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Article title: Fischer-Tropsch conversion of biomass-derived synthesis gas to liquid fuels

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Abstract

Recent and ongoing research on Fischer-Tropsch catalysts for biomass conversion typically focus on the effects of impurities common in bio-derived synthesis gas, and also on the effect of different synthesis gas compositions expected from biomass gasifiers. Cobalt and iron catalysts share the sensitivity towards some, but not all of the impurities. The most profound difference is the strong negative effect of alkali, alkaline earth and nitrogen containing compounds on cobalt catalysts while these impurities have a negligible or no effect on iron catalysts. CO_2 appears to mainly act as a diluent in cobalt-based processes while iron catalysts respond differently to this component depending on catalyst design. In particular, iron catalysts containing Al_2O_3 as a structural promoter display a high stability, C_{5+} selectivity and activity in CO_2 rich synthesis gas.

A possible link between carbon emissions and climate change, as well as diminishing non-renewable energy resources, have motivated the development of carbon neutral technologies based on renewable feedstocks. The conversion of biomass to liquid fuels may in the near future become an important complimentary source of carbon-neutral transportation fuels compatible with present infrastructure. However, it is crucial that the biomass used for transportation fuels does not compete with the production of food and that the biomass production itself does not harm the environment.[1-3] Lignocelluloses from wood or agricultural byproducts, is an attractive raw material, but the chemical composition is such that extensive processing is necessary in order to produce fuels. Key issues are molecular weight, composition (the biomass contains large amounts of oxygen, as well as trace amounts of other elements), and chemical structure.[4]

Several routes are possible for the conversion of lignocellulose to fuels. The building blocks of cellulose and hemicellulose are sugars, which after de-polymerization (e.g. hydrolysis) can be fermented to fuels such as ethanol or butanols[5], or chemically converted via so-called platform molecules[6]. The aromatic lignin structure is less easy to convert using these rather mild conditions.[7] Pyrolysis is a high temperature process where the lignocellulose is broken down to char, oil and gaseous products. A large fraction of the stored energy can be in the liquid fraction, which needs upgrading in order to be used as a fuel[8]. A very promising way for producing biofuels is through gasification and conversion of the resulting synthesis gas ($CO + H_2$) to liquid fuels (diesel) by the Fischer-Tropsch synthesis (FTS). The technology for conversion of biomass to liquid fuels (BTL) is similar to the technology for coal to liquids (CTL) or gas to liquids (GTL). The objective of this paper is to focus on the differences and challenges specific to FTS using biomass-derived synthesis gas. In particular, biomass derived synthesis gas can contain significant amounts of contaminants like alkali and alkaline earth species, sulphur (H_2S, COS), nitrogen (NH_3, HCN), dust and tars.[9] The $H_2:CO$ ratio in synthesis gas derived from biomass is typically lower than the ratio from obtained natural gas reforming, but higher than the ratio from coal gasification. Due to the high oxygen content of biomass a significant concentration of CO_2 is usually present in the synthesis gas.[10]

The industrially relevant FTS catalysts are based on cobalt or iron as the active phase. Cobalt has the highest activity and is best suited for fuel production from natural gas, but is more expensive and more sensitive to certain poisons than iron.[11] It is possible with state-of-art technology to remove the contaminants down to acceptable levels, but the cost may be high.[12] Also, the economic risk related to a trip or failure, where a breakthrough of contaminants reaches the catalyst, is very high because of the high replacement cost for the catalyst. Thus, knowing the severity of and managing this risk as well as designing catalysts which are more tolerant to contaminants will help to reduce the commercial risk for BTL. In this respect, iron catalysts are an attractive alternative. They are the conventional choice for coal-to-liquid processes with a long history of large scale production. In

general, choosing and developing the optimal catalyst for liquid fuel production may require the consideration of numerous parameters including scale of operation, operating conditions, feedstock, desired product range, infrastructure at the production site and proximity to market.

Brief historical perspective and motivation for research on FT-BTL

The Fischer-Tropsch (FT) process has an interesting and rich history spanning back to the beginning of the 20th century. In 1913 BASF patented a process for hydrogenation of CO to produce hydrocarbons[13]. BASF later abandoned this research and decided to focus their efforts on developing other processes. However, their patent sparked an interest in Professor Franz Fischer at the Kaiser-Wilhelm Institute in Mulheim, who sought to test their claims together with Hans Tropsch. The first pilot plant was constructed in 1932. By the end of 1939 nine FT plants with an annual capacity of 5.4 million barrels were in operation in Germany. A Cobalt/Thorium catalyst developed by Roelen was in use at that time. The main products were motor vehicle fuels while 28 % were different chemicals ranging from alcohols to soft waxes that produced fatty acids when oxidised[14].

The period after the 2nd world war (1950-1974) has been labelled as the "iron age" for Fischer-Tropsch synthesis. Iron catalysts were developed and commercialised, mainly in South-Africa, for the conversion of coal to liquids; a process which still remains important Later, cobalt was "rediscovered" (1975-1990) and became the preferred catalyst for the conversion of natural gas to liquids fuels (GTL)[13].

Commercial FT-GTL and CTL processes are in operation today and from this one can argue that the realization of FT-BTL plants is largely dependent on the availability of clean and cheap enough bio-derived synthesis gas. Kirkels et al.[15] investigated the annual number of publications on biomass and coal gasification from 1976 until 2009. Publication numbers for both coal and biomass spiked after the oil crisis and remained high until late 80s. Publication numbers on coal gasification has remained stable from the early 90s while there has been a remarkable increase in publications on biomass gasification in the same time-period. This lack in congruence in publication trends between these two closely related technologies demonstrates the increasing interest in green processes for production of electricity, fuels and chemicals via synthesis gas.

