Fischer-Tropsch synthesis at high conversions on Al_2O_3 supported Co catalysts with different H_2/CO levels.

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Abstract

Fischer-Tropsch experiments with different H_2/CO ratios at high CO conversions have been carried out over an alumina-supported 20wt%Co-0.5wt%Re catalyst in a stainless steel fixed-bed reactor at 210 °C and 20 bar and with H_2/CO ratios between 1.04 and 2.56. The results indicate that for H_2/CO ratios above 2.1, CO conversion levels up to at least 85% can be obtained without significant short-term deactivation or loss of selectivity towards heavier hydrocarbons. Except for very low conversion anomalies, the data collapse into a single trendline for selectivity to C_{5+} products versus average hydrogen partial pressure in the reactor irrespective of the H_2/CO feed ratio. The present results are important for development of small scale biomass to liquids plant based on a once-through process concept in order to avoid recycle streams.

1. Introduction

Fischer-Tropsch (FT) synthesis converts synthesis gas (H_2 + CO) into hydrocarbons [1]. Synthesis gas can be derived from several different carbon containing feedstocks such as natural gas (GTL), coal (CTL), or biomass (BTL). The ratio between hydrogen and carbon monoxide and the impurity content in the synthesis gas can be different depending on the feedstock and in the case of coal or biomass also depending on the gasification technology [2].

Concerns about climate change and fuel security are the main drivers for the interest in conversion of biomass to liquid fuels via FT-synthesis. According to the well-to-wheel report by the European Commission Joint Research Centre, FT-biofuels are among the bio-derived fuels with the lowest life cycle anthropogenic CO_2 emissions [3]. Typical first generation biofuels such as bioethanol and biodiesel are produced from feedstocks grown on land suitable for food agriculture. These are feedstocks such as sugar cane, corn and wheat for bioethanol production and rapeseed and palm oil for biodiesel production. Synthesis gas production does not require any specific quality or chemical structure of the feedstock. Because of this, Fischer-Tropsch biomass-to-liquids (FT-BTL) processes can utilize a wider range of biomass feedstocks than the previously mentioned processes. Examples of feedstocks suitable for FT-BTL processes that do not compete with food production are wood from forestry and non-food by-products from agriculture such as bagasse, corn stover and straw.

It is important to note that the quality of Fischer-Tropsch products only depends on the choice of catalyst and process conditions and not on the feedstock the synthesis gas is made from provided that the syngas does not contain impurities.

The metals worth mentioning that display Fischer-Tropsch activity are Ru, Fe, Ni, Co [4], but of these only cobalt and iron are considered commercially, because they offer a good compromise between catalytic activity, selectivity, stability and cost [5]. Both iron and cobalt based catalysts are in commercial use today. Although iron is cheaper and more resilient to some poisons, cobalt is preferred when hydrocarbons in the fuel range such as diesel are the target of the process.

An important difference between cobalt and iron based catalysts is the activity for water-gas-shift (WGS), converting H_2O and CO into H_2 and CO_2. Depending on the feedstock and choice of gasification technology, the hydrogen to carbon monoxide ratio of the syngas can be in the range from below 1 to 3. The water-gas shift reaction, either performed in a separate reactor or as part of the FTS process, will thus be an important feature of the process. Cobalt catalysts have no significant water-gas-shift (WGS) activity. This partly explains why cobalt-based catalysts are preferred for conversion of natural gas [6]. Synthesis gas derived from coal or biomass is typically lean in H_2 and rich in CO [7, 8]. Iron catalysts display significant WGS activity. This partly explains why it is common to use iron-based catalysts in FT-CTL processes and also why iron catalysts could be suitable for FT-BTL processes [6]. However, cobalt catalysts have many favourable properties that are desired, such as; high stability, high selectivity towards heavy hydrocarbons and they can be operated at higher CO conversion levels than iron catalysts [9]. Since cobalt catalysts usually have no significant WGS activity, the H_2/CO ratio can instead be adjusted with a dedicated WGS reactor prior to the FT reactor [10]. It has, however, been observed that Co catalysts can develop a water-gas shift activity at high CO conversion levels depending on specific criteria based on the H_2O/H_2 ratio level [11].

Compared to CTL and GTL processes, the feedstock for a BTL process must be harvested from a significantly larger geographical area. This leads to a different set of challenges in terms of logistics for transportation of the feedstock. This, in addition to the synthesis gas composition and impurity content could determine the optimal scale of FT-BTL plants and also the process design. One of the largest costs of a Fischer-Tropsch plant is the air separation unit for production of synthesis gas. With a once-through concept it is possible to omit the air separation unit and use air or oxygen enriched air instead. However, in order to efficiently use the synthesis gas in a once through concept it is important to operate at high CO conversion levels. Such a process layout could be relevant for small scale FT-BTL plants. Because of this, it is important to understand the behaviour of catalysts at high CO conversion levels with different synthesis gas compositions.

Co catalysts are usually dispersed on a refractory metal oxide such as Al_2O_3 and the catalysts deactivate with time on stream depending on the catalyst properties and process conditions. Different deactivation mechanisms have been proposed such as carbon formation, sintering and reoxidation of Co particles and a detailed review has been given previously [12].

