Advanced liquid biofuels synthesis

Adding value to biomass gasification

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Abstract

Transportion accounts for about a third of the world's energy use, half of the global oil consumption and a fifth of total GHG emissions. Increasing concerns over global climate change, depletion of fossil fuel resources and demand for transportation fuels have strongly influenced research efforts and funding programs in development and deployment of advanced biofuels. Syngas obtained from the gasification of biomass could be used as reactant in the thermochemical production of advanced (second generation) biofuels. The most relevant liquid fuels include drop-in diesel obtained through catalytic Fischer-Tropsch synthesis at an estimated 25-39 $€_{2017}$/GJ at a medium to large production scale of >200 MW. MeOH and/or DME can be obtained at a much lower production cost of 20-25 $€_{2017}$/GJ, over a Cu-catalysed system, combined with an acid catalyst for the MeOH dehydration to DME. Drop-in gasoline can be obtained indirectly from DME/methanol, via the so-called methanol to gasoline (MTG) process, at approximately 22-33 $€_{2017}$/GJ. MeOH production seems most interesting as it could be produced at low cost and relatively high overall efficiency (~60%). If desired, MeOH can be converted into DME or drop-in gasoline (via the MTG process) and it has market value as an industrially relevant platform molecule. Most liquid synthsis processes through syngas conversion are well established and have a high technological readiness level, however, the production of syngas through biomass gasification and gas cleaning are not. Low fossil fuel and high (woody) biomass prices inhibit commercialization of these processes. Along with technological innovation, more strict policies (higher CO_2 taxation) and stimulation through subsidies are needed to ensure that biomass to liquid plants will succeed.

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Summary

In this work, an overview of the main available thermochemical biomass conversion routes towards advanced biofuels is presented. The main focus is the catalytic conversion of synthesis gas, obtained via biomass gasification, into liquid fuels. The fundamentals of each synthetic route are reported, as well as their current Technology Readiness Level (TRL). The aim of this report is to evaluate and estimate the feasibility of the most viable route for the production of advanced biofuels from bio-syngas.

Transport accounts for about a third of the world's energy use, half of the global oil consumption and a fifth of total GHG emissions. Increasing concerns over global climate change, depletion of fossil fuel resources and demand for transportation fuels have strongly influenced research efforts and funding programs in development and deployment of advanced biofuels. The thermochemical conversion of biomass to synthesis gas (H_2/CO) through gasification, followed by catalytic conversion of syngas, could produce significant amounts of liquid fuels. Specifically, the catalytic conversion of syngas towards liquid hydrocarbons (via Fischer-Tropsch synthesis) and oxygenates (mainly methanol, DME and higher alcohols) are discussed.

Fischer-Tropsch synthesis is a mature commercial process for the production of liquid fuels (diesel/ gasoline/kerosene) from syngas, traditionally via coal or natural gas gasification. Liquid and gaseous hydrocarbons are formed in presence of (promoted) Fe or Co catalysts. Especially, the Co-catalysed FTS at low temperature (200-250°C) forming mainly long saturated hydrocarbons (C5+ > 80%) has become the leading technology. Up to 60% FT diesel, with naphtha and kerosene as by-products can be formed at per pass conversion of 80-90%. Although it can provide 'drop-in' fuels, it is not yet applied commercially with biomass gasification. According to current estimates, the FT liquid production costs are approximately 25-39 €/GJ.

Methanol can be used as a fuel or fuel blend (up to 3% in gasoline in EU), or can be converted to dimethylether for use as a diesel replacement or to gasoline. MeOH synthesis from coal or natural gas gasification, over a Cu-ZnO-Al_2O_3 catalyst at typical reaction conditions of 230-260°C and 50-100bar, is a well-developed and industrially practiced process, with >99.5% selectivity. This process has been proven more efficient than the production of FT liquid, with a first commercial bio-methanol plant has been started in 2015, using municipal solid waste (*Enerkem*), with a capacity of 38 million litres per year. DME is mainly produced from methanol dehydration, over an acid catalyst, but it can also be produced in one step from syngas using a dual catalyst system that allows both methanol synthesis and dehydration, overcoming the thermodynamic constraints of methanol synthesis, leading to higher per-pass CO conversions and higher DME productivities. The

current estimated production costs of MeOH and DME from biomass are about 20-25 €/GJ, with a current market price of about 20 €/GJ. MeOH and/or DME can be further upgraded to gasoline at an estimated production cost 22-33 €/GJ. Moreover, MeOH allows for a certain flexibility as it can be converted into gasoline. Other promising syngas catalytic conversion routes to valuable products (not necessarily fuels) include low olefins production via FTO, OX-ZEO or MTO processes, as well as the production of higher alcohols. However, TRL are still low so that justified cost/efficiency comparisons cannot be made.