Description of the Fischer-Tropsch process

In short, FTS is a process where a gas mixture of H_2 and CO (synthesis gas or syngas), is converted into hydrocarbons by using a transition metal catalyst, typically iron or cobalt. The hydrocarbon products are formed via a polymerization mechanism. The Anderson-Schulz-Flory (ASF) distribution is a statistical model that describes the product distribution from FTS in terms of the chain growth probability, usually termed α. Most catalyst systems give product distributions quite close to the ASF distribution. Methane and alkanes of different length are typically the main products, with some 1-alkenes and oxygenates also formed.

(Sidebar Gasification)

From the ASF distribution it can be seen that the only two products which can be produced directly from the Fischer-Tropsch reaction with high selectivity is methane (low α) and heavy paraffinic wax (high α). Instead of reporting a calculated α, the C_{5+} selectivity is often used to quantify the liquid product selectivity. Products containing four carbon atoms or less are gaseous at ambient pressure and temperature. These by-products are typically recycled or utilized for heat and/or power production. The build-up of small inert alkanes (and CO_2) in a recycle loop decreases efficiency and increases reactor parameters and costs. Because of this, it is normally desired to have as high selectivity towards heavy hydrocarbons as possible, corresponding to a high value of α. Heavy paraffinic wax can be used for production of chemicals or can easily be converted into liquids fuels (diesel) via hydrocracking. It has been reported that cobalt-based processes combined with hydrocracking can approach 80% selectivity towards diesel; based on the total plant output[16]. The main overall reactions in FT synthesis are listed in Table 1 below.

Table 1: Main reactions in Fischer-Tropsch synthesis.

Main reactions		
	Paraffins	$nCO + (2n + 1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$
	Olefins	$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$
	Water-gas shift	$CO + H_2O \rightarrow CO_2 + H_2$
Side reactions		
	Oxygenates	$nCO + 2nH_2 \rightarrow C_nH_{2n+2}O + (n\text{-}1)H_2O$
	Boudouard reaction	$2CO \rightarrow C + CO_2$

Catalysts

According to Vannice et al.[17] ruthenium, iron, nickel and cobalt are the most active metals for FT-synthesis, and the average weight of product molecules is decreasing in the following sequence: Ru > Fe > Co > Rh > Ni > Ir > Pt > Pd. Ruthenium is too expensive, leaving cobalt and iron as the only viable metals for industrial applications. The most important difference between cobalt and iron catalysts is that iron has significant water gas shift activity while cobalt exhibits almost no such activity.

It is not straightforward to compare the activity of iron and cobalt catalysts. Site time yields can easily be determined for cobalt catalysts with H_2 or CO chemisorption data together with catalytic activity measurements. Active iron catalysts can contain a mixture of oxides, carbides and also metallic phases[18, 19] and there is an on-going debate on the nature of the active phase and the active site in Fe-based FT catalysts[18]. Because of this it probably more appropriate to use some other unit for comparison. According to van de Loosdrecht et al.[20] cobalt catalysts are more active than iron on a per gram basis. In agreement with apparent activation energies on their catalysts, (~110 and ~80 kJ/mol for Co and Fe, respectively) the activity for cobalt catalysts also increases more rapidly with higher temperatures. The catalytic activity of iron catalysts also displays a strong dependence on conversion. M.E. Dry [21] used kinetic equations for iron catalysts derived from studies at fixed and

fluidized bed pilot plants at Sasol R&D[22] and the Satterfield equation[23] for cobalt catalysts to calculate conversion profiles. In Figure 1 the activity of the catalysts were deliberately set to be equal at 4% CO conversion except for one of the plots where the intrinsic activity of the iron catalyst was set to be five times higher. The figure shows how cobalt retains more of its activity at higher conversions and also is more dependent on pressure. The curve where the intrinsic activity of the iron catalyst was set 5x higher illustrate how the activity would start to drop below that of cobalt catalysts at high conversions.

(Figure 1)

Cobalt catalysts

Cobalt catalysts are usually prepared with impregnation techniques where a cobalt salt, often cobalt nitrate, is dissolved in a solvent, e.g. water and added to a highly porous high surface area SiO_2, Al_2O_3 or TiO_2 support material. Different noble metal or oxide promoters are also typically added by pre-, co- or post-impregnation in order to improve a range of properties such as reducibility, selectivity, activity, inhibition of catalyst deactivation or to improve mechanical and attrition properties. After drying to remove water and calcination to remove residual nitrates, cobalt is present as Co_3O_4. The catalyst becomes catalytically active after reduction in pure H_2 or CO or a mixture of these gases to obtain metallic cobalt. Site time yields on cobalt catalysts have traditionally been seen as independent of support variables and dispersion[24-26]. However, it has been demonstrated how site time yield decreases dramatically for very small cobalt particles, i.e. below a cobalt particle size of 6-8 nm[27], which defines an optimum on how efficiently cobalt can be used. Readers who are interested in more information on preparation and characteristics of cobalt catalysts are referred to the review by Khodakov et al[11].

The temperature range cobalt catalysts can be operated in is fairly narrow (200-240 °C) as higher temperatures will lead to a high selectivity towards methane[11, 28]. Sintering can also become a significant problem at higher temperatures as solid-state diffusion becomes faster. The Hüttig temperature of cobalt is fairly low (~250 °C) and may indicate the temperature range where sintering becomes a problem [29]. The C_{5+} selectivity of cobalt catalyst (220°C, H_2/CO = ~1.9) increases significantly until ~15 bar pressure is reached and a further increase in pressure increases selectivity only moderately[30]. According to Schanke et al[31]., catalytic activity remains more or less constant in the range of 0-60% CO conversion with varying space time velocities. They also found an optimum for C_{5+} selectivity at ~70% CO conversion and that CO conversions above 80 % will lead to a dramatic increase in CO_2 formation.

