

A comparison of cobalt- and iron-based Fischer-Tropsch catalysts for biomass-derived diesel and SNG coproduction

Javier Barrientos, Magali Boutonnet and Sven Järås

KTH (Royal Institute of Technology), Chemical Technology, Teknikringen 42, S-100 44 Stockholm, Sweden. E-mail: javbar@kth.se; Tel: +46 87908257

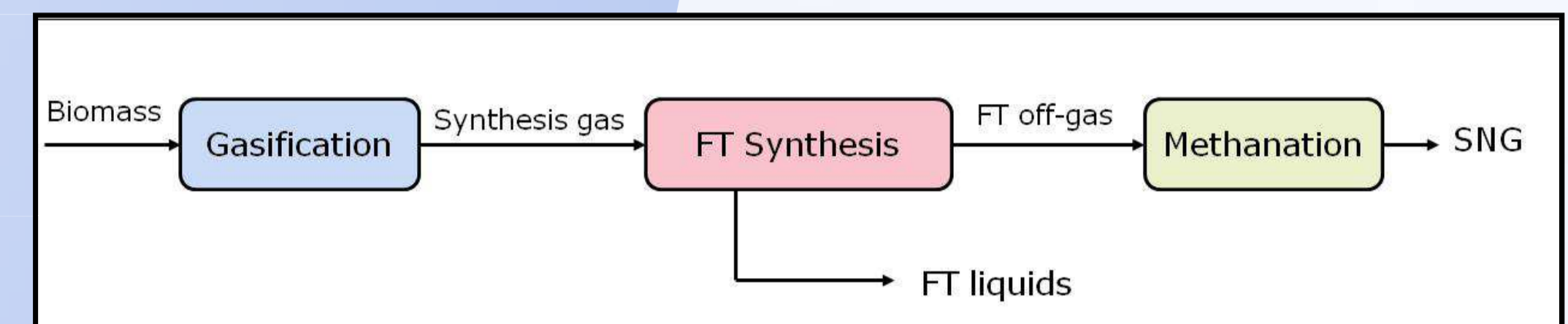
1. Introduction

Depletion of fossil fuels and awareness of environmental issues caused by the utilization of these fuels are two of the largest challenges that humankind will have to face in the coming years. Biomass is, at the moment, the only renewable energy source that can both diminish the oil share and the CO₂ emissions from the transportation sector. Therefore, the conversion of biomass into liquid fuels via gasification and Fischer-Tropsch (FT) synthesis is becoming an interesting technology [1, 2].

It has to be mentioned that the conversion of biomass into bio-synthetic natural gas (SNG) has also attracted much attention lately [3]. Moreover, the idea of co-producing diesel and SNG by methanating the off-gas resulting from the FT reactor has been technically and economically assessed, and has resulted in an increase in biomass-to-fuel efficiency [4].

Among all the metals known to catalyze the FT reaction only Co and Fe have found industrial application [5]. Conventionally, cobalt is the preferred one for Gas-to-Liquid applications while iron is for Coal-to-Liquid processes [6, 7]. At the moment, there is no conventional knowledge regarding the most suitable catalyst for Biomass-to-Liquid applications.

This work focuses on the differences between the catalytic properties of cobalt- and iron-based catalysts and provides information to evaluate the suitability of these two metals in a diesel and SNG co-production system.



FT diesel and SNG co-production block diagram

2. The catalysts

The cobalt-based catalyst was prepared by incipient wetness impregnation of Co(NO₃)₂·6H₂O and Pt(NH₃)₄(NO₃)₂ aqueous solutions on a γ-Al₂O₃ support. The sample was then calcined at 300 °C for 16h in air. The catalyst consists of 12% wt. Co and 0.5% wt. Pt.