2. Experimental

2.1 Catalyst preparation and characterization

The 20 wt% Co-0.5 wt%Re/Al_2O_3 were prepared by incipient wetness co-impregnation of $Co(NO_3)_2 6H_2O$ and $HReO_4$ on 53-90 μm γ-Al_2O_3 (Sasol GmbH Puralox SCCa, BET 174 m^2g^{-1}, pore volume 0.71 cm^3, average pore diameter 12 nm). The catalysts were dried and then calcined in air at 300 ^oC for 16 h.

Hydrogen chemisorption was performed on a Micromeretics ASAP 2010 unit. Prior to the chemisorption measurements , the catalysts were reduced *in situ* at 350 ^oC for 16 h and then cooled to 40 ^oC under vacuum. Hydrogen was dosed at 40 ^oK in order to collect data for the adsorption isotherms that was used to calculate Co dispersion with the assumption that hydrogen adsorbs in the ratio H:Co = 1.

Temperature Programmed Reduction shows the two main peaks associated with the two-step reduction of Co oxide to Co metal [13, 14].

2.2 Fischer-Tropsch synthesis experiments

Fischer-Tropsch synthesis experiments were carried out with an in-house built laboratory scale setup. In brief, the experiments were performed in a stainless steel, 10 mm ID fixed-bed reactor at 210 ^oC and 20 bar. H_2/CO ratios of 1.04, 1.33, 1.55, 1.71, 2.21 and 2.55 were used together with catalyst loadings of 2.00, 1.85, 1.70, 1.30, 1.00 and 0.88 g, respectively. The catalyst samples were diluted with 15 g of SiC particles with a size of 75-150 μm. The catalyst bed height was about 12 cm. The temperature gradient over the bed was generally smaller than 0.3 K and the average temperature over the bed did not deviate with more than 0.2 K from the desired setpoint. Cold traps to collect hydrocarbon products were maintained at 358 – 363 K after the reactor and further downstream at ambient temperature. All the gases used for the experiments were provided in 50 L gas bottles at 200 bar pressure. The helium and hydrogen gases were of 99.996 and 99.999% purity, respectively. Synthesis gas was ordered premixed with a H_2/CO ratio of 2.1 or 1 and with 3% N_2 as an internal standard. A more accurate analysis of the syngas composition was carried out with the gas chromatograph (GC) prior to and after each experiment. A HP 6890 GC equipped with a GS-Alumina PLOT column, temperature conductivity detector (TCD) and flame ionization detector (FID) were used for identification and quantification of gas phase products. All the gases used to create the syngas mixture were of 99.999% purity. Hydrogen was added with a different flow controller and mixed with the synthesis gas prior to the Fischer-Tropsch reactor when it was desired to have a H_2/CO ratio different from 2.1 or 1. In order to prevent metal carbonyls from reaching the catalyst bed, the synthesis gas was delivered in aluminium gas bottles and a PbO trap was maintained prior to the synthesis gas flow controller [15].

Since the feed gas contained a known amount of N_2 and CH_4 also can be detected by the TCD, CH_4 could be used as an internal standard to quantify the amount of hydrocarbons detected by the FID. An in-house developed spreadsheet was used to calculate the amounts of different

products from the GC data. The reduction was performed with 150 NmL/min H_2 at 1.5 bar pressure with a ramping rate of 1 K/min to the target temperature of 623 K which was kept for 16 h. After reduction, the reactor bed was cooled to 443 K and pressurized to the operating pressure with He. Temperature ramping from 443 K to operating temperature started at the same time as introduction of synthesis gas. The furnace was heated from 443 K to 20 K below the desired operating temperature with a ramping rate of 0.5 K/min and then 10 K higher in temperature with a ramping rate of 0.1 K/min. The final adjustment of the reaction temperature was done incrementally to avoid overshooting the setpoint. The standard experimental conditions were a temperature of 483 K, pressure 20 bar and an initial syngas feed rate at 250 NmL/min. The H_2/CO ratios were kept constant through each experiment.

Higher CO conversion levels were obtained by lowering the feed rate of synthesis gas every 24 hours. All the results reported here are from 24 hours after the last change in process conditions. The process conditions at 24 and 240 hours were equal allowing a measure of catalyst deactivation after 10 days on stream. Figure 1 illustrates how the experiments were carried out.

3. Results and discussion

It has previously been reported that the selectivity towards CO_2 and light hydrocarbons increases significantly when the CO conversion level exceed 70% [16] This was reported for cobalt catalysts in slurry reactors with a H_2/CO ratio of 2. Here we report on the behaviour of a 20 wt% Co – 0.5 wt% Re /Al_2O_3 catalyst in a fixed-bed reactor at high CO conversion levels with different H_2/CO ratios at 20 bar, 483 K and with an initial feed rate of synthesis gas of 250 Nml/min. Figure 2 shows the CO conversion levels throughout all of the experiments. All the reported results are from 24 hours after change in process conditions.

