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Hydrogen Rich Fuel Gas Production from 2-Propanol Using Pt/Al_2O_3 and Ni/Al_2O_3 Catalysts 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. $Pt/Al_2O_3$and Ni/Al_2O_3were the catalysts used in the gasification reactions. All of the experiments were performed under a constant pressure of 25MPa. 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, Ni/Al_2O_3, Pt/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.

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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, 0.5 M dilute solutions of 2-Propanol were used, with an initial Total Organic Carbon (TOC) content of 18000 mg/L. Two different catalysts, namely Pt/Al_2O_3 and Ni/Al_2O_3, were employed in the reactor. The experiments were performed at five reaction temperatures (400, 450, 500, 550 and 600°C) for the experiments made with Pt/Al_2O_3catalyst and at four reaction temperatures (450, 500,

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550 and 600°C) for the experiments made with Ni/Al_2O_3catalyst, as a net gaseous product yield could not be obtained at lower temperatures. For both catalysts five different reaction times (10, 15, 20, 25 and 30 s) were implemented, under a constant pressure of 25 MPa. With the aid of these experiments, it was aimed to find the effect of reaction temperature, reaction time and catalyst type on the gasification yield and biofuel composition; and to determine the optimum conditions for hydrogen production.

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 0.5 M solution with an initial TOC content of 18000 mg/L, 38.36 mL of 2-Propanol was diluted to 1 L with distilled water.

B. Catalysts

The Pt/Al_2O_3catalyst was obtained from Hach-Lange, which contained 2.95% (wt.) oxygen, 55.86% (wt.) aluminum and 41.19% (wt.) platinum. From the SEM images of the catalyst shown in Fig. 1, it can be seen that Pt/Al_2O_3particles have a spherical and a porous shape.

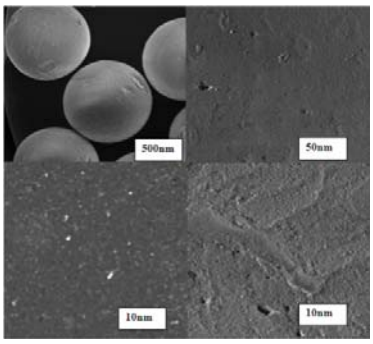


Fig. 1 SEM images of the Pt/Al_2O_3 catalyst

On the other hand theSEM images of the Ni/Al_2O_3 catalyst, which was also obtained from Hach-Lange, are shown in Fig. 2. From the analysis, it was found that the catalyst contained 9.30% (wt.) aluminum, 8.54% (wt.) calcium and 82.16% (wt.) nickel.

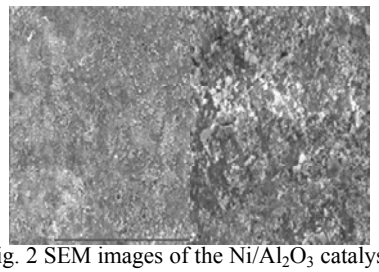


Fig. 2 SEM images of the Ni/Al_2O_3 catalyst

C. Experimental Setup

The catalytic gasification experiments were performed in the reactor system with a volume of 8.305 mL, 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 is pumped into the furnace using a high pressure pump (Autoclave Engineers, Series III pump). After exiting the furnace, the effluent is cooled rapidly by passing through a heat exchanger, and the reaction immediately stops. The possible solid particles in the effluent, which would be formed, are removed with a 0.5 μm inline filter before the stream is depressurized by a back-pressure regulator (BPR) (GO Regulator Inc.). The system pressure is kept at a constant value (±0.1 MPa) 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 are 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.