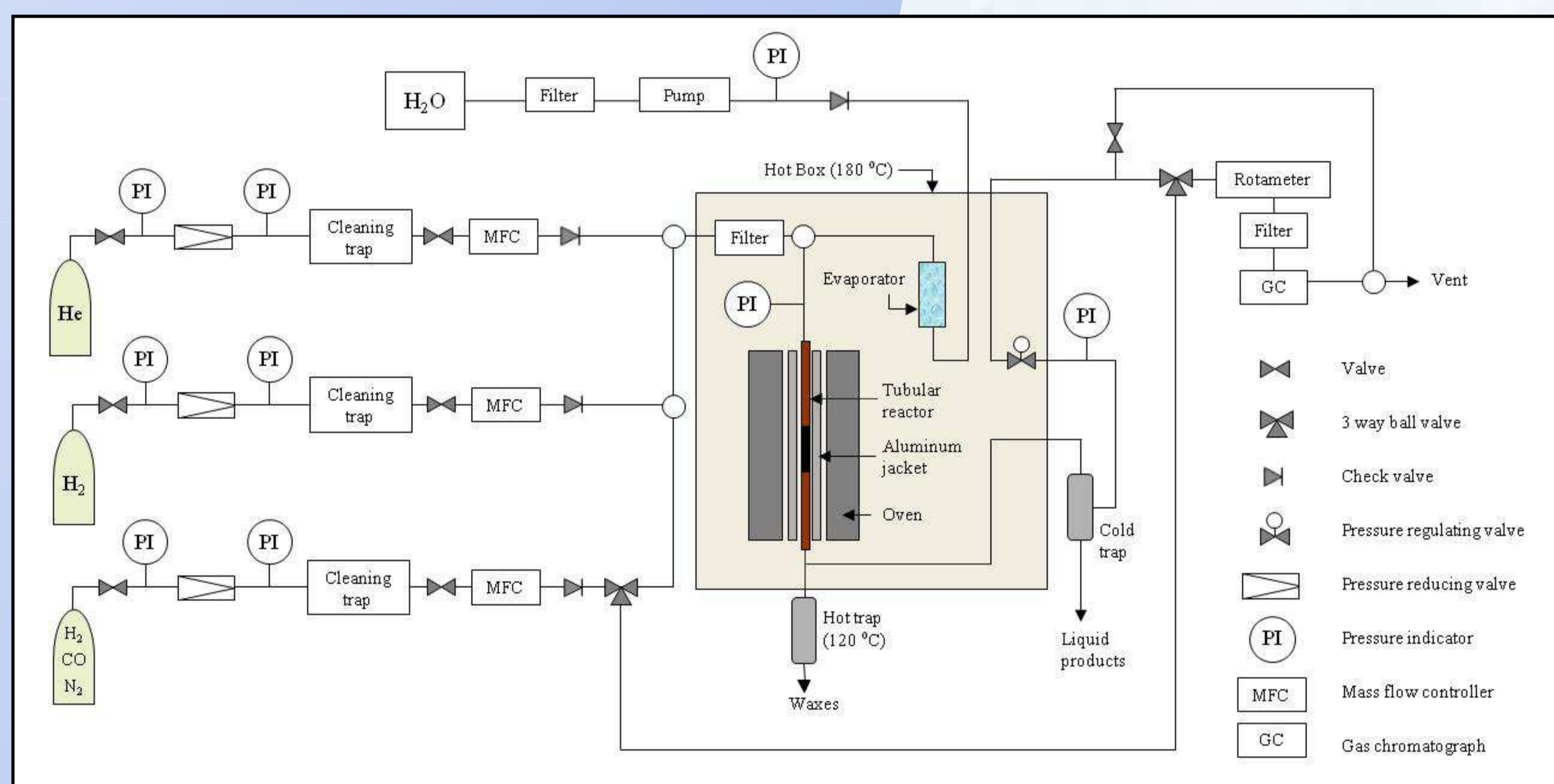
The iron-based catalyst was prepared by co-precipitation of Fe(NO₃)₃·9H₂O, Cu(NO₃)₂·3H₂O and TEOS, calcination of the sample at 450 °C during 4h in air and subsequent incipient wetness impregnation of KNO₃ aqueous solution on the sample. Finally the catalyst was calcined again at 450 °C during 4h in air. The molar composition of the catalyst is 100Fe/1.2K/1Cu/1SiO₂.

The reduction of both catalysts was performed in situ at 350 °C during 16 h in H₂ flow.

Catalyst	100Fe/1.2K/1Cu/1SiO ₂	12Co0.5Pt/γ-Al ₂ O ₃
BET Surface Area (m ² /g)	95	201
Pore volume (cm ³ /g)	0.31	0.46
Average Pore Diameter (nm)	9.7	6.9
Degree of Reduction (%)	93	97
H ₂ Uptake - Chemisorption (cm ³ /g STP)	0.6	1.1