In addition to the H_2/CO ratios, the different operating condition histories over the ten day experiments could influence how much of the initial activity that was retained at the end of the experiments for the different samples. Figure 2 shows the measured site time yield at different CO conversion levels. It is important to note that the CO conversion was increased with time on stream and the catalyst was 24 hours on stream between each point on the graphs shown in Figure 2. Because of this, the site time yield reported in Figure 2 is influenced both by the time on stream and also by the different CO conversion levels.
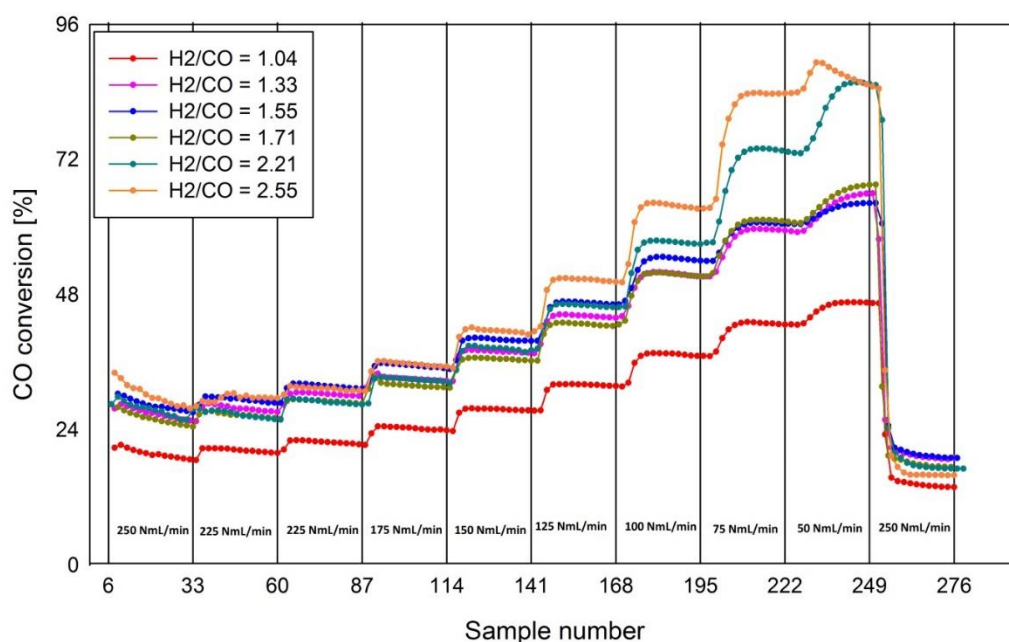
Figure 1: CO conversion throughout the experiment. Increased conversion by lowering the feed rate stepwise from 250 ml/min every 24 h. Each vertical line represents 24 h period. Conditions: 20 wt% Co-0.5 wt%Re/γ-Al$_2$O$_3$, 483 K, 20 bar. Catalyst loading from H$_2$/CO 1.04 to 2.55: 2.0 g, 1.85 g, 1.70 g, 1.30 g, 1.0 g, 0.88 g with 15 g SiC dilution. The conditions during the last 24 h were equal to the initial values.

Figure 2 shows that the site time yield (STY) decreased the most for catalysts operated at low H$_2$/CO ratios by increasing the CO conversion level. For H$_2$/CO =2.21 the STY was constant up to about 75-80 % conversion and for H$_2$/CO=2.56 the STY was constant up to about 82 % conversion. However, for all the H$_2$/CO ratios STY is reduced initially. The gradient in the partial pressures of H$_2$ and CO over the catalyst bed could contribute to this behavior. With a H$_2$/CO ratio of 1 and a CO conversion level of 47%, hydrogen will be nearly depleted at the bottom of the catalyst bed. With a H$_2$/CO ratio of 2.55, a CO conversion level at 85% and with the assumption that 2.06 mol H$_2$ is consumed per mol CO, the ratio between the partial pressure of H$_2$ and CO will be 5.3 at the outlet of the reactor. It is known that the reaction rate increases with higher H$_2$/CO ratios [17].