The economics of novel biomass to liquid concepts using state-of-art technology (including MILENA/OLGA) should be investigated both for MeOH/DME and FT production. This will establish whether, without subsidy, it is economical to build an advanced biofuel plant. For instance, co-production and isolation of by-products, such as BTX and ethylene, can lower overall production costs. Also, extra value could be created from Fischer-Tropsch co-products, e.g. via co-production of high-value waxes. Alternative feedstock such as RDF can also be considered, as biomass prices contribute significantly to production costs (~40%).

Nomenclature

ASU: Air separation unit
Bbl/day: Barrels/day
BTL: Biomass to liquid
BTX: Benzene, toluene and xylene
CTL: Coal to liquid
DME: Dimethyl ether
Drop-in fuel: Fuel that could be used directly in the EU transportation sector, without blending (in reality it will always be mixed to a certain extend due to a smaller production scale)
EUR_{2004}: Euro valuation in 2004
FTS: Fischer-Tropsch synthesis
Fuel blend: Fuel that cannot be directly used in the transportation sector in the EU. However, it can be mixed with common fuels. For example 5% ethanol in gasoline as E5
GHG: Greenhouse gas
GJ: Giga Joule
GTL: Gas to liquid
HAS: Higher alcohol synthesis
HC: Hydrocarbons
HDS: Hydrodesulphurization
HHV: Higher heating value
LHV: Lower heating value
LPG: Liquefied petroleum gas
MeOH: Methanol
MTG: Methanol-to-gasoline
MWh: Megawatt hour
O&M: Operation and maintenance
SNG: Synthetic natural gas
Syngas: Synthesis gas
TCI: Total capital investment
TRL: Technology Readiness Level
USD: US dollar
WGS: Water-gas shift

Conversions:
1 EUR = 1.20 USD
1 MWh = 3.6 GJ

1. Introduction

1.1 Why produce renewable liquid fuels?

The incentive for producing liquid fuels from biomass are both environmental and political. In the 2015 Paris agreement, it has been decided that global warming should be limited to a max. 2°C increase compared to pre-industrial temperatures. GHG emissions should therefore be lowered substantially by a switch from energy production via fossil fuel towards renewable fuels. Benefits of advanced liquid fuels produced via biomass gasification and catalytic synthesis include:

1. Low overall GHG emission as the CO_2-emissions after combustion are compensated by CO_2 consumption during growth of biomass. Even negative emissions can be obtained.
2. No competition with food/crops production.
3. High energy density of the fuels.
4. A high quality Sulphur-free fuel is produced.
5. Straightforward implementation as transportation fuel in current combustion engines. Liquid fuels can be produced and refined such that they match the properties of conventional diesel and gasoline. The infrastructure for distribution is already in place (gasoline stations).

In Figure 1, the CO_2 emissions per sector are presented. It clearly shows the major contribution of the transport sector in overall emissions. Interestingly, where the CO_2 emission for most sectors decreases, the prognosis for the transport sector remains constant. As overall energy demand in the world increases, part of the energy production is replaced by renewable resources. Especially in the electricity production sector, steady capacity increase by solar panels and wind mills affects current and projected GHG emissions positively. However, in the transportation sector, most delivered energy comes from, in decreasing order, gasoline, diesel, jet fuel, natural gas, other liquids and electricity (see Figure 2). The energy transition from fossil fuels to renewable fuels is found more difficult. Although the replacement of classic petrol cars to battery powered vehicles is promising, its total impact is small assuming the electricity required to charge the batteries is produced from fossil fuels. Bloomberg predicts that battery powered cars will be as cheap as gasoline powered cars by 2025, which leads to higher number of electric vehicles sold by 2038 [1]. However, no such substitute is available or implemented for heavier transportation vehicles that still heavily depends on fossil fuel, e.g. diesel in trucks and kerosene in aviation.

