

STEAM REFORMING OF PYROLYSIS OIL USING NICKEL-SPINEL BASED CATALYSIS

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Introduction – Rationale

In many areas worldwide, electricity is mainly produced using fuelled generators or as a supplementary power source. The energy efficiency of those units is typically below 30% excluding production and distribution costs. Replacing the fossil fuels used in electricity production with biofuels will allow for lower carbon print, although the amount of biomass available may not be sufficient in arid areas such as the Canadian arctic. It is therefore necessary to reduce the consumption of the propellant by the unit. Fuel cells, which reach an efficiency of 65%, reduce the amount of fuel required by half. Fuel cells do not use liquid fuels directly, but rather a reformer is included to the device to reform the biofuel into syngas or hydrogen-rich syngas. The challenge with reforming complex molecules into syngas lies with carbon deposition. For example, Chen et al.¹ tested the $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ catalyst, while Xing et al.² performed catalysis of Co, Ni and Rh over MgAl_2O_4 for steam reforming of pyrolytic oil from vegetal and both observed carbon deposition.

This work focuses on the steam reforming of pyrolytic oils originating from plastic and vegetal materials as biofuels. A comparison is drawn between the behavior of (a) a nickel-alumina spinel catalyst mixed with yttrium oxide stabilized zirconia (YSZ), and (b) a catalyst made of mine wastes (known as UGS), impregnated with nickel. The NiAl_2O_4 -YSZ catalyst used in this study has already been tested for steam reforming of diesel³⁻⁵ and other liquid hydrocarbons⁶ and dry reforming of methane⁷⁻⁸ while the Ni-UGS catalyst has been tested for dry and steam reforming of methane⁹.

Experimental

The NiAl_2O_4 -YSZ catalyst was produced by wet impregnation of nickel nitrate mixed with amorphous alumina and tetragonal YSZ (containing 7% mass yttria). First, the solubilized nitrate was mixed with both powders to create a suspension, which was stirred for 90 minutes at ambient conditions. The suspension was then heated at 90°C until all the water evaporated and a dry powder was obtained. The catalyst contained 5% Ni, 47.5% alumina and 47.5% zirconia by mass. The catalyst was then calcined at 900°C for 6 hours in air to form the NiAl_2O_4 spinel. The zirconia as an oxygen carrier acted as a stabilizer for alumina, preventing its transformation into the alpha phase. XRD analyses revealed that it comprised a mix of the spinel NiAl_2O_4 and gamma alumina ($\gamma\text{-Al}_2\text{O}_3$) prior to reforming. Most of the spinel phase disappeared after reforming, while metallic nickel became visible⁸.

The Ni-UGS catalyst was produced by first grinding the initial particles to less than 53 μm . Nickel nitrate was then added and the mixture was delicately blended using a pestle for 90 seconds. Only 0.1-0.5 ml of water per gram of UGS was added to the powder and the slurry homogenized using the pestle, dried for three hours at 105°C, and calcined at 900°C for 12 hours. The calcined catalyst was finally crushed and screened to less than 53 μm . The XRD analyze shows a complex mix of spinel, mainly but not exclusively NiAl_2O_4 , MgFe_2O_4 , MgAl_2O_4 , and NiFe_2O_4 . After the CH_4 reforming reaction, performed at 800°C, the Ni-spinels are reduced into metallic nickel, alumina and Ni-Fe compound⁹.

The experimental setup (figure 1) was a tubular oven in which the catalyst was maintained in place with quartz wool. An emulsion of pyrolytic oil and water was injected into the reactor using a peristaltic pump. Argon was added as carrier gas and standard (to double check the exit flow). The reaction temperature range was 600-800°C, while the injection flow was 0.2 ml of emulsion/min. The ratio of carbon over oxygen in the emulsion was set at 2, and the amount of water added to the emulsion calculated accordingly. The produced syngas was dried using an ice bath, filter-cleaned, and its composition analyzed with a gas chromatograph (GC). The volume of the exhaust gas was measured with a mass flow meter at the GC exit.

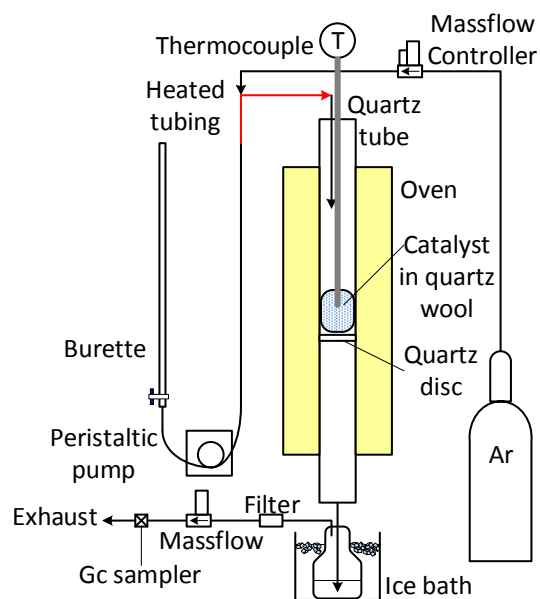


Figure 1: Schematic of experimental setup for steam reforming of pyrolytic oil.