Catalyst physicochemical properties

3. Experimental setup



Rig Scheme

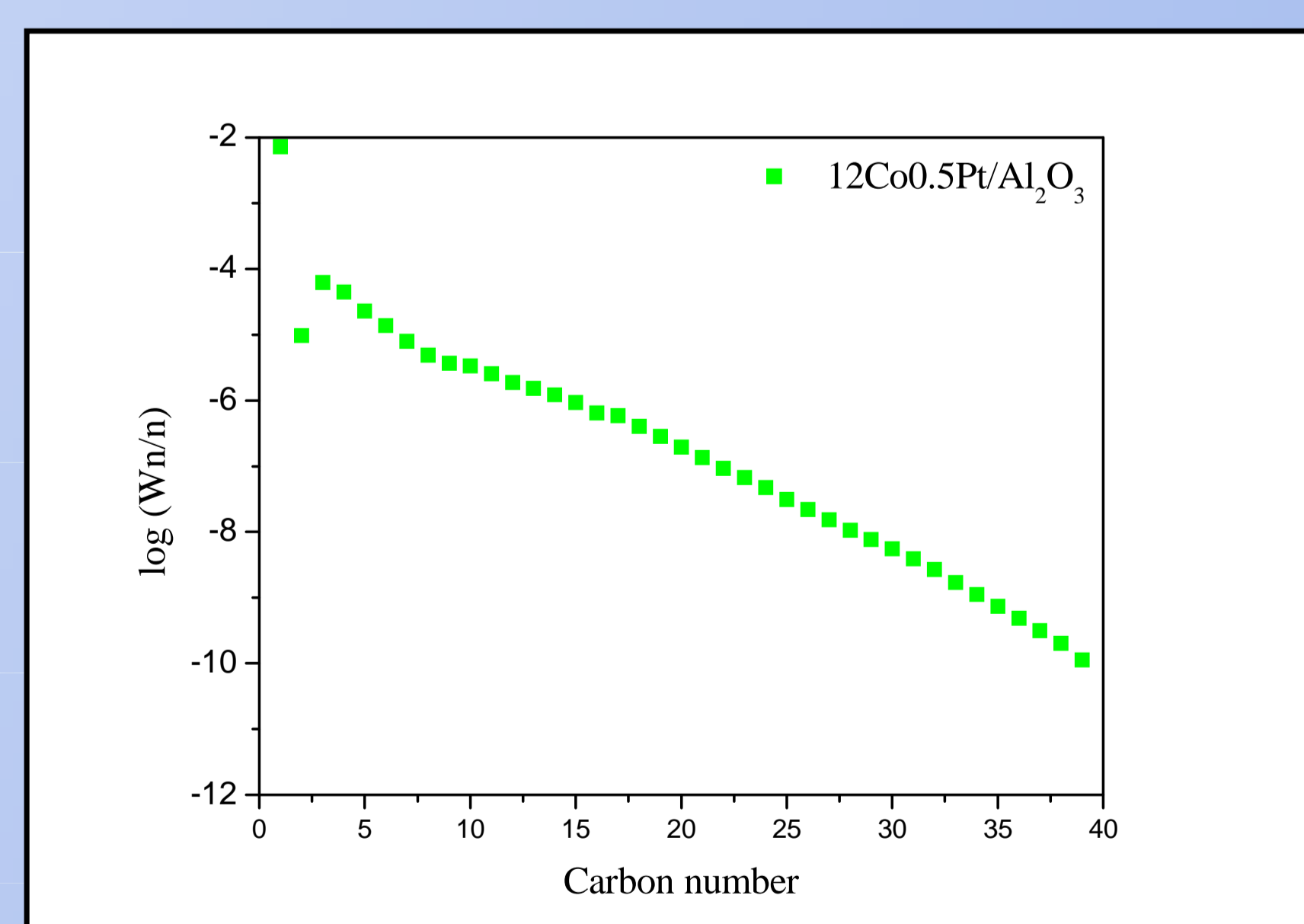
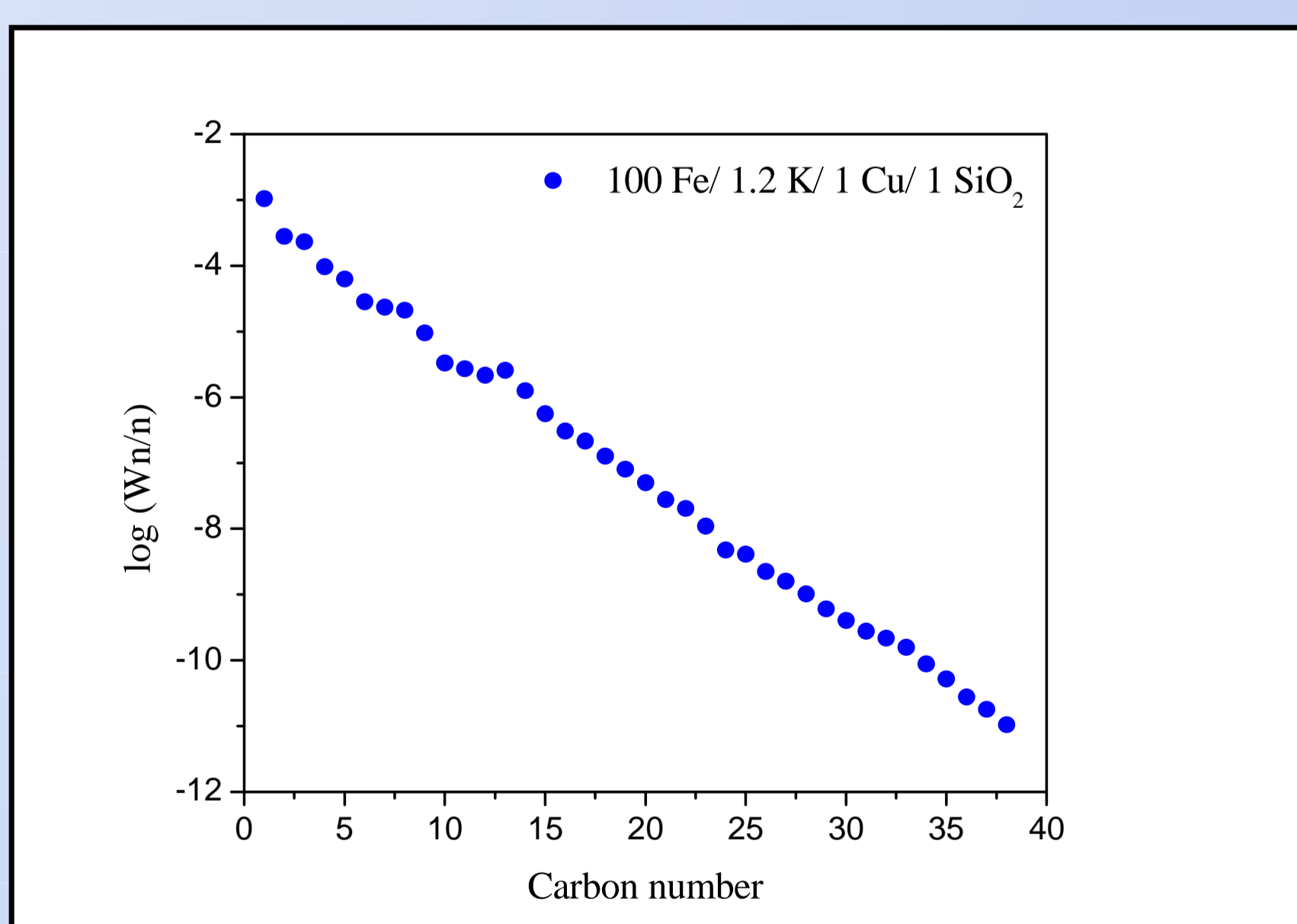
4. Experimental results