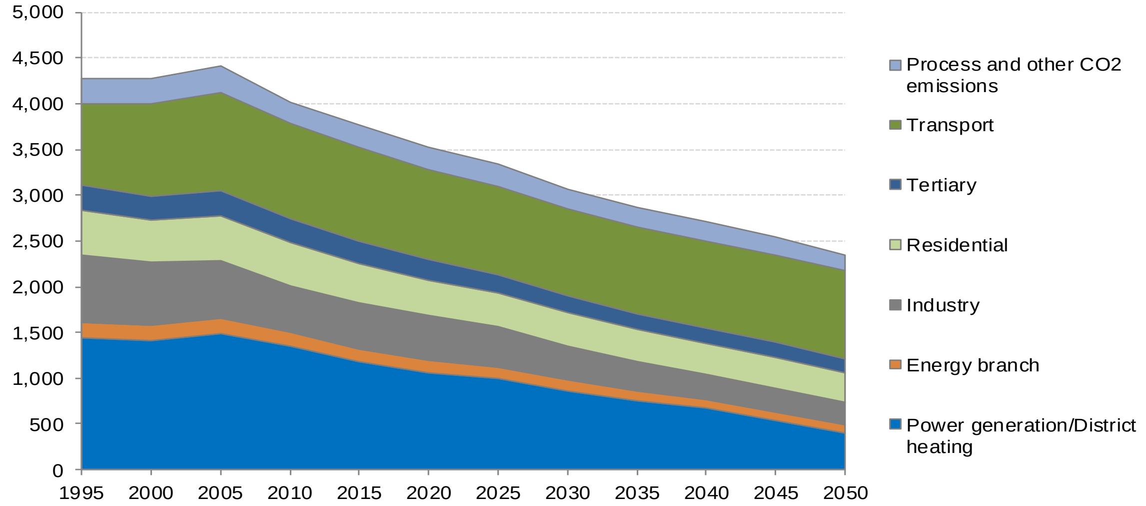


Figure 1: Prognoses of the CO_2 emissions (Mt) development by sector in the EU until 2050 [2].

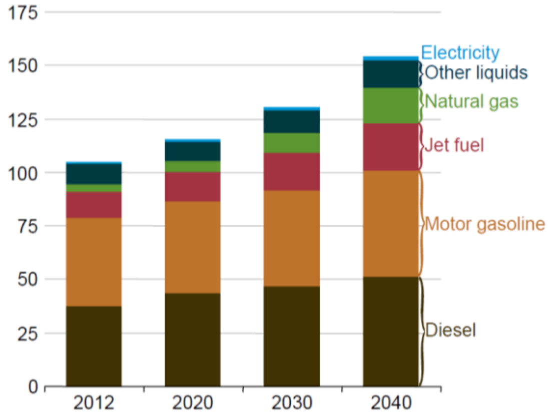


Figure 2: World transportation sector energy consumption by fuel (quadrillion Btu); projection 2012-2040 by the US Energy Information Administration (EIA) [3].

In 2009, the European Commission's Renewable Energy Directive was issued [4] in order to set national targets for the share of renewable energy in the final energy use of each EU country. That target was set at 20% renewable energy share in the EU by 2020 with a 10% target for liquid transportation fuels. This commission was revised in 2015 following concerns about the impact of indirect land use on GHG emissions savings. These revisions include a cap on the conventional biofuels contribution from crops for food or feed to national renewable energy targets in 2020, and a voluntary subtarget for advanced biofuels. The new target suggests [5]:

- The contribution of biofuels and bio-liquids from food and feed crops will be up to 7% of the energy consumption in road and rail transport by 2020. By 2030 this will be reduced to 3.8%.
- The use of baking and frying oil, animal fats and molasses may amount up to 1.7% in the calculation of the percentage sustainable energy in the transport sector.
- Fuel delivered to aircraft or seagoing ships is accounted 1.2 times, and thus receives a 20% bonus.
- The proportion of sustainable fuels (excluding starch crops) should rise from at least 1.5% in 2021 to 6.8% by 2030. In this definition sustainable fuels are: advanced biofuels and other biofuels and biogas produced from non-food feedstock (waste excluding baking and frying oil, animal fats and molasses). The percentages aforementioned are mandatory for fuel suppliers.
- Within this total share, the contribution of advanced biofuels and biogas produced from non-edible feedstock (waste excluding baking and frying oil, animal fats and molasses) shall be at least 0.5% in 2021 and should increase to at least 3.6% by 2030. These percentages are mandatory for fuel suppliers.

