints that can be implemented and commercialized efficiently. Shota et al in 2007 has successed in producing 1-butanol from the engineered Escherichia Coli and opening the possibility for using non-native, easily manipulated organisms for 1-butanol production [12].
Considering all of recent technologies in bioprocess, strain development, fermentation method and efficiently fuel separation, biobutanol will be the new generation fuel that can be utilized as cost-effective fuel and enhances environmental friendly and sustainability. Whether it will be used as a transportation fuel directly or an additive component to gasoline, butanol will offer a better flexibility as an alternative fuel in the future. While awaiting for commercially production of biobutanol, the current isobutanol can be used as an attractive choice to overcome the lack of ethanol quality.

The aim of this research work is to examine and prove experimentally the effect of isobutanol addition in gasoline on the physical and chemical properties based on the standard fuel specification of gasoline 88 dan gasoline 92 for typical spark-ignition engines.

2. Material and Methods

The experimental work was carried out through the following steps:

2.1. Base gasoline preparation, by mixing of low and high octane mogas components to get bas gasoline with octane number 84.
2.2. Isobutanol sampel came from BASF product
2.3. Blending of base gasoline and isobutanol at some variate of compositions
2.4. Laboratory testing according to standard gasoline fuel parameters

| No | Properties | Results |
|----|------------|---------|
| 1  | Isobutanol purity, %wt | 99.7 |
| 2  | Water, %wt | 0.01 |
| 3  | Colour | Colourless |
| 4  | Acidity as acetic acid, %wt | < 0.001 |
| 5  | Density, g/cm3 | 0.802 |
| 6  | Flash Point, °C | 27 |
| 7  | pH value | 7 |
| 8  | Viscosity Dynamic @ 20 °C, MPas | 3.9 |
| 9  | Boiling range at 1013 mbar, °C | 106 -108 |
| 10 | Vapour pressure @20 °C, mbar | 9.5 |

Base gasoline was prepared by mixing low octane mogas component and high octane mogas component supplied from national oil refinery to get a certain quality with 84 octane number. The right compositions of blending components will determine the gasoline quality.

The methodology to prepare gasohol from isobutanol was by mixing process using batch stirring reactor at mixing speed 300 rpm for about 3 minutes. The composition of blending component was varied and the product was tested in laboratory according to standard test parameters for gasoline fuel. The simplified process flow diagram of gasoline-isobutanol is shown in figure 1.
Figure 2. Simplified process flow diagram of gasohol production from isobutanol

The evaluation of gasohol from isobutanol is also done by comparing some test parameters with neat gasoline prepared by mixing of low and high octane mogas components. The test parameters evaluated at the same octane number are Reid vapor pressure (RVP), density at 15°C and sulfur content.

3. Results and Discussion

The key properties for motor gasoline fuels are ignition quality, volatility, corrosivity and stability. The occurrence of knocking in spark ignition engine can be reduced by increasing the gasoline’s resistance to autoignition, which is expressed by its octane rating. Octane rating is measured relative to a mixture of 2,2,4-trimethylpentane (an isomer of octane) and n-heptane using CFR engine according to ASTM D2699-86 test method. The typical unit for octane ratings is research octane number (RON) and motor octane number (MON). The research octane number (RON) describes the behavior of the fuel in the engine at lower temperatures and speeds, and is an attempt to simulate acceleration behavior. Whereas motor octane number (MON) describes the behavior of the fuel in the engine at high temperatures and speeds—a full-throttle range, comparable to driving fast on a highway. The spread between the two numbers (MON & RON) is known as the fuel sensitivity. Octane rating parameter for commercial gasoline fuel specification normally use research octane number (RON).

The key gasoline characteristic for good driveability is volatility namely a gasoline’s tendency to vaporize. Gasoline that vaporizes easily allows a cold engine to start quickly and warm up smoothly. Warm-weather gasoline is blended to vaporize less easily to prevent engine vapor lock and other hot fuel handling problems and to control evaporative emissions that contribute to air pollution.

With respect to gasoline, vapor pressure (RVP) is the single most important property for cold-start and warm-up driveability. Cold-start means that the engine is at ambient temperature, not that the ambient temperature is cold. Higher values of vapor pressure generally result in better cold-start performance, but lower values are better to prevent vapor lock and other hot fuel handling problems.

The normal range of vapor pressure for gasoline 88 is 69 kPa maximum and in range of 45-60 kPa for gasoline 92.

