Fischer-Tropsch Synthesis for the production of biofuels with a low ILUC-risk

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Introduction and background

Metal pollution resulting mainly from industrial production intensification, has a serious impact on human health and environment. The remediation of heavy metals contaminated soil becomes necessary to reduce these negative effects. Bioenergy production is compromised by the risk of diversion in agricultural land for fuel production to the detriment of food supply, which led to "food versus fuels" issue.

To respond to these two challenges, The HORIZON 2020/GOLD Project, involving R&D activities of many collaborators (Greece, Italy, France, Poland, China, Germany, Netherlands, Portugal, United Kingdom, Canada), provides a potential solution based on phytoremediation and biofuels production, through the conversion of high-yield lignocellulosic crops on contaminated lands (miscanthus, switchgrass, willow, biomass sorghum and industrial hemp) into clean low ILUC biofuels. The first part of the Canadian component of this project comprises the pyrolysis of contaminated biomass in a continuous bubbling fluid-bed autothermal pyrolysis (BFB-ATP), in order to capture and concentrate biomass-contaminating metals in the solid phase products, the char. The second part consists of using pyrolysis gases as a feedstock for biofuel production through a 3-φ slurry reactor by Fischer-Tropsch Synthesis (FTS). The BFB-ATP and the 3-φ slurry reactor are both components of an innovative process intensification technology.

This work is aimed at studying the activity and the selectivity of new supported metal FTS catalysts, using syngas produced by pyrolysis of contaminated biomass as a feedstock. The first option is to use hydroxyapatite [$(Ca_{10}(PO_4)_6(OH)_2)$] as a catalyst support. HAP presents interesting characteristics such thermal, mechanical and chemical stability and amphoteric character[1]. The second option is to valorize the char of biomass as a support for FTS catalyst. For this purpose, the char is to be treated chemically to create mesopore material with high specific surface.

FTS is the catalyzed reaction of carbon monoxide (CO) and hydrogen (H_2), to produce hydrocarbons with various chain and molecular weight. The reaction pathways are complex, and the reactants conversion and products selectivity depend largely on, catalyst features. The main metals catalysts used in FTS are cobalt (Co), iron (Fe) and nickel (Ni). Each catalyst has a different active phase and different selectivity. Nickel is used as metallic form (Ni°), Ni has high selectivity for methane formation and forms nickel carbonyl at higher temperature which leads to catalyst desactivation[2]. Iron has different active phases, which are metallic iron (Fe°), magnetite (Fe_3O_4) and carbide (Fe_xC)[3]. Carbides are considered as the most active phases. Iron based catalysts are characterized by a high-water-gas-shift (WGS) reaction activity, a higher selectivity of lower olefines and it is used at a large range of temperature (220-360°C)[4]. Where cobalt is used, the metallic cobalt (Co°) is considered as the most catalytically active phase. Co-based catalysts have a low WGS reaction activity, a higher selectivity to long chain hydrocarbons and longer lifetime compared to Fe[5]. The choice of an appropriate support is an important step in catalyst preparation, in order to have a higher active phases dispersion and a good activity. Many metal supports have been studied for FTS. Zeolites have been used for their pore structure and catalytic cracking action, which favorize formation of short chain of hydrocarbons and higher isomerization[6]. Oxide supports such alumina (Al_2O_3), silica (SiO_2) and titania (TiO_2), offer higher strength (mechanical) stability, but form complex oxides with the active metal, so high-cost promoters were necessary for better reducibility and dispersion of metal particles[7]. Other studies focus on carbon materials (activated carbon, nanotube, nanofilament) as supports for FTS, due to their inertness and high surface area[8], which make them a suitable support for the deposition of the active species. However high price and sintering catalyst limit their uses on an industrial scale.

Research hypothesis

Our research is based on 2 projects: the first project is directly related to the contaminated biomass, that will be pyrolyzed in our proprietary Autothermal Pyrolyzer (ATP). The second project that is discussed in detail for this presentation concerns: (a) the char produced by pyrolysis that is transformed into an activated carbon by chemical treatment and used as support for catalyst preparation; (b) the fluids products of the pyrolytic treatment that are used as a feedstock for FTS.