All the above reasons constitute global drivers for advanced biofuels production. Their production might be costly, but when the technology is developed and proven, it is the best alternative for replacing fossil fuels in transportation. Along with technological innovation, policies and business models are needed to bridge the way, ensuring that plants continue to be built and production costs continue to decline.

1.2 Definition of advanced biofuels

The term 'Biofuel' refers to all liquid and gaseous transportation fuels produced from biomass, such as biodegradable agricultural and forestry products and residues, or biodegradable industrial and municipal waste. Biofuels can be classified differently according to a number of key characteristics, such as feedstock type, conversion process, GHG emissions and technical specification of the feedstock. Biofuels are commonly divided into 'first-, second- and third-generation', but also into 'conventional' and 'advanced' biofuels.

Conventional biofuel technologies include well-established processes that are already producing biofuels on a commercial scale. These biofuels, commonly referred to as first-generation, include bioethanol obtained by microbial fermentation of sugar- or starch-based crops, biodiesel produced by transesterification, where lipids (oils and fats) are reacted with alcohols (ethanol or methanol), as well as biogas derived through anaerobic digestion [6]. Typical feedstocks used in these processes include food or animal feed crops, such as sugarcane, starch, corn and wheat, soybean and oil palm, and in some cases animal fats and used cooking oils.

Advanced biofuel technologies are conversion technologies which are still in the research and development (R&D), pilot or demonstration phase, commonly referred to as second-generation. Typical feedstocks used in these processes are non-food crops, agricultural and forest residues and other waste materials. A key characteristic is that these feedstocks cannot be used for food [6]. This category also includes novel technologies that are mainly in the R&D and pilot stage, referred to as third-generation, such as algae-based biofuels and the conversion of sugar into diesel-type biofuels using biological or chemical catalysts.

The main pathways for advanced biofuels production can be classified into biochemical, thermochemical and chemical technologies. Biochemical technologies are usually based on lignocellulosic feedstock which is pretreated, hydrolyzed into sugars and then fermented to ethanol. Most thermochemical technologies use gasification to convert lignocellulosic feedstock into synthesis gas, which can be converted into Methanol, FT-Diesel, SNG, DME or mixed alcohols. Alternative thermochemical pathways include pyrolysis of biomass and upgrading of the resulting pyrolysis oil. The most successful chemical pathway is the hydro-treatment of vegetable oil or fats to produce diesel-type hydrocarbons [6]. Figure 3 shows an overview of the available conversion technologies from biomass to biofuels including gasification with consecutive catalytic conversion, anaerobic digestion, pyrolysis and esterification of bio oils. This report will be focused on the thermochemical biomass conversion, via gasification, for the production of 'advanced biofuels' and specifically FT hydrocarbons and oxygenated products (Methanol, DME and higher alcohols).