From the variation of isobutanol addition in base gasoline, it was obtained the octane rating data as shown in figure 2.
From the octane testing data, gasoline 88 grade was achieved by adding isobutanol at 12% volume, gasoline 90 was achieved at 16% volume of isobutanol, whereas gasoline 92 was obtained by adding 20% volume of isobutanol into base gasoline. The sensitivity of isobutanol addition to octane rating increment in the gasoline blend is about 2.5% per-octane unit.

The octane rating of typical commercially available gasoline varies by country. In Indonesia, RON 88 is the standard for regular unleaded gasoline named as Premium 88 or gasoline 88, whereas RON 90 is equivalent to standard gasoline of Pertalite and RON 92 is used for standard gasoline 92 called as Pertamax.

Higher values of vapor pressure of 12% and 20% isobutanol containing gasohol result in better cold-start performance than neat gasoline 88 and 92 respectively.
Lower values of sulfur content as isobutanol contained gasohol increased can reduce sulfur dioxide emission because SO$_2$ is produced primarily from the combustion of fuels containing sulfur.

Gasoline fuel specifications in Indonesia are regulated under three different regulations based on their Research Octane Number (RON), that are Premium RON 88 by SK 933/2013 as of 19 November 2013, Pertalite RON 90 by SK313/2013 as of 22 March 2013 and Pertamax RON 91 & 95 based on SK 3674/2006 as of 17 March 2006.

In the experimental work, gasoline 88 dan gasoline 92 produced by isobutanol addition are tested to the complete test parameter based on National gasoline standard specfications as shown in table 4 and 5.

**Table 4. Laboratory Test Report of 12% Isobutanol in gasohol**

| No | Properties                  | Unit  | Gasoline 88 Specification | Method  | Results |
|----|-----------------------------|-------|---------------------------|---------|---------|
| 1  | Octane Number               | RON   | Min. 88                   | D 2699  | 88.0    |
| 2  | Oxidation Stability         | minutes | Min. 360          | D 525  | >360 |
| 3  | Sulfur Content              | %/m/m | Max. 0.05               | D 2622  | 0.008  |
| 4  | Lead Content                | g/l   | Max. 0.013              | D 3237  | 0.004  |
| 5  | Metal content (Mn, Fe)      | mg/l  | Not detected            | D 3831  | -      |
| 6  | Oxygen content              | %/m/m | Max 2.7                 | D 4815  | 2.91   |
| 7  | Distillation :              |       |                          |         |         |
|    | 10% vol. evap               | °C    | Max. 74                  |         | 56     |
|    | 50% vol. evap               | °C    | 75 - 125                |         | 92     |
|    | 90% vol. evap               | °C    | Max. 180                |         | 138    |
|    | End Point                   | °C    | Max. 215                |         | 171    |
|    | Residue                     | % vol | Max. 2.0                |         | 1.0    |
| 8  | Sediment                    | mg/l  | Max. 1.0                | D 5452  | -      |
| 9  | Unwashed gum                | mg/100ml | Max. 70       | D 381  | -      |
| 10 | Washed gum                  | mg/100ml | Max. 5        | D 381  | 1      |
| 11 | Reid Vapour Pressure        | kPa   | Max. 69                 | D 323   | 57     |
| 12 | Density at 15°C             | kg/m$^3$ | 715.0-780.0     | D 1298  | 752.7  |
| 13 | Copper Strip Corrosion      | Merit | Max. Class 1           | D 130   | Class 1 |
| 14 | Mercaptane Sulfur           | %/m/m | Max. 0.002             | D 3227  | 0.001  |
| 15 | Appearance                  |       | Clear & Bright         | Visual  | Clear & bright |
| 16 | Colour                      |       | Yellow                 | Visual  | -      |
| 17 | Dye Content                 | gr/100 l | Max. 0.13        |       | -      |
| 18 | Odour                       |       | Marketable            | Visual  | Marketable |

Based on laboratory test report data as shown in table 4, the addition of 12% isobutanol into gasoline can meet the gasoline 88 or premium 88 specification for all of test parameters. By adding 12% isobutanol (equivalent to 2.6% oxygen) in base gasoline may yield a gasohol with energy density is less than energy density of neat gasoline alone. For comparison, all modern cars are designed to operate on concentrations of up to 10% denatured ethanol gasoline (3.5% oxygen), which has about 96% of the energy of gasoline alone. Because the energy density can roughly be estimated based on the oxygen concentration, any blend with an oxygen content less than or equal to that of E10 will have an energy density within the range for which modern vehicles have been designed.
The extra oxygen in gasoline allows for adding more fuel to the engine and therefore making more heat energy to push the piston down in the cylinder. The extra oxygen also helps the cylinder burn all of the fuel within it more efficiently. The more fuel an engine can burn, the more power the engine can make.

