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Hydrogen and Biofuel Production from 2-Propanol Over Ru/Al_2O_3 Catalyst in Supercritical Water

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***Abstract*—**Hydrogen is an important chemical in many industries and it is expected to become one of the major fuels for energy generation in the future. Unfortunately, hydrogen does not exist in its elemental form in nature and therefore has to be produced from hydrocarbons, hydrogen-containing compounds or water.

Above its critical point (374.8°C and 22.1MPa), water has lower density and viscosity, and a higher heat capacity than those of ambient water. Mass transfer in supercritical water (SCW) is enhanced due to its increased diffusivity and transport ability. The reduced dielectric constant makes supercritical water a better solvent for organic compounds and gases. Hence, due to the aforementioned desirable properties, there is a growing interest toward studies regarding the gasification of organic matter containing biomass or model biomass solutions in supercritical water.

In this study, hydrogen and biofuel production by the catalytic gasification of 2-Propanol in supercritical conditions of water was investigated. Ru/Al_2O_3 was the catalyst used in the gasification reactions. All of the experiments were performed under a constant pressure of 25 MPa. The effects of five reaction temperatures (400, 450, 500, 550 and 600°C) and five reaction times (10, 15, 20, 25 and 30 s) on the gasification yield and flammable component content were investigated.

***Keywords*—**2-Propanol, Gasification, Ru/Al_2O_3, Supercritical water.

I. Introduction

THE growing population of the world, combined with the gradually increasing demand for consumption lead to a proportional increase in production, and therefore the energy amount required to provide it. So far, the majority of this energy has been supplied from fossil fuel reserves, such as coal, petroleum and natural gas [1]. However, the unfortunate fact that these nonrenewable reserves will cease someday brings a necessity to search for other alternative energy sources.

One of these alternative energy sources is hydrogen, which is a prominent chemical in many industries such as the chemical industry (production of ammonia, methanol, hydrogenation, etc.), petrochemical industry (hydrotreatment), food processing, semiconductor industry and metallurgical industry. The growth in hydrogen demand is already increasing significantly, and since hydrogen fuel cells is now near commercialization, it is expected to become one of the major fuels for energy generation in the future. But hydrogen does not exist in nature in its elemental form and, therefore, has to be produced from hydrocarbons, other hydrogen-containing compounds or water.

Supercritical water gasification (SCWG) is a process that currently attracts considerable attention for the production of hydrogen or other combustible gases of economic value from aqueous biomass solutions. It is basically a hydrothermal gasification process, in which the conversion of a material into gaseous products takes place at conditions exceeding the critical temperature (374.8°C) and critical pressure (22.1 MPa) of water. Above its critical point, water has very interesting properties as a reaction solvent, altering between a polar liquid and a nonpolar fluid in a very wide temperature range. It has a lower density and viscosity, and a higher heat capacity than those of ambient water. Mass transfer in supercritical water is enhanced due to its increased diffusivity and transport ability. What is more, the reduced dielectric constant makes supercritical water a better solvent for organic compounds and gases [2]-[4]. Hence, due to the aforementioned desirable properties, there is a growing interest toward studies regarding the gasification of organic matter containing biomass or model biomass solutions in supercritical water.

In this study, hydrogen and biofuel production by the catalytic gasification of 2-Propanol in supercritical conditions of water was investigated. 2-Propanol (isopropyl alcohol, isopropanol or propan-2-ol) is a colorless and a flammable chemical with a formula of C_3H_8O. It is used in cleaning and pharmaceutical industries, mainly taking part in the production of acetone and its derivatives [5]. It is also used as a solvent and an antifreeze agent.

During the gasification experiments, 0.5M dilute solutions of 2-Propanol were used, with an initial Total Organic Carbon (TOC) content of 18000mg/L. A commercially obtained Ru/Al_2O_3catalyst was employed in the reactor. The experiments were performed at five reaction temperatures (400, 450, 500, 550 and 600°C) and five different reaction times (10, 15, 20, 25 and 30s) were implemented, under a constant pressure of 25MPa. With the aid of these experiments, it was aimed to find the effect of reaction temperature and reaction time on the gasification yield and biofuel composition; and to determine the optimum conditions for energy production.

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II. Materials and Methods

A. Raw Materials

For the preparation of the model biomass solutions, 2-Propanol of 99.8% purity (Merck) was used. In order to make a 0.5M solution with an initial TOC content of 18000mg/L, 38.4mL of 2-Propanol was diluted to 1L with distilled water.