Cobalt only displays a negligible WGS activity, thus a H_2/CO ratio slightly above 2 is required to satisfy the ratio of H_2 and CO consumed in the Fischer-Tropsch reaction. This ratio is not always attainable in biomass gasification, so in order to provide sufficient H_2 some WGS activity can be desirable. Chanenchuck et al.[32] suggested to use a mechanical mixture of a cobalt catalyst with a Cu-ZnO/Al_2O_3 water gas shift catalyst in a slurry Fischer-Tropsch reactor. This way it would be possible to benefit from the characteristics of cobalt catalysts in FT-synthesis while also being able to feed CO rich synthesis. They reported a stable Fischer-Tropsch activity for 400h comparable to the activity with the cobalt catalyst operating alone. Lualdi et al.[33] performed a similar study but used a fixed bed plug flow reactor in their experimental work. They reported a lower productivity of hydrocarbons per gram Co-catalyst with increasing amounts of WGS catalyst. Escalona et al[34]. added Cu and Co on the same support but found a dramatic decrease in FT activity. They speculated that formation of surface spinels or possibly blocking of surface Co sites by Cu could explain this behaviour. Because of the interaction between Cu and Co it can prove difficult to make this kind of bi-metallic catalysts with both WGS and FT activity.

With increasing partial pressures of CO_2 the ratio of paraffin to olefins has been found to increase exponentially until $CO_2/(CO+CO_2)=0.7$ where paraffins are formed almost exclusively[35]. Several researchers believe that readsorption of α-olefins to the catalyst surface for further chain growth plays an important role in the selectivity of cobalt catalysts[36, 37], and lower formation of olefins might correlate with lower C_{5+} selectivity in CO_2 rich feeds. Riedel et al.[38] found a methane selectivity at 10% with pure CO and as they increased the partial pressure of CO_2 they observed an exponential increase in methane selectivity. When pure CO_2 was fed to the reactor the selectivity towards methane was 95%. They speculated that with lower concentrations of CO in the synthesis gas, hence also lower CO coverage on the catalyst surface, the probability of desorption of the growing chains increases. In this way CO_2 acts mainly as a diluent by replacing CO in the synthesis gas. It is well known that high H_2/CO ratios lead to a methanation regime for cobalt catalysts. This is also important for the design of the catalyst in terms of the physical parameters of supported catalyst. If diffusion limitations become significant, hydrogen diffusion in pores will be faster than CO diffusion. This could lead to CO-deficient areas in catalyst particles, with methanation, lower weight hydrocarbon products and higher paraffin/olefin ratio as the consequence[39, 40].

Iron catalysts

Iron catalysts can be used under two different process regimes, high temperature (HTFT) or low temperature Fischer-Tropsch (LTFT). HTFT (300-350 °C and 20-40 bar pressure) yields hydrocarbons in the C_1 to C_{15} range, with a large fraction of light olefins. This regime is suitable for fluid bed reactors which do not tolerate liquid phase products at reaction conditions. In LTFT (200-240 °C and 20 – 45 bar pressure) the main product is heavy paraffinic wax (C_1-C_{100}), comparable to a cobalt-based process.

Conventional iron catalysts typically contain SiO_2, Cu and potassium. The role of Cu is to improve the reducibility of iron. In hydrogen, Fe_2O_3 reduces to Fe_3O_4 and then to metallic Fe, while in CO, a mixture of $Fe_{2.5}$ and Fe_3C is formed[41]. Smit et al.[42] reported that CuO was reduced to Cu^0 at 180 °C and at this temperature reduction of Fe_3O_4 also started. They explained the promotion effect by spillover of hydrogen and/or CO from metallic Cu^0. According to Li et al.[41] Cu increases CH_4 and paraffin selectivity while addition of K suppresses these effects. The effect of alkali promoters is complex as they increase WGS activity, FT activity, hydrocarbon selectivity, 1-alkene selectivity and resistance against re-oxidation by water.[43, 44]

Iron-based FTS processes are typically operated with synthesis gas that is lean in CO_2 and with a H_2/CO ratio lower than the required stoichiometric ratio consumed by the FT reaction. The required amount of H_2 is obtained by formation of H_2 along with CO_2 at the expense of CO and H_2O through the WGS reaction. With an inlet H_2/CO ratio of about 0.7 WGS can become rate controlling at approximately 50% CO conversion, when the production of hydrogen becomes a rate limiting factor[45, 46]. If the ratio of partial pressures between H_2O and CO reaches high enough levels (significantly higher than one) the catalyst can suffer severe oxidation and lose more or less all of its activity[46]. In general, the advantages of operating at conversion levels of 50% or lower is a higher activity per gram of iron catalysts (as demonstrated in Fig. 1), avoiding excess production of H_2 and CO_2 and also a higher selectivity for CO towards hydrocarbon products[46].

Effect of alkali promoters

Comparison of different alkali promoters and loadings is not straightforward as their ranking in terms of activity differs with the test conditions; especially with the CO conversion. According to Ngantsoue-Hoc et al.[45] the activity ranking for different alkali elements is in the order Li= K > Na = un-promoted > Rb = Cs at 20 % CO conversion, while at 60% CO conversion the ranking is different; K > un-promoted > Na > Rb > Cs > Li. The data was gathered with the same atomic ratio of 1.44/100 for alkali/iron on a 100Fe/4.6Si precipitated catalyst.[45] Riedel et al.[38] performed a similar series of

experiments with Fe/Y-zeolite catalysts and found an activity ranking in the following order Na > K > Li = Rb > un-promoted. The catalysts were tested with the same feed flows and CO conversions were in the range of 17-22%. They also found that the heavier alkali elements increased the C_{5+} selectivity the most. The high cost of Rb would most likely prohibit the use of this rare element as a promoter in industrial applications. This makes potassium the most practical choice in order to obtain both high activity and selectivity. Yang et al.[47] found 0.7 wt% potassium to be the optimal loading on an iron-manganese catalyst. At this loading, FT and WGS reaction rates as well as C_{5+} selectivity were at a maximum. It should be noted that other studies have identified different optimums for potassium loadings, most likely because of other differences in the catalyst design or in the operating conditions.