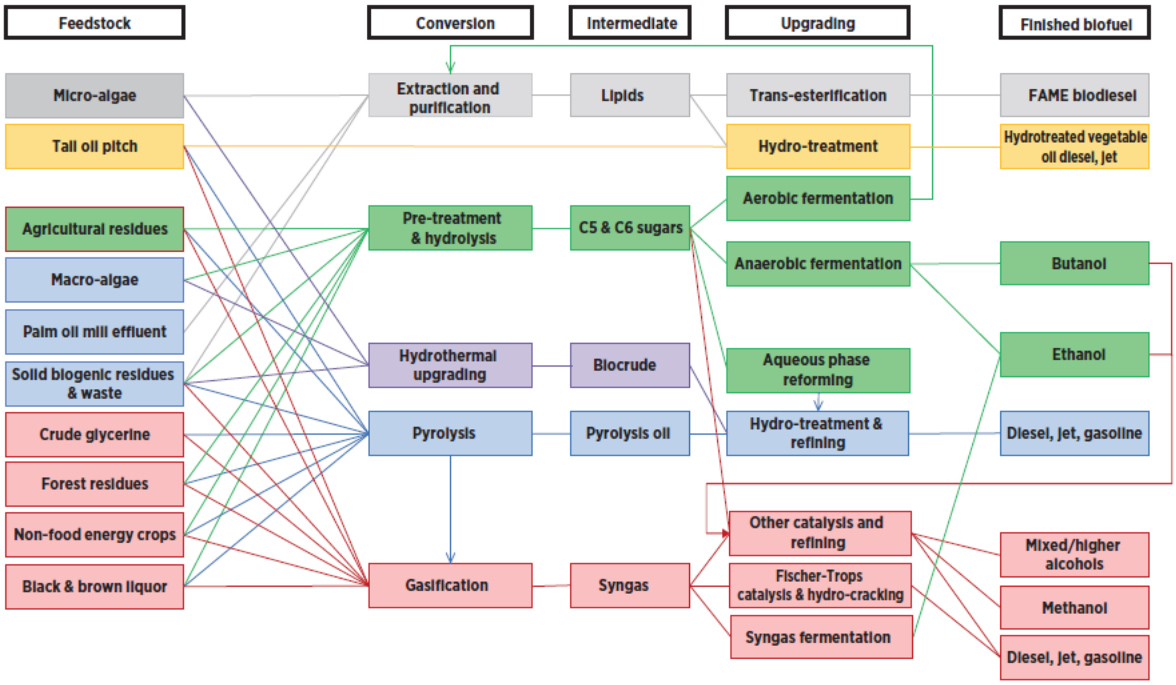


Figure 3: Overview of conversion technologies from biomass to biofuels [7].

Liquid biofuels may be used in road and rail, substituting gasoline and diesel. In shipping and aviation they replace diesel, bunker and jet fuels. Fuels used in all transport sectors are required to meet national or international standards. Advanced biofuels may therefore be blended with conventional fossil fuels according to their properties. Most liquid biofuels are expected to be blended with fossil fuels at different points in the distribution chain depending on their type and require zero to minor engine modifications.

1.3 Bio-syngas production via gasification

Gasification converts biomass into a gaseous mixture of bio-syngas consisting mainly of hydrogen, carbon monoxide, carbon dioxide, methane and other hydrocarbons, as well as impurities such as tars, NH_3, HCl and H_2S which are highly depending on the source of biomass. There are many technologies available for syngas production, some of them are presented in Figure 4. Biomass gasifiers can be classified as air-blown, oxygen-blown or steam-blown, as atmospheric or pressurized, as fixed bed, fluidized bed or entrained flow, and as allothermal (indirect heating) or autothermal (direct heating by combustion of part of the feedstock). Gasification takes place in the presence of a gasification agent that can be air, oxygen, steam, CO_2 or combination of some of them. The operating conditions (pressure, temperature) greatly influence the economy of both gasifier and downstream equipment, e.g. due to the different product gas compositions. Some gasifiers, used for biomass gasification, are briefly discussed below.

Fixed Bed gasifiers can be separated in updraft and downdraft gasifiers. Both gasifiers are operated in 'dry' mode, which means that the ash in the gasifiers is not usually in a molten state. This is achieved by keeping the operating temperature below the melting temperature of the ash. Both gasifiers use air as gasification agent.

In the *Entrained Flow gasifier* the biomass is injected in co-current flow with the oxidant (usually oxygen). The residence time of an entrained flow gasifier is on the order of seconds or tens of seconds. Because of the short residence time, entrained flow gasifiers must operate at high temperatures (1000-1300°C) to achieve high carbon conversion. The feedstock in an entrained flow gasifier is typically fed pneumatically and needs to be in very fine form. Biomass pre-treatment, e.g. torrefaction, is required to require the right feedstock properties.

Fluidized bed gasifiers can be divided into three main categories: Bubbling Fluidized Bed (BFB), Circulating Fluidized Bed (CFB) and Indirect or Allothermal twin bed gasifier. All Fluidized bed gasifiers use a bed material (sand, ash from the fuel or catalytically active bed material) in order to distribute and transport the heat in the gasifier. The CFB gasifier (shown in Figure 4), is used for high gas velocities (between 3 and 10 m/s), where the bed material gets entrained and a circulation of the material is required. In this gasifier, biomass and oxygen are fed separately into the fluidized circulating bed that contains a bed material such as sand for proper fluidization. The typical gasification temperature is 850-950°C.