B. Catalyst

The Ru/Al_2O_3catalyst was commercially obtained (Alfa-Aesar), which contained 3.795% (wt.) ruthenium, 70.794% (wt.) aluminum, 7.905% (wt.) oxygen and 17.596% (wt.) chlorine. The catalyst tablets were in cylindrical shape, with a diameter and length of both 3.2mm. The density of the Ru/Al_2O_3catalyst was measured as 1.82g/cm^3. The SEM image of the catalyst, which was obtained from scanning electron microscope (JEOL-5410LV) using Bath Scatter Electron Detector and Secondary Electron Detector, is shown in Fig. 1. On the other hand, its XRF spectrum, which was obtained by using Energy Dispersive Spectroscopy (EDS), is presented in Fig. 2.

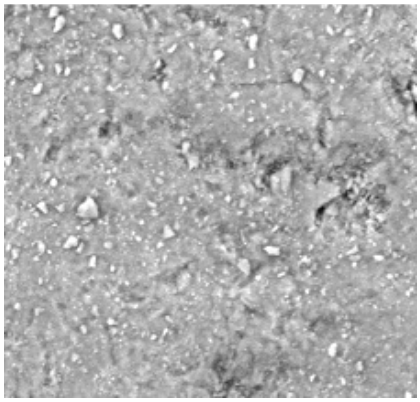


Fig. 1 SEM image of the Ru/Al_2O_3 catalyst (10 nm)

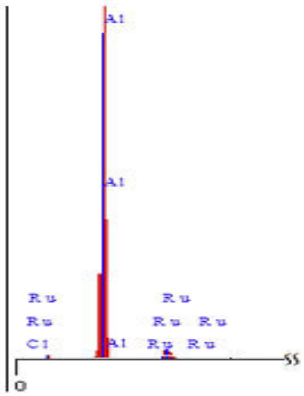


Fig. 2 XRF spectrum of the Ru/Al_2O_3 catalyst

C. Experimental Setup

The catalytic gasification experiments were performed in the reactor system with a volume of 8.305mL, which is placed into a PID controlled split furnace (Protherm, model SPT 11/70/750). From the feed pump to the gas–liquid separator, all of the wetted parts of the system, such as tubing, fittings, etc., were made of 316 SS. The 2-Propanol solution was pumped into the furnace using a high pressure pump (Autoclave Engineers, Series III pump). After exiting the furnace, the effluent was cooled rapidly by passing through a heat exchanger, and the reaction immediately stopped. The possible solid particles in the effluent, which would be formed presumably, were removed with a 0.5µm inline filter before the stream was depressurized by a back-pressure regulator (BPR) (GO Regulator Inc.). The system pressure was kept at a constant value (25±0.1MPa) by the BPR set at the exit of the reactor and monitored through a digital pressure indicator. The system temperature is also kept stable (±1°C) through the PID-controlled split furnace. The products leaving the BPR were separated by a gas-liquid separator. The gaseous effluent taken from the top portion of the separator is transported for quantitative analysis by a gas chromatograph capable of online sampling. On the other hand, the samples taken from the liquid effluent leaving the system are sent for TOC analysis. The experimental setup is schematically demonstrated in Fig. 3.

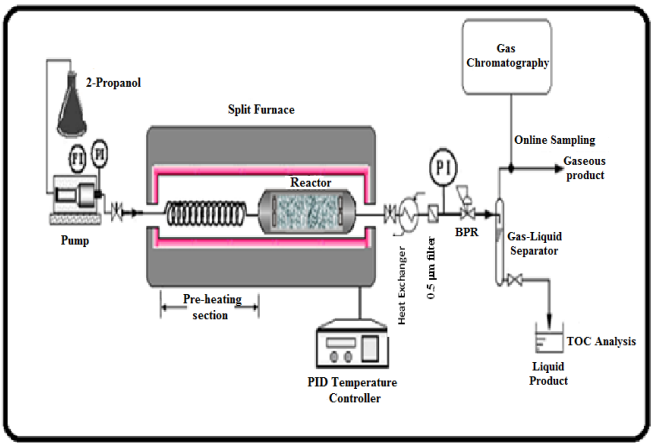


Fig. 3 Schematic demonstration of the experimental setup

D. Gaseous Product Analysis

The gaseous product obtained from the top portion of the gas-liquid separator was taken to a gas chromatograph for quantitative analysis. The instrument used for this aim was a Perkin Elmer Arnel brand, Clarus 500 model gas chromatography device, coupled with one FID and two TCD detectors.