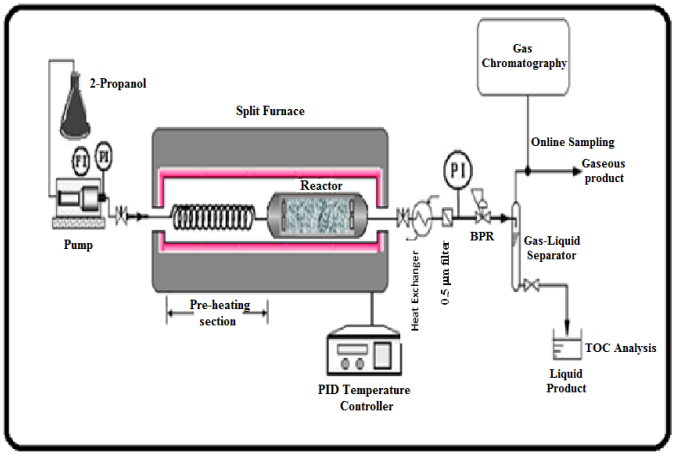


Fig. 3 Schematical demonstration of the experimental setup

D. Gaseous Product Analysis

Thegaseous product obtained from the top portion of the gas-liquid separator is 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).

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III. Results and Discussion

A. Experiments Performed with Pt/Al_2O_3 Catalyst

The experiments with Pt/Al_2O_3 catalyst were made under a constant pressure of 25 MPa, and it was aimed to investigate the effect of five different temperatures (400, 450, 500, 550 and 600°C) and five different reaction times (10, 15, 20, 25 and 30 s) on the gasification yield and flammable component content.

Fig. 4 shows the change of TOC conversion of the liquid effluent with temperature and time. Accordingly, it can be seen that TOC conversion increased with temperature and reaction time; and the maximum amount of conversion was reached at the experiment performed at 550°C, 30 s (83%). However, the minimum amount of TOC conversion was obtained at the experiment performed at 400°C, 10 s (36%). The figure also demonstrates that temperature had a more prominent effect on TOC reduction that that of reaction time.

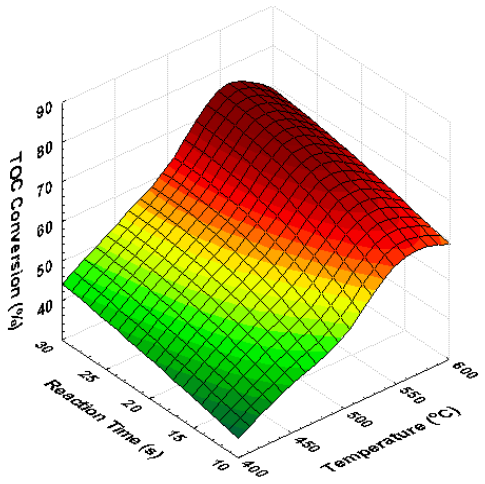


Fig. 4 The change of TOC conversion with temperature and reaction time, for Pt/Al_2O_3 catalyst

The gas product yield (Fig. 5), which stands for the amount of gaseous product obtained per mL 2-Propanol fed to the reactor, also increased with reaction temperature and time. At 600°C and 30 s, a maximum gas product yield of 7.71 mL/mL 2-Propanol was obtained.

Considering the content of the aforementioned gas product, quantitative analysis indicated that the majority **o**f the produced effluent involved flammable components like hydrogen, methane, ethane, propane and propylene. Fig. 6 shows the change of the total biofuel content of the gas product with temperature and reaction time. As it can be seen from the figure, almost all of the effluent was composed of flammable components at low temperatures. This content decreased with increasing reaction temperature, having a minimum value of 52% at 600°C and 20 s.

A significant portion of the gas product consisted of hydrogen, the change of which is demonstrated in Fig. 7. Accordingly, low temperatures and fast reaction times were found to favor hydrogen production. For example, the reaction conducted at 400°C and 10 s yielded a gaseous effluent composed of 96% hydrogen. At this condition, for every mL

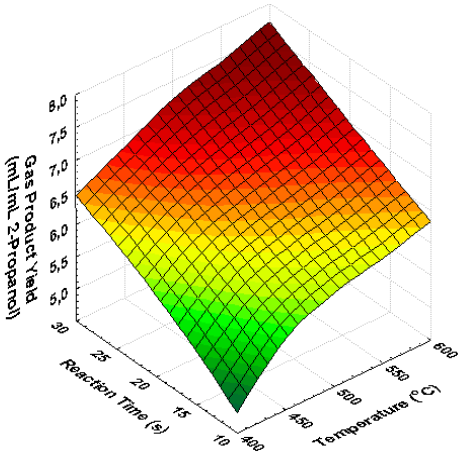


Fig. 5 The change of gas product yield with temperature and reaction time, for Pt/Al_2O_3 catalyst