The experimental conditions were returned back to the initial conditions for the last 24 hours of the experiments. After 240 hours on stream it was the catalysts that were operated at the lowest H$_2$/CO ratios that retained the most of the initial activity.
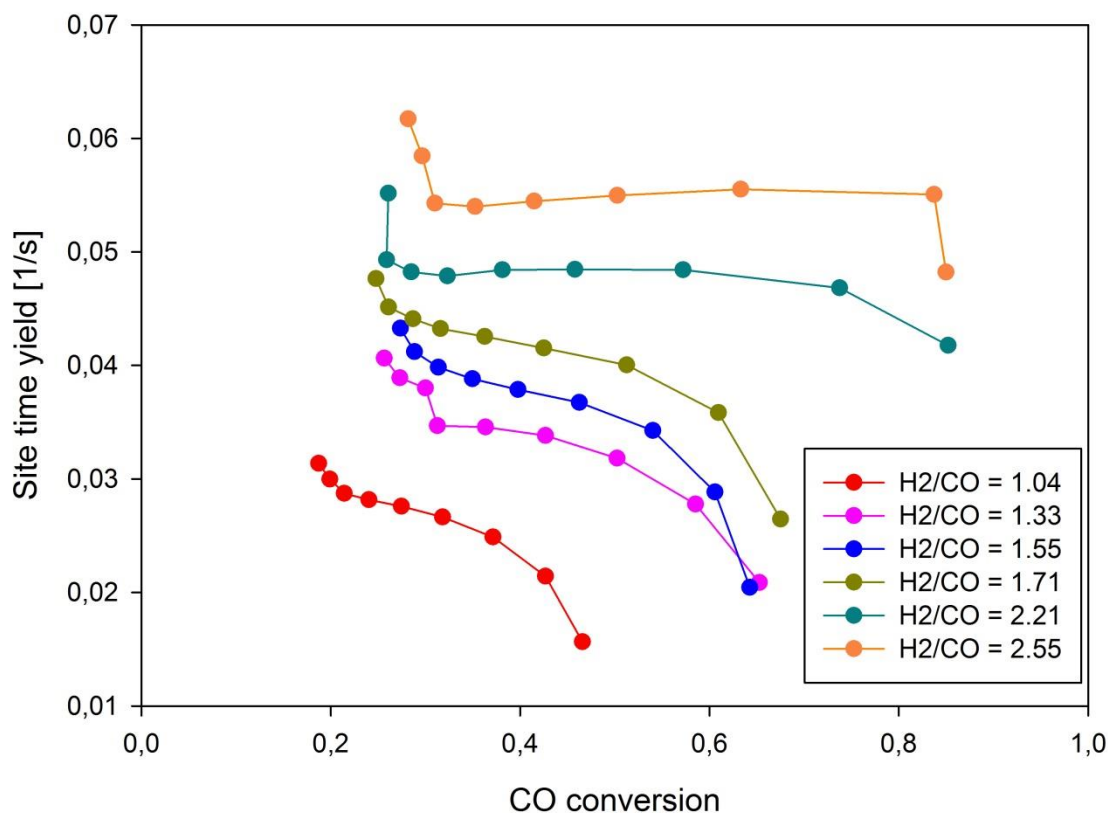
Figure 2: Site time yield at different CO conversion levels. Increased conversion by lowering the feed rate stepwise from 250 ml/min every 24 h. Conditions: 20 wt% Co-0.5 wt%Re/γ-Al_2O_3, 483 K, 20 bar. Catalyst loading from H_2/CO 1.04 to 2.55: 2.0 g, 1.85 g, 1.70 g, 1.30 g, 1.0 g, 0.88 g with 15 g SiC dilution.

Figure 3 shows the CO_2 selectivity at different CO conversion levels. With H_2/CO ratios of 2.21 and 2.55, we measured higher CO_2 selectivity at the lowest CO conversion levels than what we measured at intermediate conversion levels. With a H_2/CO ratio of 2.55 we did not observe any increase in selectivity towards CO_2 at high conversion levels.

For all the experiments with a ratio between H_2 and CO that was lower than the ratio of consumption by the FT-reaction, the trends we observed were similar. The CO_2 selectivity was lowest at the lowest CO conversion levels, and the selectivity towards CO_2 increased exponentially as we approached depletion of H_2 in the reactor. The highest CO_2 selectivity we measured was 1.38% with a H_2/CO ratio of 1.04 at 47% CO conversion.

Our results show that selectivity towards CO_2 will not be significant at any conversion level with H_2/CO ratios higher than 1.33. We did not approach depletion of the limiting reactant with a H_2/CO ratio of 1.54 or higher. This is related to how we performed our experiments. It becomes difficult to maintain the pressure in the experimental setup at high conversion levels

if the syngas feed rate becomes too low. However, we did not observe high selectivity towards CO_2 at the CO conversion levels we managed to obtain.

In CSTR reactors much higher selectivities to CO_2 have been obtained at high conversions [11,18]. As an example it has been reported a selectivity to CO_2 of 9.7 % at a conversion of 87.9 % and 16.9 % at a conversion of 96.3% [11].
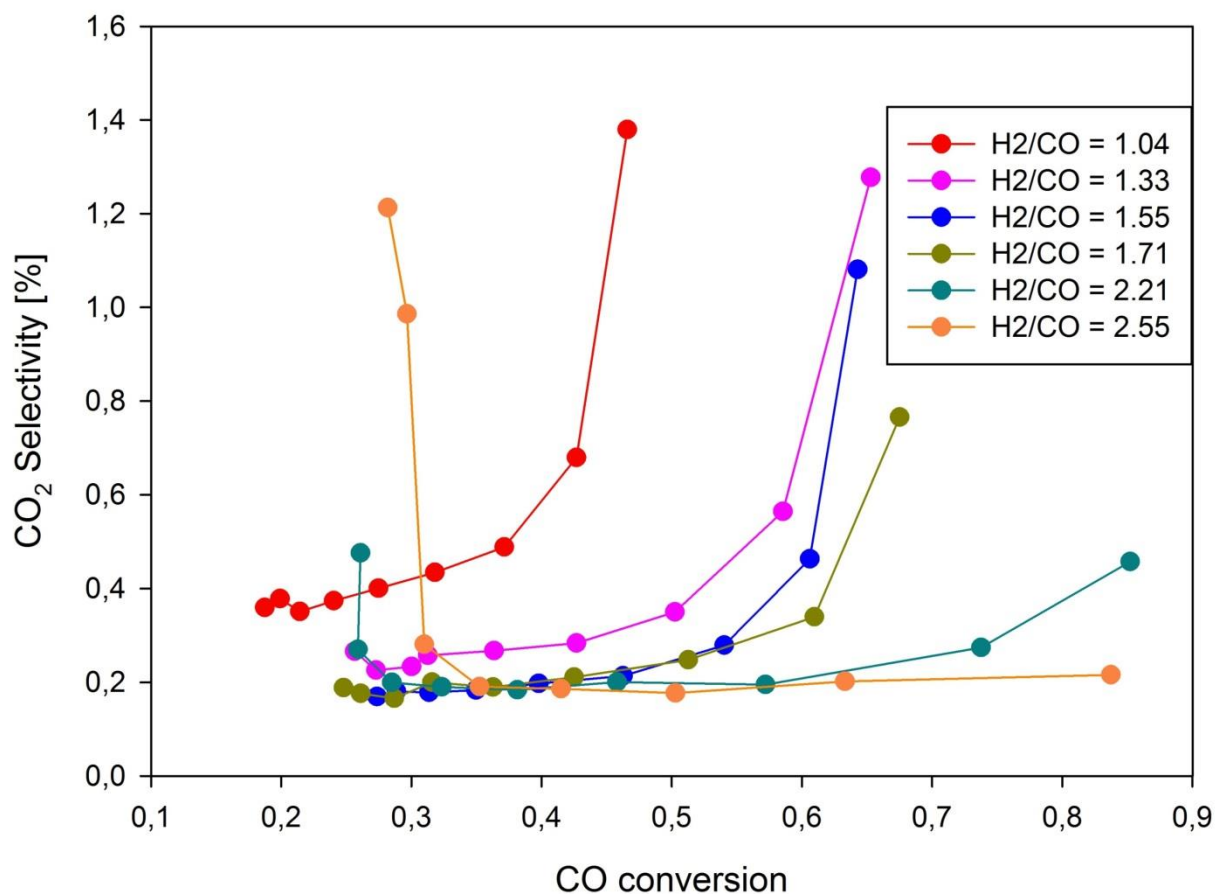