New formulations of FTS catalyst are set out, by varying the type of active metal, the support and the metal compositions. Cobalt (Co) and Iron (Fe) are used as active metal, supported on hydroxyapatite (HAP) or the ATP-biomass-derived char (C). Catalyst performances are carried out on a 3-φ slurry reactor, which presents many advantages such as a good heat exchange, homogeneous mixture and non-diffusion limitations.
The following hypotheses are tested in this study:

- The acid-basic character of hydroxyapatite support will facilitate the reduction of metals oxides species;
- The contact between Fe nanoparticles and carbon support facilitates the formation of iron carbides, considered as being the most catalytically active FTS phases;
- Particles size of catalyst has to be larger than 6 nm, because if the size of particles is less than 6nm, the activity of the catalyst will decrease by edge and corner sites blocking[9].

Experimental design of the 3-φ slurry reactor

Catalyst activity is evaluated on a 3-φ-Continous stirred reactor. The feed containing a mixture of hydrogen, carbon monoxide and nitrogen as an internal inert standard, is entered by the bottom of the slurry reactor and bubbled through an inert solvent hexadecane, in which catalyst particles are suspended and slurried. The reaction is carried out at 20 bar, 230°C and a ratio of H2/CO = 2. Vigorous mixing is applied for maintaining CSTR conditions. The products are exiting into two cold traps, in order to separate liquid from the uncondensed vapors. The entrained not trapped droplets are accumulated on the filter. Products are then analyzed using two Gas Chromatographs, one for gas injections and the other for liquid samples.

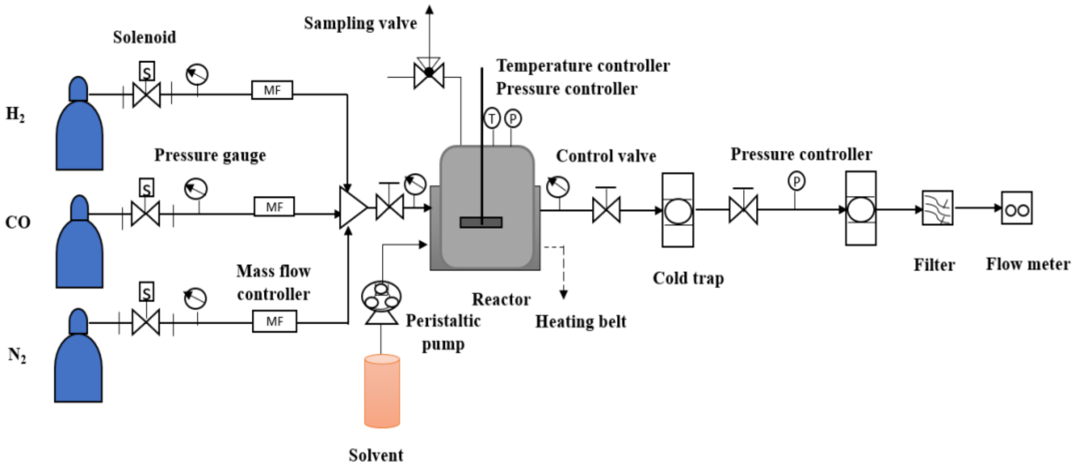

Figure. Schematic design of the 3-φ slurry reactor

The project has just started and some preliminary results towards validating the research hypotheses will be presented by the time of the conference.

Conclusion

Integrating phytoremediation with the production of clean biofuels from biomass conversion is a promising route for a viable and sustainable solution for issues of both bioenergy security and remediation of polluted soils. Pyrolysis of biomass to use for producing char for metals concentration. Converting non-fossil-carbon feedstock into liquids fuels by FTS is a very promising practical-approach. With the use of the char as catalytic support, and/or a bio-catalyst, should provide a complete solution for the revalorization of contaminated plants. many factors needs to be monitored and optimized for higher selectivity/conversion, such as: (a) the nature of the active metal and the support, (b) the operational conditions, and (c) the design of the reactor. Hydroxyapatite and char are both promising new supports for Fisher-Tropsch synthesis and their efficiency/selectivity will be benchmarked with catalysts used industrially for FTS.

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