Separating the gasification of the biomass and the combustion of char, leads to the Allothermal or *Indirect gasification.* An example of an indirect biomass gasifier is MILENA, developed at ECN. It operates based on indirect gasification with a combustion and a gasification zone in a refractory lined reactor vessel. Heat required for the endothermic gasification is produced in the combustion zone. Gasification is normally operated at a relatively low temperature of 700-850°C. Gasification of biomass takes place in the presence of steam, which is used as fluidization medium into the CFB riser. In the riser it mixes with the fluidization material/bed material (e.g. sand) at a velocity between 3 and 10 m s^{-1}. The char that is left after gasification of the biomass flows, together with the bed material, into the combustor section where complete combustion to flue gas (and white ash) takes place in the presence of air. Hence, a high carbon conversion up to 100% can be obtained. As the combustor and gasification are separated, the flue gas and producer gas are separated i.e. minimum nitrogen dilution in the producer gas. Moreover, no air separation unit is required as air is used for combustion in the combustion zone.

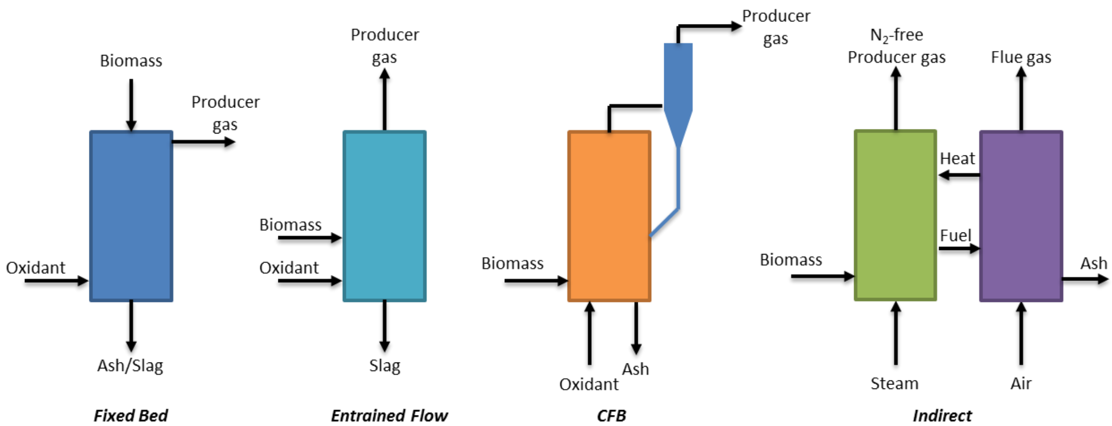


Figure 4: Schematic representation of a fixed bed, an entrained flow (EF), a circulating fluidized bed (CFB) and an indirect gasifier (e.g. MILENA).

In Table 1 some typical gas compositions are reported for different biomass gasifiers (Indirect MILENA, CFB, BFB and EF Shell). Producer gas from the MILENA and the CFB gasifier contains a lot of methane, hydrocarbons and tar due to the low temperature of operation. Clearly, indirect gasification technologies is especially suitable for SNG production, because the producer gas contains already much methane. On the other hand, due to the specific conditions in MILENA much of the energy in the product gas is contained as chemical energy in the form of hydrocarbons (C2+, BTX and tar). For liquid fuels synthesis (such as Methanol and FTS) the presence of large quantities of hydrocarbons is unwanted, because mainly H_2 and CO are converted into the desired product. Also hydrocarbons have negative effects on the downstream catalytic process due to the risk of deactivation. Impurities such as, HCl, NH_3 and H_2S are not included in the table due to the lack of information, but these are more dependent on the feedstock than the gasifier type. Overall S/N levels in woody biomass are low. For instance beech wood contains up to 0.4 wt% nitrogen and up to 0.04 wt.% sulphur [8].

Table 1: Typical syngas compositions from different gasifiers using woody biomass as feedstock.

	Indirect (*MILENA*)	**CFB**	**IGT BFB**	**EF (*Shell*)**
Feed	woody biomass	woody biomass	biomass	biomass
Gasification medium	Steam	O_2/steam	O_2/H_2O	O_2/H_2O
T (°C)	700-850	700-850	982	1085
P (bar)	1	1	34	24.3
Moisture (vol%)	25	35-50	31.8	18.4
	Dry basis:	Dry basis:	Dry basis:	Dry basis:
CO (vol%)	32.8	28.0	21.9	47.8
H_2 (vol%)	26.3	23.0	30.3	37.6
CO_2 (vol%)	16.4	28.2	36.4	14.5
N_2 (vol%)	1.6	2.24	0.61	n.d.
Ar (vol%)	0.066	4.82	n.d.	n.d.
CH_4 (vol%)	14.8	9.11	12.5	0.1
C_2H_4 (vol%)	4.8	3.08	C_{2+}=0.3	C_{2+}=0
C_2H_6 (vol%)	0.33	0.25	-	-
C_2H_2 (vol%)	0.33	0.16	-	-
benzene (ppmV)	11,490	6813	-	-
toluene (ppmV)	1,641	710	-	-
SPA tars (ppmV)	4000-10,000	4114	-	-
H_2/CO	1.25	0.82	1.39	0.79
Reference	--	[9]	[10]	[11]