E. Liquid Product Analysis

The liquid samples taken from the bottom of the gas-liquid separator were characterized by their TOC concentrations. TOC analyses were performed by a total organic carbon-total nitrogen analyzer (Hach-Lange IL550 TOC-TN), which is based on the combustion catalytic oxidation method, using a highly sensitive multi-channel, non-dispersive infrared detector (NDIR).

III. Results and Discussion

The experiments with Ru/Al_2O_3 catalyst were made under a constant pressure of 25MPa, and it was aimed to investigate

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the effect of five different temperatures (400, 450, 500, 550 and 600°C) and five different reaction times (10, 15, 20, 25 and 30s) on the gasification yield and flammable component content.

From the TOC analyses, it was seen that under hydrothermal conditions, 2-Propanol was almost completely converted to gaseous products. It was also seen that the TOC conversion increased with temperature and reaction time. This situation can also be verified when the change of gaseous product yield, which stands for the amount of gaseous product obtained per each mL of 2-Propanol fed to the reactor, is investigated (Fig. 4). Accordingly, the gas product yield showed an increasing tendency with temperature and time, signifying the breakdown of the organic content of the 2-Propanol solutions to the gaseous products. The gas product yield showed a little decrease above 550°C, and this situation was attributed to the transformation of the gas products to the final reaction products (carbon dioxide and water) with the effect of temperature. The maximum yield of the gaseous product was obtained at 550°C and for a reaction time of 30 s, having a value of 27.2mL/mL 2-Propanol fed to the reactor. At these conditions, the gas product involved 40.1% methane, 11.4% hydrogen, 0.8% ethane, 0.8% propane, 0.01% propylene and 49.3% carbon dioxide. On the other hand, the minimum amount of gas product yield, which was 8.2mL/mL 2-Propanol, was obtained at the experiment conducted at 400°C and with a reaction time of 10s. At these conditions, the gas product involved 65.2% methane, 1.5% hydrogen, 1.8% ethane, 0.2% propane, 0.2% propylene and 37.5% carbon dioxide.

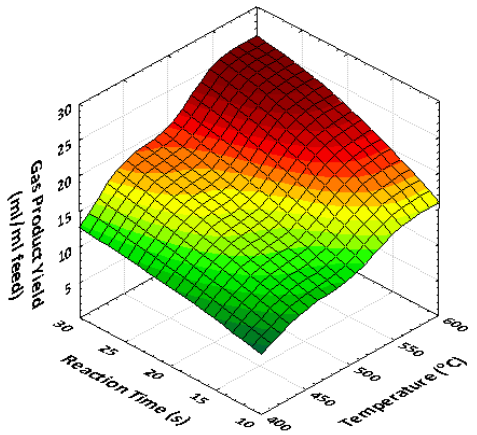


Fig. 4 The change of gas product yield with temperature and reaction time

Considering the composition of the aforementioned gas product, quantitative analysis indicated that the majority **o**f the produced effluent involved flammable components like methane and hydrogen. Besides these components carbon dioxide, ethane, propane, propylene and scarce amounts of n-butane, i-butane, 1-butene, iso-butene, T-2-butene, C-2-butene, 1,3-butadiene, n-pentane and iso-pentane were also obtained.

During the gasification experiments, it was seen that Ru/Al_2O_3 catalyst showed a very high gasification activity towards methane. Fig. 5 shows the change of the main flammable component obtained, methane, with temperature and reaction time. Accordingly, it can be said that temperature had a prominent effect on methane production, rather than reaction time; and that methane production increased at low reaction temperatures. The fact that methanation reactions of carbon monoxide and carbon dioxide are exothermic can be one of the reasons that methane formation was favored at low reaction temperatures. The minimum amount of methane in the gas product was 28.3%, which was obtained at 600°C and at a reaction time of 15s. On the other hand, the maximum amount of methane, 67.5%, was obtained at the experiment carried out at the temperature of 400°C and with a reaction time of 15s.