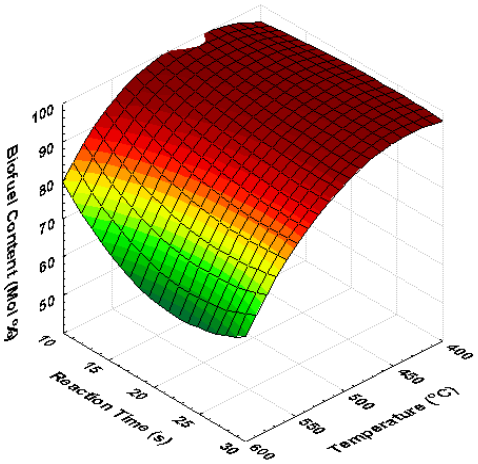


Fig. 6 The change of total biofuel content with temperature and reaction time, for Pt/Al_2O_3 catalyst

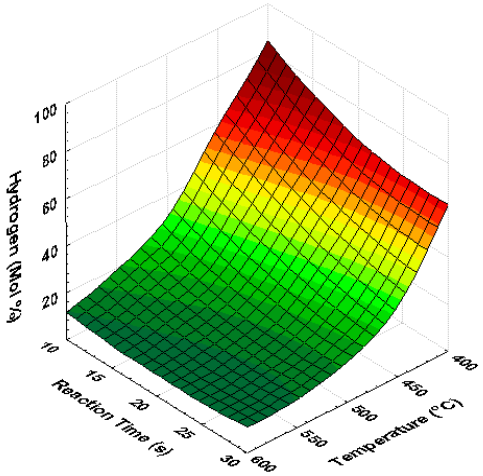


Fig. 7 The change of hydrogen content with temperature and reaction time, for Pt/Al_2O_3 catalyst

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mLof 2-propanol fed to the reactor, a gas product yield of 4.73 mL was obtained. The minimum amount of hydrogen, 10%, was obtained at 600°C and 30 s. On the contrary, high temperatures and slower reaction times favored methane production. The maximum amount of methane in the gaseous product was 53%, which was obtained at 600°C with a reaction time of 30 s, the conditions at which the hydrogen content was found to be minimum.

B. Experiments Performed with Ni/Al_2O_3 Catalyst

For the case of Ni/Al_2O_3 catalyst, the effect of four different temperatures (450, 500, 550 and 600°C) and five different reaction times (10, 15, 20, 25 and 30 s) on the gasification yield and flammable component content was investigated. The deduction of the 400°C set was due to not obtaining a net gaseous product yield at this condition. Again, all of the experiments were performed under a constant pressure of 25 MPa.

Fig. 8 shows the change of TOC conversion of the liquid effluent with temperature and time. Just like the case of Pt/Al_2O_3 catalyst, TOC conversion increased with temperature and reaction time; and the maximum amount of conversion was reached at the experiment performed at 550°C, 30 s (86%). The figure also demonstrates that temperature had a more prominent effect on TOC reduction that that of reaction time.

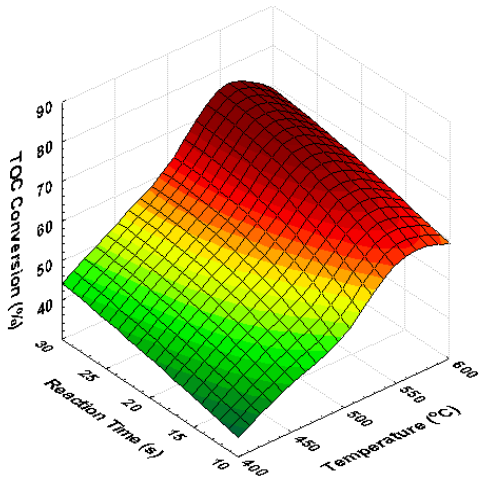


Fig. 8 The change of TOC conversion with temperature and reaction time, for Ni/Al_2O_3 catalyst

The gas product yield change with temperature and reaction time is demonstrated in Fig. 9. Just like the results obtained for Pt/Al_2O_3 catalyst, it is seen that the gas product yield increased with temperature and reaction time, though especially at low temperatures, the yield amounts were much smaller. The maximum amount was obtained at 600°C and 25 s, with a value of 6.15 mL/mL 2-Propanol.