Figure 3: CO_2 selectivity at different CO conversion levels. Increased conversion by lowering the feed rate stepwise from 250 ml/min every 24 h. Conditions: 20 wt% Co-0.5 wt%Re/γ-Al_2O_3, 483 K, 20 bar. Catalyst loading from H_2/CO 1.04 to 2.55: 2.0 g, 1.85 g, 1.70 g, 1.30 g, 1.0 g, 0.88 g with 15 g SiC dilution.

Figure 4 shows the C_{5+} selectivity at different CO conversion levels. The C_{5+} selectivity was highest with the lowest H_2/CO ratios. In the experiments with a H_2/CO ratio of 2.21 and 2.55 in the synthesis gas, the C_{5+} selectivity increased rapidly with only a marginal increase in the CO conversion level in the beginning of the experiments. This change occurred at the same time as the selectivity towards CO_2 decreased. For the experiments with H_2/CO ratios of 1.04, 1.33, and 1.55 it can be seen in Figure 4 that the C_{5+} selectivity stopped to increase or decreased slightly when the highest CO conversion levels were reached. In general, the C_{5+} selectivity

increased linearly with higher CO conversion levels in all experiments. It is known that the selectivity towards heavier products increases with decreasing H_2/CO ratios [17] and also with increasing CO conversion levels 11. As shown in Table 1, there is of course a limit for CO conversions for H/CO ratios below the stoichiometric consumption ratio.
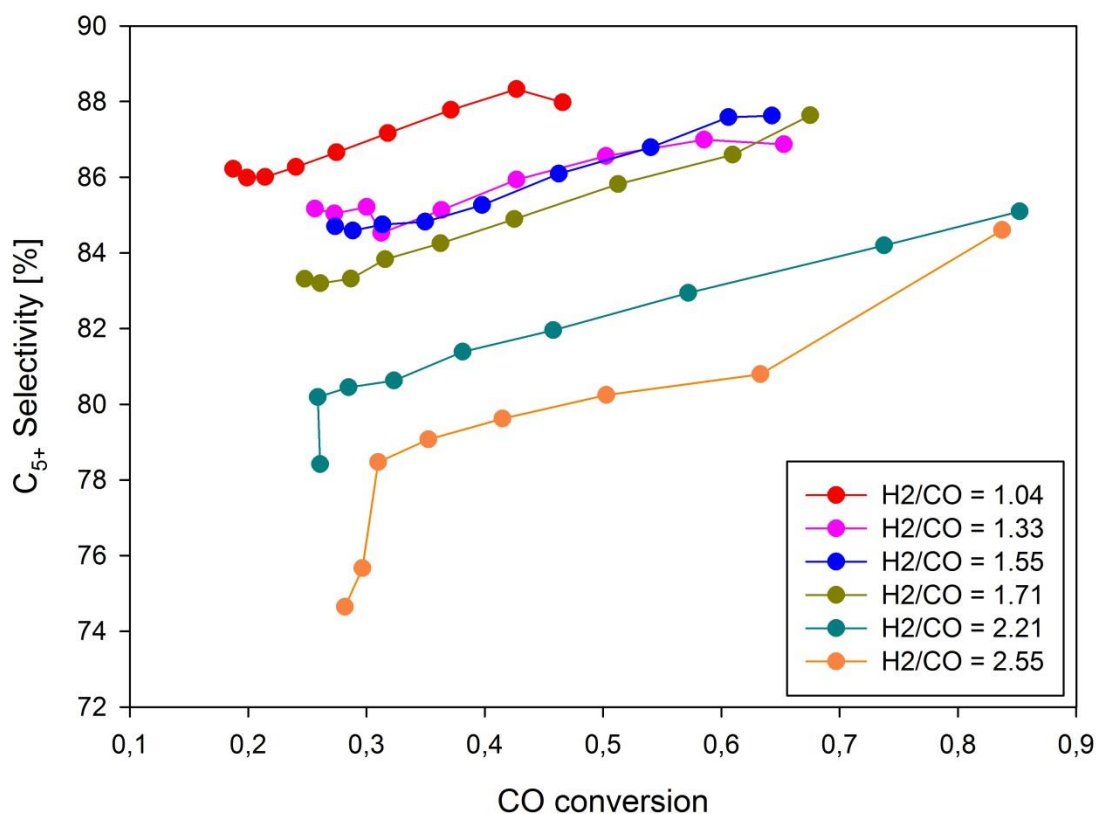