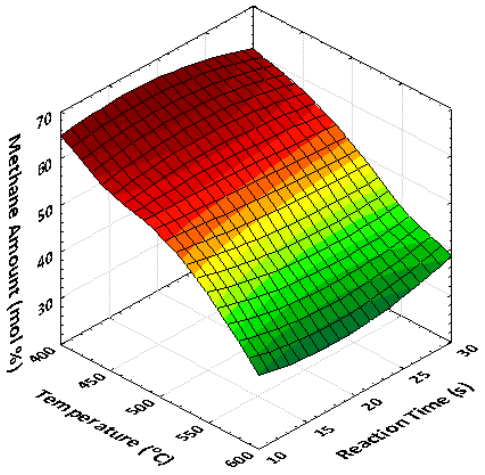


Fig. 5 The change of methane amount with temperature and reaction time

Fig. 6 shows the change of the second abundant flammable gaseous product, hydrogen, with respect to reaction temperature and time. From the figure, it can be seen that hydrogen showed an opposite trend with temperature when compared with methane. Accordingly, hydrogen production increased at elevated temperatures and long reaction times. The effect of reaction time on hydrogen production was more pronounced at low temperatures. The minimum amount of hydrogen obtained was 1.5%, obtained at a reaction temperature of 400°C and a reaction time of 10s. On the other hand, the maximum amount of hydrogen in the gaseous effluent was 11.8%. This value was obtained during the experiment carried out at 600°C and with a reaction time of 25 s.

Another abundant gas product was carbon dioxide, the change of which with reaction conditions is presented in Fig. 7. Accordingly, temperature was the main parameter that affected carbon dioxide production. The minimum amount of carbon dioxide in the gaseous effluent was 28.0%, obtained at 400°C and for a reaction time of 15s; whereas the maximum

amount of carbon dioxide, 60.6%, was encountered at 600°C for the experiment made with 15s of reaction time.

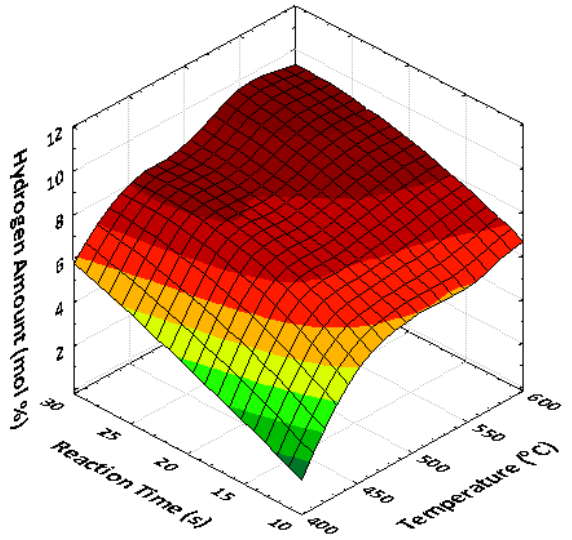


Fig. 6 The change of hydrogen amount with temperature and reaction time

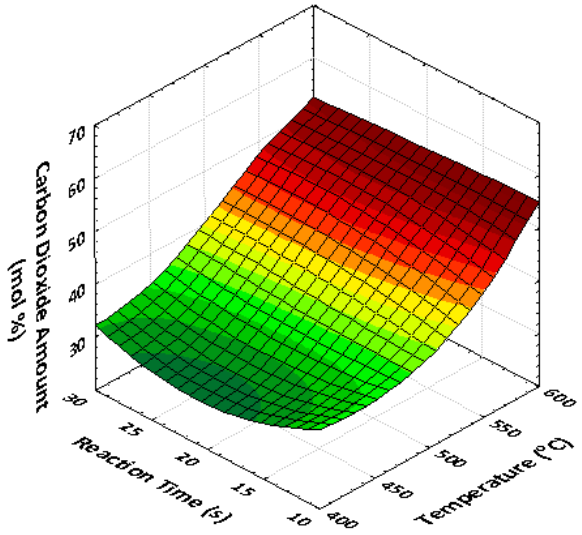


Fig. 7 The change of carbon dioxide amount with temperature and reaction time

IV. Conclusion

In conclusion, it can be said that the use of Ru/Al_2O_3 catalyst in the gasification of 2-Propanol in supercritical water enhanced flammable component production in the gaseous effluent, in very short reaction times. It was seen that $Ru/Al_2O_3$was especially selective for methane production, giving methane yields up to 67.5%. A significant reduction in the TOC contents of the liquid effluents was observed. What is more, gas product yields up to 27.2mL/mL 2-Propanol were obtained during the catalytic gasification reactions.

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