Impurities in bio-syngas

Diversity of biomass feedstocks in combination with partial gasification leads to contaminants in syngas, which are mainly classified as tars, particulate matter (PM), alkali, nitrogen (NH_3, HCN), sulphur (H_2S, COS), halides and trace elements. Tars are a mixture of a variety of aromatic hydrocarbons such benzene, poly-aromatic hydrocarbons such as naphthalene and hydroxyl aromatics. Often they are classified according to their dew point, which is the temperature at which the real total partial pressure of tar equals the saturation pressure of tar. Tar and other impurities are responsible for downstream problems in the gasifier such as corrosion, clogging, equipment fouling and catalyst deactivation. They also render syngas unsuitable for bio-methanol production, FT synthesis, fuel cells and other applications. Syngas specification for the CO hydrogenation reactions to methanol and higher alcohols and the Fischer-Tropsch synthesis are shown in Table 2.

Table 2: Synthesis gas specification for the CO hydrogenation reactions to oxygenates and Fischer-Tropsch synthesis [12]

Impurity	**Oxygenates synthesis**	**Fischer-Tropsch synthesis**
Tars	< 0.1 mg/Nm^3	< 0.1 mg/Nm^3
Sulphur species (H_2S, COS)	H_2S: 0.1ppmv-60ppb and100 ppmv (MoS_2–based)COS: < 9ppm	0.2 ppm, 1 ppmv, 60 ppb
Halogen species (Cl, Br, F)	1 ppb	10 ppb
HCN	10 ppb	10 ppb
NH_3	10 ppm	10 ppm
As, Se, Hg	ppb levels	ppb levels

The nature of the catalytic material obviously affects the maximum acceptable concentration of impurities in syngas. The above-listed impurity concentrations refer to general limits reported in literature for oxygenates (mainly alcohols) and FT synthesis. In general, tar content should be limited below 0.1 mg/Nm^3 for all catalysts. Regarding the H_2S concentration, the specification ranges between 60 ppb and 0.1 ppmv (depending on the reference) for the Methanol and Fischer-Tropsch catalysts, respectively. Sulfide-based catalysts, such as MoS_2, do not have the strict sulphur clean up requirements of the other catalysts. In fact, these materials may require relatively high levels of sulphur (100 ppmv) in the syngas in order to operate more efficiently. The limitting HCl content, is more severe than for H_2S and is below 1 ppb for Methanol and less than 10 ppb for FT catalysts. The referenced nitrogen-species levels reported are 10 ppmv for NH_3, 0.1 ppmv for NOx and 10 ppb for HCN. Heavy metals (As, Se, Hg) must be removed to parts per billion (ppb) levels prior to the synthesis reactor to prevent catalyst poisoning. It is proven that alkali metals increase the production of higher alcohols, thus unless this is the desired product, removal might be necessary in order to maximize selectivity. Other catalyst poisons that need to be avoided are metal carbonyls, particularly Ni and Fe carbonyls as they affect the selectivity of the catalysts. Metal carbonyl concentrations should be kept below 5 ppb. Finally, poisons to be avoided are As and P [12].

1.4 Catalytic conversion of bio-syngas

Gasification of biomass, followed by catalytic conversion of synthesis gas can lead to the production of various liquid fuels and/or chemicals. Figure 5 shows the most important chemicals produced via metal-catalysed reactions of syngas. Depending on the reaction conditions, water and CO_2 are produced as typically by-products. Examples include formation of MeOH and higher alcohols formed over Cu-Zn catalysts and the Fischer-Tropsch synthesis (FT or FTS) in which saturated/unsaturated higher (liquid) hydrocarbons can be obtained in presence of Fe or Co catalysts. The hydrocarbon FT product, which is mostly liquid, can be processed into fuels such as gasoline and diesel. Integration of the Fischer-Tropsch synthesis with syngas from renewable resources (bio-syngas) has attracted much attention in the last decades [13]. Such process is referred to as (amongst others) biomass to liquid via Fischer Tropsch synthesis (BtL-FT).