Figure 4: C_{5+} selectivity at different CO conversion levels. Increased conversion by lowering the feed rate stepwise from 250 ml/min every 24 h. 20 wt% Co-0.5 wt%Re/γ-Al$_2$O$_3$, 483 K, 20 bar. Catalyst loading from H$_2$/CO 1.04 to 2.55: 2.0 g, 1.85 g, 1.70 g, 1.30 g, 1.0 g, 0.88 g with 15 g SiC dilution.

The parallelism of the lines in Figure 4 indicates a common cause of the displacement between them. In addition to water, it is obvious that the hydrogen partial pressure, as dictated here by the H_2/CO ratio for the different series, is the main candidate to be explored. As a consequence we have in Figure 5 plotted the C_{5+} selectivity, S_{C5+}, multiplied by an exponent of the partial pressure of hydrogen instead of only S_{C5+}. The exponent has been adjusted to give a horizontal trend line, excluding the highest water pressures, and to ensure maximum collapse of the individual series.

The distinction to Figure 4 is striking; an essentially constant value is obtained for all conditions up to an average P_{H2O} of 4.5 bar, corresponding to an exit pressure for 9 bar. These pressure

ranges covers most relevant FTS conditions. Deviations for the highest P_{H2O} values is to be expected as other mechanisms likely play a role; specifically bulk or surface oxidation of cobalt. The result can simply be formulated as:

$$S_{C5+} = 142 \cdot P_{H2}^{-0.22} \qquad (1)$$

with selectivity in C% and pressure in bar. That this expression apparently is independent of water vapor pressure is deceiving. As the pressure of hydrogen is reduced, either due to a lower partial pressure in the feed, or as a result of conversion, the pressure of water increases. Nevertheless, the correlation between P_{H2} and P_{H2O} is weak using the entire dataset ($R^2=0.65$ for an exponential decay).
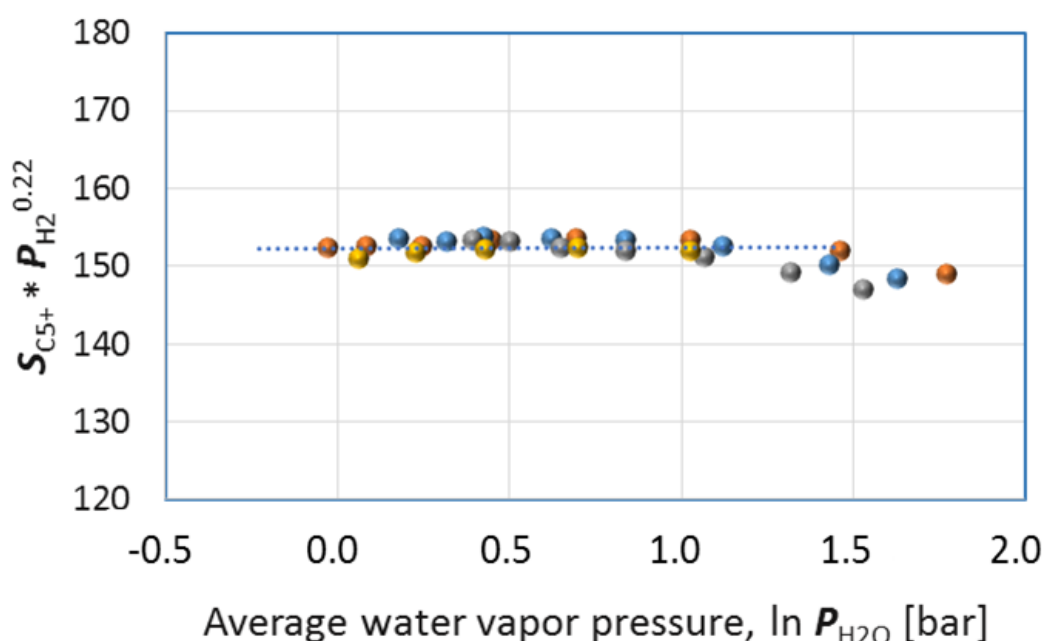

Figure 5. C_{5+} selectivity multiplied by an exponent of $\boldsymbol{P}_{H2}$ as a function of *in situ* generated water by stepwise increase of conversion as shown in Figure 1. Conditions: 20wt% Co/0.5wt% Re/γ-Al$_2$O$_3$; 210 °C; 20 bar. Catalyst loading from H$_2$/CO 1.04 to 2.55: 2.0 g, 1.85 g, 1.70 g, 1.30 g, 1.0 g, 0.88 g with 15 g SiC dilution. Outliers for low CO conversion were omitted, ref. Figure 4