Effect of CO_2 with different mechanical promoters

Iron-based catalysts typically contain one or several promoters for improvement of mechanical and attrition properties. However, the choice of metal oxide promoter seems to have a profound effect on the performance of the catalysts with different synthesis gas compositions. In order to study the effects of SiO_2 as a mechanical and structural promoter, Dlamini et al measured the activity with H_2/CO =2. No CO_2 was present in the feed. Their SiO_2 free catalysts had higher activity than catalysts prepared by adding SiO_2 before or after precipitation and also for catalysts where SiO_2 were added after drying or calcination. Yang et al.[49] reported similar effects on iron-manganese catalysts. With increasing SiO_2 loadings, the surface area increased while catalytic activity decreased. They speculated that a lower degree of reduction and carburization with increasing SiO_2 loading was responsible for this behaviour. These observations are also supported by Zhang et al.[50] who found that the degree of reduction for iron catalysts containing SiO_2 is lower than for silica-free catalysts. Wan et al.[51] found that SiO_2 suppresses H_2 adsorption and increases CO adsorption and carburization compared to Al_2O_3. Both FT and WGS activity, and also C_{5+} selectivity was higher in samples containing SiO_2 than Al_2O_3 under CO hydrogenation conditions. However, Al_2O_3 containing samples did display better stability under their experiments. From the available literature there seems to be an agreement that SiO_2 is the preferred mechanical promoter in CO_2 lean environments.

However, during CO_2 hydrogenation (H_2/CO_2 = 3) the activity of iron catalysts on different supports follow this order $Al_2O_3 > TiO_2 > SiO_2$ [38]. In a gas composition where the volume percent of CO, CO_2, Ar and H_2 is 11, 32, 5, and 52 %, respectively, comparable to bio-derived synthesis gas[52], it is also found that Fe/Cu/Al/K catalysts have significantly higher activity than the silica containing catalysts[53]. The difference in activity under such conditions seems to arise from a higher resistance towards oxidation and higher stability of the carbide phases with alumina as structural promoter [38, 53]. One significant difference between alumina and silica supports is the ability of K containing alumina to chemisorb CO_2[38, 54]. Addition of K to co-precipitated Fe-Cu-Al catalysts was also found to promote CO2 hydrogenation activity and hydrocarbon selectivity, it also shifted the product distribution in the direction of olefins and long-chain hydrocarbons[55]. Addition of silica was reported to be unfavorable in spite of an increased surface area. This was explained by a decreased interaction between Fe and K.[56] These results indicate that Fe/K interaction could play an important role during CO_2 hydrogenation, and that conventional iron catalysts may not be appropriate for a BTL process with CO_2 rich synthesis gas.

According to Yao et al.[35] iron catalysts follow the same trend as cobalt in regard of paraffin to olefin ratio with increasing partial pressures of CO_2. A previous study of 10 wt% Fe on TiO_2 also showed higher selectivity towards lighter hydrocarbons with increasing amounts of CO_2 in the feed[57]. Riedel et al.[38] performed FT synthesis over a 100 Fe/13 Al_2O_3/10 Cu/10 K with H_2/CO = 2.3 and H_2/CO_2 = 2.3 synthesis gas. The product distribution in terms of hydrocarbon weight was near identical at both conditions, while the olefin selectivity was slightly higher in the CO_2 containing synthesis gas. Using

an intermediate $H_2/CO/CO_2$ mixture the olefin selectivity fell between the selectivity at pure CO and pure CO_2 conditions. The very different results obtained with different catalyst designs exemplify the importance of careful selection of an appropriate catalyst for FT-BTL processes.

Impurities in bio-derived synthesis gas

Coal, which originates from biomass, typically contains all of the same inorganic impurities found in biomass[58]. Hence, technologies for the removal of these impurities have already been developed in connection with large-scale CTL plants. However, these plants normally operate with iron catalysts, while most BTL concepts to this date are based on cobalt catalysts. Iron and cobalt catalysts share the sensitivity towards some, but not all of the impurities commonly found in coal and biomass derived synthesis gas. The difference between the catalysts are mainly the detrimental effect of alkali and alkaline earth elements on cobalt catalysts, while these elements often can have a beneficial or negligible effect on iron catalysts. In addition, cobalt catalysts seem to be very sensitive towards NH_3 and HCN, while iron catalysts are largely unaffected by these impurities. This raises some interesting challenges when determining sensitivity levels and synthesis gas cleaning requirements. Table 2 shows the content of inorganic materials in two types of coal and three types of biomass.

Biomass- derived synthesis gas can contain both organic and inorganic impurities such as: tars, benzene, toluene, xylene, NH3, HCN, H2S, COS, HCl, volatile metals, dust and soot60. Table 3 summarizes proposed impurity limits by different authors, though without reference to a specific catalyst or cleaning process.