The use of 12% isobutanol in gasoline blend can improve the environment impact as shown in low sulfur content 80 ppm that meets EURO III specification of 500 ppm.

The use of 20% concentration of isobutanol in base gasoline as shown in table 5 can meet mainly the gasoline 92 specification or pertamax having octane number 92 minimum.

| No | Properties                  | Unit | Gasoline 92 Specification | Method | Results |
|----|-----------------------------|------|---------------------------|--------|---------|
| 1  | Octane Number               | RON  | Min. 92                   | D 2699 | 92.1    |
| 2  | Oxydation Stabilitly        | minutes | Min. 480          | D 525  | >480    |
| 3  | Sulfur content              | % m/m | Max. 0.05               | D 2622 | 0.006   |
| 4  | Lead content                | g/l  | Max. 0.013              | D 3237 | 0.005   |
| 5  | Metal content (Mg, Fe)      | mg/l | Not detected            | D 3831 | -       |
| 6  | Oxygen content              | % m/m | Max. 2.7               | D 4815 | 5.3     |
| 7  | Distillation :              |      |                          | D 86   |         |
|    | 10% vol. evap               | °C   | Max. 70                 |        | 54      |
|    | 50% vol. evap               | °C   | 77 - 110                |        | 90      |
|    | 90% vol. evap               | °C   | 130 - 180              |        | 138     |
|    | End Point                   | °C   | Max. 215               |        | 182     |
|    | Residue                     | % vol | Max. 2.0            |        | 1.0     |
| 8  | Sediment                    | mg/l | Max. 1.0               | D 5452 | -       |
| 9  | Unwashed gum                | mg/100ml | Max. 70           | D 381  | -       |
| 10 | Washed gum                  | mg/100ml | Max. 5             | D 381  | 3       |
| 11 | Reid Vapour Pressure        | kPa  | 45 - 60                 | D 323  | 59      |
| 12 | Density at 15 °C            | kg/m³ | 715.0-770.0          | D 1298 | 757.5   |
| 13 | Copper Strip Corrosion      | Merit | Max.Class 1           | D 130  | Class 1 |
| 14 | Doctor Test                 |      | Negative               | IP 30  | Negative|
| 15 | Mercaptane Sulfur           | % m/m | Max. 0.002            | D 3227 | 0.0008  |
| 16 | Colour                      |      | Blue                    | Visual | -       |
| 17 | Dye Content                 | gr/100 ltr | Max. 0.13          |        | -       |
| 18 | Appearance                  |      | Clear & bright         | Visual | Clear & bright |

The increasing of oxygen content in gasohol to more than 3.5% may reduce fuel energy content and will increase the nitrogen oxide emission during combustion, but the ignition quality as represented by octane number for this oxygenate fuel is still in the range of limit. In addition to ignition quality, the use of gasohol from 12% and 20% of isobutanol additions generally showed the normal properties in case of volatility, corrosivity and stability according to minimum requirement for typical gasoline fuel. The decreasing in sulfur content to about 60 ppm in gasohol from 20% isobutanol is approximate to EURO IV specification, so it can improve the exhaust gas emission from sulphur dioxide and minimizing the acid rain impact.
4. Conclusion

Isobutanol is an alternative oxygenate that can be used to overcome the lack of ethanol quality as gasoline blending component in spark-ignition engine. The use of 12% and 20% isobutanol in gasohol resulted in fuel quality that comply with standard fuel specification of Gasoline 88 or Premium and Gasoline 92 or Pertamax respectively. The increasing of oxygen content as isobutanol increased tend to lower energy content, but the fuel ignition quality as expressed by octane rating, as well as its volatility, corrosivity and stability has met the standard quality specifications of gasoline fuel. The decreasing of sulfur content in isobutanol-gasoline blend can reduce the formation of sulfur oxide emission during fuel combustion in engine and will be an alternative of environmental friendly fuel. The production of gasohol using isobutanol can be implemented at early stage by utilizing the existing isobutanol while awaiting for efficiently and commercially production of biobutanol.

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