However, plotting Eq. 1 in a S_{C5+} - P_{H2} diagram together with the experimental data points show systematic deviations in curvature and led to exploration of alternative expressions. We favor a linear plot as given in Figure 6 forcing interception at 100% selectivity when depletion of all hydrogen is approached:

$$S_{C5+} = 100 - k(T) \cdot P_{H2} \quad = 100 - 1.48 \cdot P_{H2} \quad (210\,°C) \qquad (2)$$

Note that this relationship is valid for a given temperature and catalyst, but for large variations in conversion and inlet H_2/CO ratios; *i.e.* variations in H_2, CO and H_2O partial pressures. The blue diamonds were excluded from the fit in Figure 6. These data points represent extreme conditions; specifically 85.5% conversion and exit water pressure of 12 bar, and the maximum hydrogen concentrations for an inlet H_2/CO ratio of 2.55. The apparent slight curvature for the lowest hydrogen pressures is represented by experiments with exit H_2/CO ratios as low as 0.85 and 0.63, and high H_2O/H_2 ratios. All in all, the simple correlation between selectivity and hydrogen pressure is striking and is in line with previous qualitative statements.
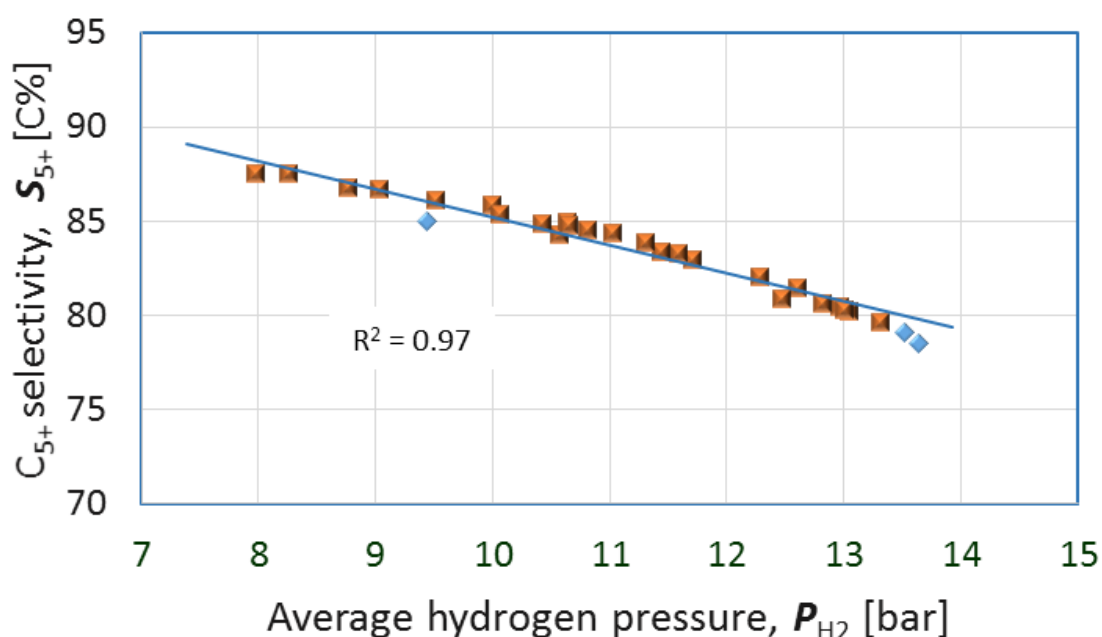

Figure 6 Selectivity to C_{5+} as a function of average hydrogen partial pressure by stepwise increase of conversion as shown in Figure 1. Conditions: 20wt% Co/0.5wt% Re/γ-Al$_2$O$_3$; 210 °C; 20 bar. Catalyst loading from H_2/CO 1.04 to 2.55: 2.0 g, 1.85 g, 1.70 g, 1.30 g, 1.0 g, 0.88 g with 15 g SiC dilution