Impurities in synthesis gas can be removed in wet processes such as the Rectisol process®. This is essentially an absorption process for removal of acid gases (H2S and CO2) with methanol at low temperatures (-20 to -60 °C) and high pressures (30-80 bar)63. This process requires cooling and re-heating of the synthesis gas12, 64, which results in exergy loss. Therefore, large efforts are now directed towards the development of high temperature synthesis gas cleaning processes. According to a recent review paper there are several technological challenges to overcome before hot gas-cleaning is commercially ready65. However, it is evident from the ratio of impurities in common feedstocks and the suggested impurity limits that extensive cleaning will be required. It is also necessary to determine tolerance levels and possible consequences in case of a process upset, which could cause impurities to enter the FT-reactor. Especially cobalt catalysts are known for high stability and Shell has indicated a lifetime of five or more years for the catalysts at their GTL plants66. With run times of this length it is essential to remove potential catalyst poisons down to very low concentrations.

Table 2: Analysis of 2 types of coal and 3 types of biomass. Adapted with permission from Dayton et al.[59].

	Pittsburgh No. 8 coal	Eastern Kentucky coal	red oak	Danish wheat straw	Imperial wheat straw
	proximate (wt % as received)				
Moisture	1,14	1,63	4,76	5,41	7,99
Ash	7,90	7,43	1,15	7,33	13,49
Volatile	36,80	35,44	82,88	73,39	65,14
fixed carbon	54,16	55,50	11,21	13,87	13,38
heating value (HHV as received - Btu/lb)	13691	13351	7800	7355	6318
	ultimate (wt % as received)				
Moisture	1,14	1,63	4,76	5,41	7,99
C	78,02	76,83	49,02	44,44	39,14
H	4,87	4,88	5,34	5,10	4,34
N	1,36	1,47	0,19	0,98	0,99
S	2,78	0,88	0,02	0,16	0,30
Ash	7,90	7,43	1,15	7,33	13,49
O	3,93	6,88	39,52	36,58	33,75
Cl	0,09	0,17	<0,01	0,60	2,00
	elemental ash analysis (wt % of fuel as received)				
SiO_2	3,411	3,897	0,464	2,909	5,016
Al_2O_3	1,786	2,453	0,097	0,062	0,097
TiO_2	0,073	0,107	0,065	0,003	0,005
Fe_2O_3	1,318	0,340	0,092	0,058	0,063
CaO	0,385	0,080	0,155	0,586	0,495
MgO	0,066	0,030	0,012	0,136	0,177
Na_2O	0,134	0,017	0,005	0,052	2,064
K_2O	0,108	0,098	0,104	2,507	3,049
P_2O_5	0,045	0,024	0,012	0,355	0,360
SO_3	0,885	0,096	0,022	0,302	0,762

Table 3: Gas cleaning requirements: target levels of major contaminants. Adapted with permission from Leibold et al.[12] (n.s.: not specified).

	SASOL	Newby 2001[61]	Vogel(ref 6 in [12])	Boerrigter 2003[62]
CO_2	< 10 %	n.s.	< 5 vol. %	< 5 vol. %
Particulate	n.s.	<0.1 ppm	n.s.	<0.1 ppm
HCN	< 20 ppb	< 10 ppb	< 20 ppb	< 1 ppm
NH_3		< 10 ppm		
H_2S	< 10 ppb	< 60 ppb	< 10 ppb	< 1 ppm
COS				
HCl	< 10 ppb	< 10 ppb	< 10 ppb	< 10 ppb
Br,F		n.s.	n.s.	< 10 ppb
Alkalis	< 10 ppb	n.s.	< 10 ppb	< 10 ppb
Tar	n.s.	n.s.	Below dew point	Below dew point

Sulphur on cobalt

Sulphur is known as a poison to several catalysts because of its tendency to chemisorb strongly to metallic surfaces. In addition to physically blocking up to several surface atoms, it can possibly alter neighbouring atoms electronically and by that affecting their ability to adsorb and/or dissociate reactant or product molecules[67]. Pansare et al.[68] investigated the effect of low concentrations of H_2S in the synthesis gas on a cobalt catalyst. During experiments lasting ~150 hours they did not find any detectable deactivation if the synthesis gas contained 50 ppbV H_2S, while higher concentrations (≤300 ppbV) caused a significant and irreversible deactivation. In Figure 2 the deactivation of a cobalt catalyst in a slurry reactor shows two regimes[30]. The loss in activity during period A was mainly attributed to initial build-up of heavy hydrocarbon wax inside the catalyst pores, while the gradual loss of activity in period B was correlated to the sulphur content (~0,03 mgS/m^3) in the coal-derived synthesis gas. Run times exceeding one year with this level of sulphur in the synthesis gas may not be obtainable for cobalt catalysts unless a proper sulphur guard is used [21].

Figure 2

Borg et al.[69] tested a cobalt catalyst at 20 bar pressure, 210 °C and H_2/CO=2.1 in fixed-bed. After 82 h on stream they introduced 2.5 ppmV H_2S to the synthesis gas feed. After 168 h on stream they cut the sulfur addition and adjusted the CO conversion back to 50 % before again increasing the sulfur feed rate; first to 4.8 and then to 9.5 ppmV. Figure 3 displays the catalytic activity during this experiment. Note that the feed flow is adjusted to obtain 50% CO conversion after 24 hours on stream, which explains the coinciding shift in activity. The decline in activity when adding 2.5 ppmV sulphur was extrapolated to zero using a linear expression for catalyst deactivation. This was used to calculate the catalyst dispersion assuming a 1:1 stoichiometry of S on Co. This *in operando* dispersion measurement correlated well with dispersion measurements from H_2-chemisorption on a fresh catalyst. In their study they also found an apparent decline in C_{5+} selectivity with time on stream during sulphur addition. This reflects the effect of CO conversion on selectivity. When CO conversion was adjusted back to 50%, the initial selectivity was obtained. Hence, it can be concluded that sulphur itself did not influence C_{5+} selectivity to any significant degree.