The emulsion was prepared by adding NH_4OH solution diluted with water to a pyrolytic oil – n-pentanol ($\text{C}_5\text{H}_{12}\text{O}$) - oleic acid ($\text{C}_{18}\text{H}_{34}\text{O}_2$) mixture. The pyrolytic oil mixture was put under rapid stirring at 22°C , and the water added to the oil with a burette at a maximum flow rate of 5 ml/min. It was important to have an emulsion of water in oil to assist in the atomization of the oil droplets. The recipe to obtain a stable emulsion had to be redone every time the oil composition changed. In this study, the oils used were: vegetal pyrolytic oil, which were short molecules, highly oxygenated, with high-water content, and plastic pyrolytic oil (short molecules, no oxygen and no water). The recipe for the pyrolytic oil was 132 g of water and 1.4 ml of NH_4OH and 50 ml of pyrolytic oil, 5 ml of $\text{C}_5\text{H}_{12}\text{O}$ and 10 ml of $\text{C}_{18}\text{H}_{34}\text{O}_2$, and this recipe was stable for several weeks. The important parameters to control in order to obtain a stable emulsion were: the $\text{C}_5\text{H}_{12}\text{O}/\text{water}$ ratio, the $\text{C}_{18}\text{H}_{34}\text{O}_2/\text{NH}_4\text{OH}$ ratio and the $\text{C}_5\text{H}_{12}\text{O}/\text{C}_{18}\text{H}_{34}\text{O}_2$ ratio. Other beneficial parameters included high stirring speeds and low injection speeds, in order to avoid a very viscous emulsion (from slow stirring) or rapid inversion (with rapid injection).

The emulsification process is an important procedure in this set-up because it atomizes the pyrolytic oil, but other approaches may be improvised on larger scale applications. When the emulsion drops enter into the heated reactor, the water vaporizes before the oil, and the expansion of water forces the oil layer around it to shatter. In doing so, the process increases the oil surface, thereby allowing the oil to reach the reaction temperature faster. If the emulsion process is reversed before reaching the heating zone, a chain of reactions leads to the carbonization of the oil on the catalyst and it deactivates within a few seconds.

Results obtained and future work

The preliminary tests have shown a complete conversion of the pyrolytic oil into H_2 , CO , CO_2 and CH_4 . Sulfur poisoning is an issue that has to be addressed because both catalyst starts to deactivate in less than 1 hour. However the deactivation rate of the Ni-UGS catalyst is comparatively slower. Carbon deposition occurs as well, but it is not clear yet if it happens in parallel of the sulfur poisoning or if it happens because of the latter. The first few tests will determine the better catalyst choice. Then, the formulation of the catalyst will be optimized to guarantee a maximum compatibility with various oil sources and operation conditions. The optimized temperature, gas hourly space velocity and gas carrier flow rates will be investigated and presented. Biofuels with biomass origin have little to no sulfur, but since pyrolytic oil can be obtained from waste or materials containing plastics, the catalyst may be exposed to sulfur on a regular basis. Since fuel cell have low sulfur tolerance, it is more beneficial to remove sulfur from syngas as H_2S than removing the sulfur as a left over from vulcanization process from a liquid. The catalyst will be exposed to pyrolytic oil containing such sulfur and the result of these tests will be presented.

References

- 1- Chen, G.; Yao, J.; Liu, J.; Yan, B.; Shan, R. (2016) Biomass to hydrogen-rich syngas via catalytic steam reforming of bio-oil. *Renewable Energy*, 91, 315-322.
- 2- Xing, R.; Dagle, V. L.; Flake, M.; Kovarik, L.; Albrecht, K. O.; Deshmane, C.; Dagle, R. A. (2016) Steam reforming of fast pyrolysis-derived aqueous phase oxygenates over Co, Ni, and Rh metals supported on MgAl₂O₄. *Catalysis Today* (in press)
- 3- Achouri, I. E.; Abatzoglou, N.; Braid, N.; Bastien, S. (2015) New insights on the role of YSZ in a NiAl₂O₄/Al₂O₃-YSZ catalyst, *Applied Catalysis, A: General*, 497, 42-50.
- 4- Achouri, I. E.; Abatzoglou, N.; Fauteux-Lefebvre, C.; Braid, N. (2013) Diesel steam reforming: Comparison of two nickel aluminate catalysts prepared by wet-impregnation and co-precipitation. *Catalysis Today*, 207, 13-20.
- 5- Fauteux-Lefebvre, C.; Abatzoglou, N.; Braid, N.; Achouri, I. E. (2011) Diesel steam reforming with a nickel-alumina spinel catalyst for solid oxide fuel cell application. *Journal of Power Sources*, 196(18), 7673-7680.
- 6- Fauteux-Lefebvre, C.; Abatzoglou, N.; Blanchard, J.; Gitzhofer, F. (2010) Steam reforming of liquid hydrocarbons over a nickel-alumina spinel catalyst, *Journal of Power Sources*, 195(10), 3275-3283.
- 7- Abatzoglou, N., Blanchard, J., Achouri, I. E., (2014), A Novel Ni-Al Spinel-Based Catalyst for Dry Reforming of CH₄-Rich Gasification Tail Gas Streams, 22nd European Biomass Conference and Exhibition, p. 1004 – 1007.
- 8- Blanchard, J.; Achouri, I.; Abatzoglou, N. (Accepted manuscript online: 16 JAN 2016) H₂S poisoning of NiAl₂O₄/Al₂O₃-YSZ catalyst during methane dry reforming. *Canadian Journal of Chemical Engineering*
- 9- Chamoumi, M.; Abatzoglou, N.; (Provisional, 17/07/2015) Process for producing catalysts from metallurgical tailings and catalysts produced therefrom. PROVISIONAL PATENT : US 62/193,650.