We have previously reported that a linear relationship exists between the selectivities to C_1 and C_{5+} provided that the process conditions are kept constant except for adjustng GHSV for operation at constant conversion. This holds for different catalyst properties such as cobalt particle size and loading, type of alumina support and Re promoter [19]. As shown on Figure 7 the relationship between the selectivity to CH_4 and C_{5+} is valid also for different H_2/CO ratios emphasizing that there is a mechanistic link between the formation of CH_4 and higher hydrocarbons (C_{5+}).
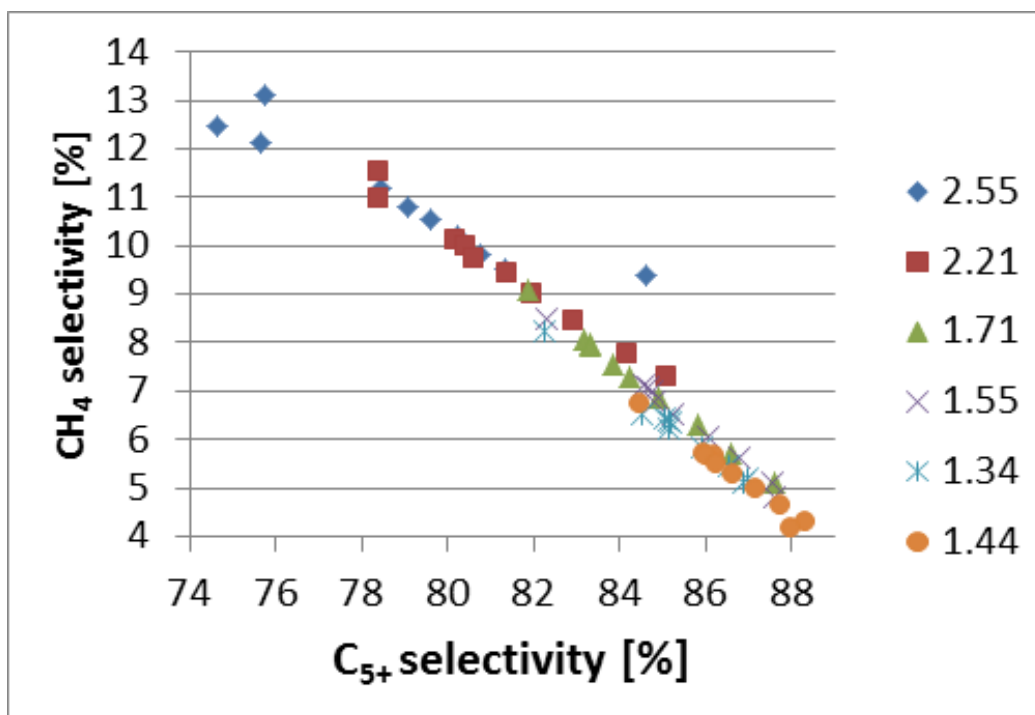
Figure 7. Relationship between the selectivity to CH_4 and the selectivity to C_{5+} for different H_2/CO ratios. Conditions: 20wt% Co/0.5wt% Re/γ-Al_2O_3; 210 °C; 20 bar. Catalyst loading from H_2/CO 1.04 to 2.55: 2.0 g, 1.85 g, 1.70 g, 1.30 g, 1.0 g, 0.88 g with 15 g SiC dilution

Data on H_2/CO ratios, calculated limit for CO conversion, obtained CO conversion and selectivity towards CO_2, CH_4 and C_{5+} is summarized in Table 1. The data reported in this table is from the highest CO conversions that we obtained. As these results show, we did not observe a significant increase in selectivity towards CO_2 and lighter hydrocarbon products. These results are different from what has been reported previously. This can at least in part be explained by a difference in reactor design (fixed bed vs CSTR). It will be a lower degree of back-mixing in fixed-bed reactors than in CSTR reactors. The conditions that lead to increased selectivity towards CO_2 and lighter hydrocarbons will most likely only be present towards the outlet of the catalyst bed in the fixed bed reactor.

Table 1. The data reported here are obtained at 483 K, 20 bar pressure and with H_2/CO ratios as specified in the table. The reported data are from 216 h time on stream and 24h after the last change in process conditions. The calculated maximum CO conversion, the obtained CO conversion, CO_2, CH_4 and C_{5+} selectivities are also reported.

H_2/CO ratio	Calculated limit for CO conversion [%]	Highest obtained CO conversion [%]	CO_2 selectivity [%]	CH_4 selectivity [%]	C_{5+} selectivity [%]
1.04	50	47	1.38	4.2	89.2
1.33	65	65	1.28	5.1	86.9
1.54	75	64	1.08	4.8	88.6
1.71	83	68	0.77	5.1	87.6
2.21	100	85	0.46	7.3	85.1
2.55	100	85	0.24	9.5	81.5

Our results show that laboratory fixed-bed reactors can be operated at high CO conversion levels with high selectivity towards heavy hydrocarbons. Since loss in reactor pressure was the limiting factor for the maximum CO conversion we obtained with a H_2/CO ratio of 1.54 or higher ratios in the synthesis gas, it cannot be excluded that stable operation with high C_{5+} and low CO_2 selectivity at even higher conversion levels can be obtained.

We have previously observed that high C_{5+} selectivity can be maintained at high CO conversions in microstructured reactors [20]. Due to the excellent heat and mass transfer properties of microstructured reactors, these reactors could be operated at severe conditions, yielding high conversions without losing selectivity of C_{5+} and without severe catalyst deactivation. In fact, a catalyst containing 40 wt% Co was operated at a conversion of CO of more than 90 % without losing selectivity to C_5+ [21]. The present results show that similar results can be obtained in laboratory scale fixed-bed reactors operated at isothermal conditions.

5 Conclusions

Previous reports have shown that the selectivity towards heavy hydrocarbons is lowered and that selectivity towards CO_2 increases as CO conversion is increased above 70-80% in CSTR reactors. We attempted to obtain as high CO conversion as possible with a 20 wt% Co – 0.5 wt% Re / Al_2O_3 catalyst in a laboratory fixed-bed reactor. The results show that high selectivity towards heavy hydrocarbons with only a minor increase in CO_2 selectivity can be obtained at high CO conversion levels. This result can possibly be important for development of small scale once through process concepts for conversion of biomass to liquid fuels.

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