Figure 3

Phosphourus, which is also present in biomass, seems to have a similar effect to sulphur on cobalt catalysts. Borg et al.[69] added H_2PO_4 via incipient wetness impregnation (IWI) to one of their samples and measured H_2-chemisorption and catalytic activity. The results from H_2-chemisorption and catalyst testing confirmed that the loss in catalytic activity was proportional to the loss cobalt surface area.

Sulphur on iron

According to Kritzinger[70], early studies of sulfur on iron catalysts were performed at accelerated conditions; meaning high levels of sulphur. The conclusions from these studies were a strong poisoning effect and rapid loss of activity. This has led to an operating philosophy where sulfur was seen as highly undesirable and kept at as low levels as possible (lower than 5 ppb). However, new data indicates that sulfur in slightly higher concentrations can have positive effects on olefin selectivity and catalyst stability in iron HTFT processes[70].

In a pilot plant, Duvenhage et al.[71] studied precipitated iron catalyst using fixed bed reactors with industrially purified synthesis gas (low ppb sulfur levels). They were able to remove parts of the catalyst from different positions in the bed during the study. The samples were tested using micro-reactors to determine the relative activity compared to a fresh catalyst. In a plot of activity versus position in the reactor, a clear inverse V-shape appears with the maximum activity present at around

a quarter of the bed height down from the top of the pilot plant reactors. Further characterization revealed high sulfur content in the top fraction of the pilot plant bed. Iron carbides were also mainly present near the top whereas iron oxide phases increased in the lower parts of the bed. The fraction of iron oxides also increased with time on stream, coinciding with loss in catalyst activity. This indicates two different deactivation regimes. Sulfur poisoning blocks active sites at the beginning of the bed, while oxidation becomes dominant further down as the H_2O/H_2 ratio increases with increasing CO conversion.

Alkali and alkaline earth elements on Co and Fe

Nordheim et al.[72] calculated the thermodynamic amounts of different alkali species present in bio-derived synthesis gas after steam gasification. Their results indicate that there will be significant amounts of alkalis in the synthesis gas. Potassium and sodium will mainly be present as hydroxides, but chlorides are favoured with high Cl content in the synthesis gas. The question is then how will this affect long term catalyst activiy? Borg et al. calculated that if the synthesis gas contains 5 to 50 ppbw Ca and all of it sticks to the catalyst (in this case a supported Co catalyst), an average concentration of 100 to 1000 ppmw is obtained after 20 000h on stream (2.5 years)[69].

Several studies show that low concentrations of alkali and alkaline earth impurities have a detrimental effect on the catalytic activity of Co-based Fischer-Tropsch catalysts [43, 69, 73-75]. However, C_{5+} selectivity increases moderately with increasing loadings of group 1 alkali elements and CO_2 selectivity increases slightly[69, 73]. The alkaline earth elements Ca and Mg decreases C_{5+} selectivity while it has a similar effect on CO_2 selectivity as the alkali metals[69, 73].

Figure 4 illustrates results on a γ-alumina supported cobalt-rhenium catalyst[73]. It shows the effect on site time yield from sodium in weight fractions ranging from 0 to 1000 ppm, and 200 ppm of lithium, potassium or calcium. Impurities in this concentration range had no measureable effect on dispersion from H_2-chemisorption and only slightly increased reduction temperatures during temperature programmed reduction. The effect on reducibility was in agreement with previous studies[69, 74]. The activity data in Figure 5 was obtained at 50 % CO conversion, 210 °C, 20 bar pressure and $H_2/CO = 2$.

Figure 4

Figure 5

With 200 ppm K the number of potassium atoms per cobalt surface atom is slightly less than 2% of the number of cobalt sites. In contrast, the loss in activity was roughly 22%. Assuming that all the cobalt surface atoms contribute equally to the activity, the authors suggest that site blocking is an unlikely explanation for the loss in activity, especially when taking into consideration that some of the alkali is likely present on the support material. A previous study on SiO_2 supported Ru catalysts by Uner et al.[76] supports the latter conclusion

Balonek et al.[73] attributed the effect of alkali contaminants to electronic effects, but the conclusion was not supported by direct evidence of electronic interactions. Uner[75] and Trépanier et al.[74] speculated that alkali atoms may block edge and corner sites for dissociative adsorption of hydrogen. In this way the alkali can act as modifiers on adsorption/desorption mobility of hydrogen while not interfering with the electronic structure.

The studies reported here typically added alkali *ex-situ* by incipient wetness impregnation (IWI) in the form of nitrates and treated the samples in flowing air or argon at high temperature (300 – 350 °C) to remove the nitrates before characterisation and activity testing. It is unclear if addition of impurities in this manner gives a representative picture of the effect of these species under real process conditions in a FT-BTL plant. The available literature indicates that alkali and alkaline earth

elements may be the impurities commonly found in biomass that have the strongest impact on catalytic activity for Co catalysts.

In contrast to the effect on Co catalysts, alkali is known to promote desirable effects in iron catalysts and potassium is commonly added as a promotor[27, 33]. A recent study have also shown that *in operando* addition of 400 ppbw KCl and NaCl, and also 40 ppmw $NaHCO_3$ and $KHCO_3$ with the synthesis gas, did not have any measureable impact on catalytic activity on a precipitated iron catalyst after 400 hours of operation[77].

Ammonia and HCN

The amount of information on the effect of impurities such as NH_3 and HCN in literature is very limited. An Exxon patent[78] claims that a combined concentration of 100 ppb of NH_3 and HCN in synthesis gas will result in a catalyst half-life of only four days for supported cobalt catalysts in a slurry reactor. However, the patent also describes that the catalyst can be rejuvenated by hydrogen treatment to restore the initial activity. More recent work have found that he effect of NH_3 on cobalt catalysts is quantitatively similar to that of H_2S and that activity was not recovered after removing ammonia from the feed gas [79]. In the same study they found no effect of ammonia on the activity of iron catalysts. This is supported by Ma et al.[80], who did not find any negative effect of ammonia on the catalytic activity or selectivity for iron catalysts.