1) Activity

Catalyst	100Fe/1.2K/1Cu/1SiO ₂	12Co0.5Pt/γ-Al ₂ O ₃
Reaction Pressure (bar)	20	20
Reaction Temperature (K)	503	483
Feed H ₂ /CO molar ratio	1	2.1
SV Feed Synthesis Gas (Nml/min·g)	60	89.4
SV Feed CO (Nml/min·g)	29.1	28
CO Conversion (%)	40.5	39.2

2) Selectivity

Catalyst	100Fe/1.2K/1Cu/1SiO ₂	12Co0.5Pt/γ-Al ₂ O ₃
Selectivity to CO ₂ (%)	42	0.3
Selectivity to CH ₄ (%)	2.5	10.3
Selectivity to C ₁₁₊ (%)	20.4	55.5
Selectivity to CH ₄ (CO ₂ -free) (%)	4.3	10.4
Selectivity to C ₁₁₊ (CO ₂ -free) (%)	35.4	55.6

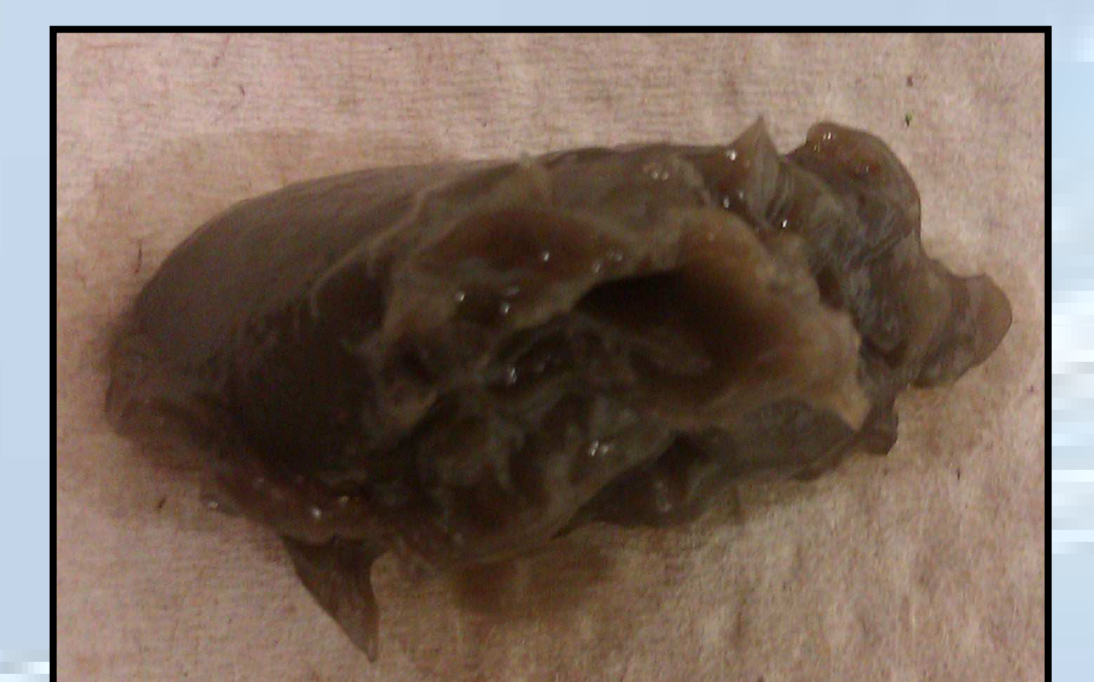


Experimental product distribution after 4 days on stream for the iron-based catalyst (left) and the cobalt-based catalyst (right) expressed as the logarithm of the weight fraction divided by the number of carbon atoms versus the carbon number.

- A significant amount of CO is converted to CO₂ when using the Fe-based catalyst at these conditions. It has to be mentioned that, for Co-based catalysts, a water gas shift unit is required prior to FT synthesis to adjust the inlet H₂/CO ratio. In such unit, the quantity of CO converted to CO₂ can be as high as for the FT process using Fe-based catalysts.



Fischer-Tropsch cobalt waxes



Fischer-Tropsch iron waxes

- There is no significant difference in the activity of these two catalysts tested at their respective relevant industrial conditions.
- The selectivity to diesel is larger for Co-based catalysts at the reaction conditions presented. However, the suitability of cobalt and iron catalysts depends strongly on the resulting H₂/CO ratio from the biomass gasifier.
- Detailed information about the catalyst life time and resistance towards poisons such as sulphur is necessary to evaluate the suitability of these catalysts in this specific application.

References:

- [1] Luaidi, M. *Fischer-Tropsch Synthesis over Cobalt-based Catalysts for BTL Applications*. 2012 Thesis.
- [2] Löfgberg, S. *Development of Fischer-Tropsch Catalysts for Gasified Biomass* 2007 Thesis.
- [3] Göteborg Energi A.B. Available from: http://www.goteborgenergi.se/English/Pages/coaltoGas_Gothenburg_Biomass_Gasification_Project.
- [4] Zwart, R.W.R. and Boerrigter, H. *High efficiency co-production of synthetic natural gas (SNG) and Fischer-Tropsch (FT) transportation fuels from biomass*. Energy and Fuels, 2005. 19 (2): p. 591-597.
- [5] Schulz, H. *Short history and present trends of Fischer-Tropsch synthesis*. Applied Catalysis A: General, 1999. 186 (1-2): p. 3-12.
- [6] Wood, D.A., Nwaoha, C., and Towler, B.F. *Gas-to-liquids (GTL): A review of an industry offering several routes for monetizing natural gas*. Journal of Natural Gas Science and Engineering, 2012. 9 (0): p. 196-208.
- [7] Leckel, D. *Diesel production in coal-based high-temperature Fischer-Tropsch plants using fixed bed dry bottom gasification technology*. Fuel Processing Technology, 2011. 92 (5): p. 959-969