Quantitative analysis again indicated that hydrogen, methane, ethane, propane and propylene constituted the majority **o**f the produced effluent. Fig. 10 shows the change of the total biofuel content of the gas product with temperature and reaction time. Similar to the results obtained for Pt/Al_2O_3

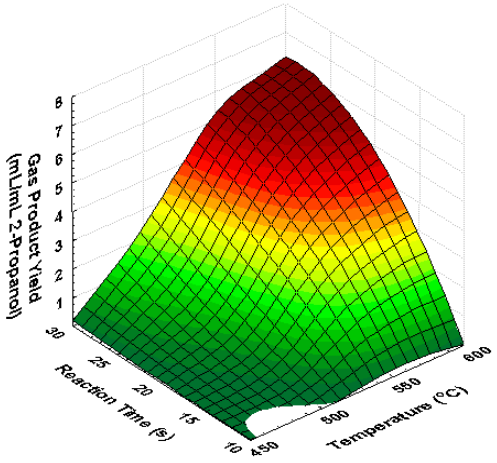


Fig. 9 The change of gas product yield with temperature and reaction time, for Ni/Al_2O_3 catalyst

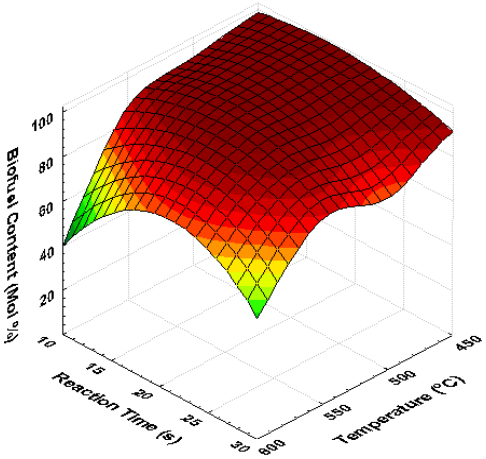


Fig. 10 The change of total biofuel content with temperature and reaction time, for Ni/Al_2O_3 catalyst

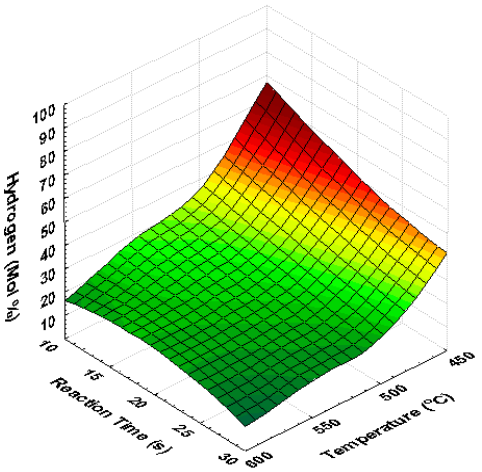


Fig. 11 The change of hydrogen content with temperature and reaction time, for Ni/Al_2O_3 catalyst

catalyst, almost all of the effluent was composed of flammable components at low temperatures. This content decreased with increasing reaction temperature, having a minimum value of 26% at 600°C and 10 s.

Similar hydrogen (Fig. 11) and methane tendencies with temperature and reaction time were observed; however their maximum amounts (65% for hydrogen, 46% for methane) were lower than those obtained with Pt/Al_2O_3 catalyst.

IV. Conclusion

In conclusion, it can be said that the use of Pt/Al_2O_3 and Ni/Al_2O_3 catalysts in the gasification of 2-Propanol in supercritical water both enhanced hydrogen and flammable component amounts in the gaseous effluent, in very short reaction times. However, Pt/Al_2O_3 was much more selective for hydrogen production. A significant reduction in the TOC contents of the liquid effluents was observed. What is more, gas product yields up to 7.71 mL/mL 2-Propanol for Pt/Al_2O_3 catalyst, and 6.15 mL/mL 2-Propanol for Ni/Al_2O_3 catalyst were obtained.

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