BTL plant layout

There are several different design options for a FT-BTL process. The choice of gasification technology and FT-catalyst dictates most of the design requirements, but also open up different possibilities for upstream process design.

Production of synthesis gas from solid carbon-containing materials is performed in a gasification reactor. There are several different designs and optimum process conditions depend on the gasifier. However, the main difference is the choice of gasification medium, including direct heating by partial oxidation with air, oxygen enriched air or pure oxygen in atmospheric or pressurised reactors; all possible in the presence of varying partial pressures of steam[81]. Another possibility for synthesis gas production is gasification by indirect heating with steam as a gasification medium. This allows production of N_2 free synthesis gas without the need of an air separation unit (ASU) for production of pure oxygen[82].

In many cases biomass-derived synthesis gas has a low H_2/CO ratio and contains light hydrocarbons such as methane. Additional hydrogen must be introduced prior to the FT reactor unless WGS activity is present in it. Adjustments of the H_2/CO ratio can be done with addition of steam in the gasifier, with a dedicated WGS reactor and/or from steam reforming of natural gas or the C_1-C_4 by-product from the FT process. Hydrogen enrichment using the WGS reaction also increases the amount of CO_2. The effects of CO_2 on the FT-synthesis with different catalysts have already been discussed, and in many cases it may be required to remove this gas prior to the FT reactor. This can be done with amine absorption or physical absorption (i.e. Selexol process)[83]. It is also possible to include a reformer to convert light hydrocarbons from the gasifier into synthesis gas. In once-through (OT) concepts auxiliary units are typically added, such as a gas turbine for power generation or other units where the energy content of the light gases can be utilized if an additional reformer is not included. However, it is for processes with low inert concentrations that the full potential of auxiliary reformers can be achieved, since recycling of unconverted synthesis gas is more economic in the absence of inert gases. The design of recycle loops becomes more complicated if WGS activity

is present in the reactor, as CO_2 removal must be incorporated in the loop, otherwise higher total pressures is required to maintain the desired partial pressures of H_2 and CO. Water is known to inhibit the activity of iron catalysts.[19, 21] Because of this it can be beneficial to use synthesis gas that is lean in hydrogen in order to consume water in the WGS reaction. This will enable higher conversions per pass.

 OT designs with one reactor or several reactors in series become more relevant when the synthesis gas contains significant amounts of inert gases. Higher total pressure is probably also required in order to compensate for the dilution with inert. Using membranes to separate CO, H_2 and C_1-C_4 compounds from the tail gas may be an option, and this valuable feedstock can be injected back into the gasifier to increase the efficiency [84]. Another option for utilisation of the tail gas is power generation[85]. Processes with cobalt catalysts can attain higher conversions than iron based catalysts per pass, but require higher pressures in order to maintain high selectivity[30]. Reactors in series with water and product knock-out in between might be a more relevant option for iron based processes[86, 87], as product selectivities are less dependent on pressure and the conversion per pass is lower[30]. In summary, the determination of an optimal plant design is complex and depends on several factors. Most likely several different designs for commercial plants will appear as different process solutions can be optimal depending on variable factors such as the type of feedstock, plant scale and location. Figure 6 shows a possible layout of an FT-BTL process including the option for production of electricity and heat from the tail gas.[88]

Figure 6

Economy of FT-BTL plants

In general, feedstock transportation costs are not decisive for the economy for GTL and CTL plants. Compared to coal, geographical distribution of biomass is much higher and energy density in terms of both volume and weight is significantly lower. Given that wood chips are milled down to the same particle size (100 μm) as in coal gasification it can still not be used in the same type of plants due to the fibrous nature of biomass[89]. It will not fluidize properly and fluffs are formed which can plug the piping. Hence, the feedstock must go through pre-treatment before it can be introduced to the gasifier, otherwise new feeding technology must be developed. Torrefaction or pyrolysis prior to gasification has been proposed. If the feedstock has to be transported over large distances, it may be feasible to perform pre-treatment near the location biomass production in order to increase the bulk density before shipment[89]. These factors complicate economic modeling of FT-BTL plants as feedstock transportation and pretreatment must be included in the evaluations. Table 4 shows the required land area biomass must be gathered from for sustainable biomass supply for relevant plant sizes[90].

Table 4: Required minimum radius for biomass harvest for sustainable supply of biomass for FT-BTL processes. Adapted from Perego et al.[90].

Plant Size (Barrels per day)	Radius of collection (km)		
	North European Forest (1 t/ha/y)	Switch grass (15 t/ha/y)	Arundo Donax (40 t/ha/y)
11-16000	109	28	17
22-32000	154	40	24

Boerrigter[91] estimated the investment costs and costs of scale using the 34,000 bbld ORYX-1 GTL plant of Sasol-QP as the basis for comparison. This study employed an oxygen blown pressurized slagging entrained flow gasification process for synthesis gas production and a low temperature cobalt synthesis process. According to his estimates, a FT-BTL plant would require 60% higher capital investment costs compared to the GTL plant with similar production capacity. The largest source of added investment cost was the air separation unit (ASU). This must provide 50% more oxygen compared to a GTL process for the production of an equivalent amount of heating value synthesis gas. The gasifier is also more expensive than natural gas reformers and additional costs also arise from more complicated synthesis gas cleaning and conditioning processes. The sensitivity analysis showed that the decrease in specific capital investment costs with increasing plant size offsets the added transportation costs of biomass as seen from Figure 7. Because of this, larger plants (16,000-32,000 bblp capacity) are favoured with this type of plant design.

Figure 7

From figure 7 it appears that the increase in transportation costs are significantly lower than the decrease in conversion costs with increasing plant scales. The effect of scale on plant economy is strong on FTS processes, and new plants are typically of very large size. From this figure it appears that small scale plants may require new technology, which allows lower conversion costs compared to large plants based on conventional technology. One possibility is so-called process intensification using micro-structured reactor technology. This may play an important part in bringing down the cost of small scale plants, which can benefit from close proximity to biomass production areas. Significant advances in the development of FT processes based on this technology have been made in the last few years[92]. Better heat transfer properties allow more active catalysts to be used under severe conditions without losing control of the highly exothermic FT reaction[93]. However, it is disputed whether the productivity of micro reactors per reactor volume is higher due to the thin layer of catalyst that can be applied to the reactor walls[92, 94, 95]. Currently both Velocys[96] and CompactGTL[97] have demonstrated their proprietary microchannel reactor technology; both are reported to be commercially ready[98]. Velocys have also demonstrated their process with bio-derived synthesis gas at Güssing in Austria[99]. An additional development which may contribute to bringing down the costs of small scale plants is the bi-functional cobalt/zeolite catalysts developed by Chevron. These catalysts are reported to yield slightly more C_1-C_4 products, but also a wax free product that does not require downstream hydrocracking or hydroisomerization[100, 101].

Conclusion

Research on catalysts for biomass conversion by Fischer-Tropsch synthesis is mostly aimed at achieving better understanding of the effects of impurities in the synthesis gas and also the effects of different synthesis gas compositions. From current research it appears that alkali, alkaline earth, ammonia and HCN only have a negative impact on cobalt catalysts while iron catalysts are not affected by these impurities to any significant degree. The benefit of cobalt catalysts is higher CO conversion per pass and also longer catalyst lifetime. Biomass derived synthesis gas also typically contains significant amounts of CO_2. If this gas is not removed it will mainly act as a diluent, replacing other gases in cobalt-based processes, whereas the effects are more significant for iron-based

processes. Iron based catalysts containing SiO_2 and TiO_2 appears to have low activity and selectivity towards heavier hydrocarbons in CO_2 rich feeds, while Al_2O_3 promoted catalysts seem to retain more of its activity and selectivity.

The availability of biomass feedstock and transportation costs will have an effect on plant scale and design. A consensus on the optimal approach is not yet established. Most likely several different concepts will appear as different designs may be feasible with depending on location and feedstock. The benefit of costs of scale with increasing plant size significantly outweighs the higher transportation costs of biomass with increasing size. Breaking this relation will require new technologies allowing the constructing of smaller plants with improved economic performance. Large scale plants will require the development of an extensive infrastructure including facilities for biomass densification in close proximity to the areas where it is harvested. This is required to increase the energy to volume ratio and the stability of the biomass before shipment. Small scale plants do not suffer from this problem and can benefit from closer proximity to the sources of biomass. However, in order for small scale plants to become economically competitive it is necessary to develop new technology. Promising developments in micro-structured reactor technology and bi-functional cobalt/zeolite catalysts may help with bringing down the costs of small scale plants

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Sidebar : Gasification

Gasification, the technology used to produce the synthesis gas, is in principle an incomplete combustion, sometimes combined with gasification with steam. The process is a high temperature reaction, with steam and a limited amount of air or oxygen giving a product gas containing CO, H_2, CO_2, CH_4 and, depending on the conditions, some heavier hydrocarbons and tar. Traditionally this is done in fixed bed reactors with controlled inlet of air from the top (downdraft) or bottom (updraft) of the slowly moving bed, giving a gas (often called producer gas). The most relevant technology for chemical applications is entrained flow gasification, where small biomass particles are blown co-currently with oxygen into the reactor. The feed can also be coal particles or liquid fuel droplets. The temperature is very high, so that tar is not formed, but the inorganic part of the biomass will melt and form slag. In a fluid bed gasifier the temperature is kept below the melting point of the ash. Several configurations are possible. The dual fluid bed gasifier in Güssing in Austria uses air in a combustion bed where a part of the biomass is burnt to provide heat. The hot bed material (sand and biomass) passes to a separate bed where the rest of the biomass is gasified with steam. This way the syngas is not diluted with nitrogen.

Figure 1: Calculated conversion profiles for LTFT operation for cobalt and iron catalysts. Figure reproduced with permission from Dry[21].

Figure 2: Typical deactivation profile for cobalt catalysts during Fischer-Tropsch synthesis. Reproduced with permission from van Berge et al.[30].

Figure 3: CO reaction rate versus time on stream with H2S addition. Fischer-Tropsch synthesis conditions were 210°C, 20 bar pressure, $H_2/CO=2.1$ and a 12 wt.% $Co/0.3wt.\% Re/NiAl_2O_4$ catalyst. Reproduced with permission from Borg et al.[69].

Figure 4: Site time yield with increasing alkali impurity loading at 50% CO conversion with a γ-alumina supported 20wt% Co, 0.5wt% Re catalyst. Impurity loading (ppm) actually denotes the weight fraction of impurities in the sample. Reproduced with permission from Balonek et al.[73].

Figure 5: A schematic of key components in a FT-BTL plant including a gas turbine (combined cycle) for power generation. Reproduced with permission from Tijmensen et al.[81].

Figure 1: An example of a possible process layout for an FT-BTL process including electricity and heat production from the tail gas. Reproduced with permission from Kavalov et al.[88].

Figure 7: Scale dependency of FT fuel production costs. ~4000 MW biomass input equals ~34,000 bbld FT products. Reproduced with permission from Boerrigter [91].

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