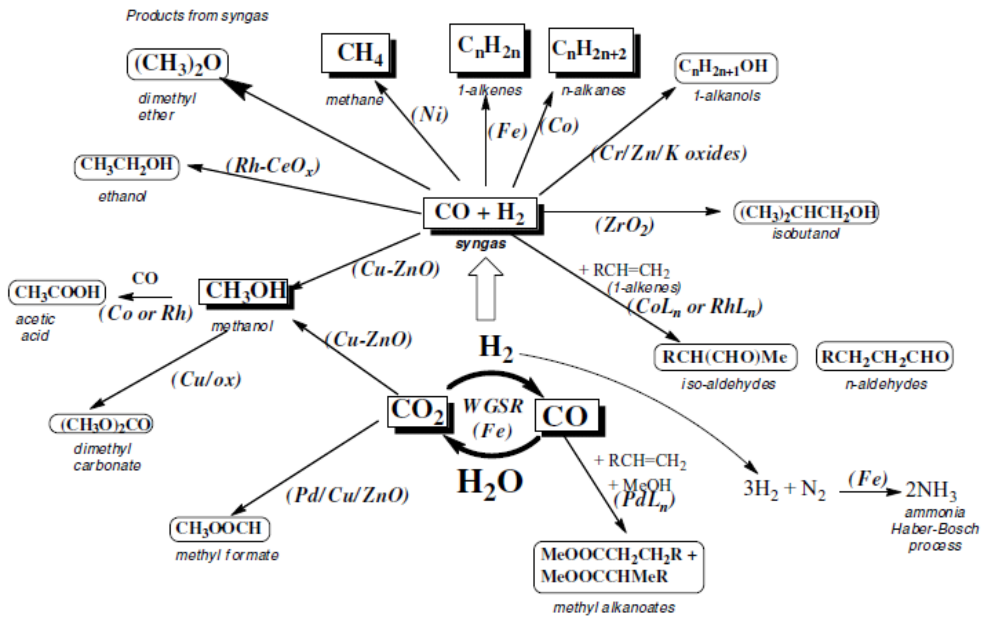


Figure 5: Syngas conversion to higher-value products via metal-catalysed reactions [14].

In addition to methanol and FTS, there are many other industrially important catalytic processes for which syngas provides the basic feedstock. These include the manufacture of dimethyl ether, higher alcohols, dialkyl carbonates, formic acid, formates, aldehydes and hydrogen gas production. Many of these reactions take place only over heterogeneous catalysts, but some are best conducted in solution under homogeneous conditions. The latter include the hydroformylation of alkenes to aldehydes and alcohols, the acetic acid syntheses, and the formation of alkanoates. The WGS reaction can be conducted either homogeneously or heterogeneously, though the latter is practiced in conjunction with the methanol and the FT synthesis plants.

1.5 This report

The aim of this report is to evaluate and recommend the most viable route for the production of advanced biofuels from bio-syngas (via thermochemical conversion). This report will mainly address the catalytic conversion of syngas towards liquid hydrocarbons (via Fischer-Tropsch synthesis) and oxygenates (mainly Methanol, DME and higher alcohols). An extensive literature review on the technological status of the different processes will be presented, including background, history and fundamentals of the syngas conversion steps to liquid fuels and chemicals (Chapters 2-5). An overview of commercial syngas conversion routes (from fossil feedstocks), pilot- and demo-scale routes (via biomass gasification) and some of the latest academic innovations/progress will be included with emphasis on liquid fuels. Finally, a short literature review on published techno economic evaluations is presented in Chapter 6 for Fischer-Tropsch, Methanol, DME and Gasoline (MTG) synthesis integrated with biomass gasification.

2. Fischer-Tropsch synthesis

2.1 Background and chemistry

The Fischer-Tropsch synthesis is named after Prof. Franz Fischer and Dr. Hans Tropsch who reported on the preparation of hydrocarbons over an iron catalyst around 1924 [15, 16]. Hence, the reaction became affiliated with their names. In 1902, Sabatier and Sendersen reported on the formation of methane from CO and hydrogen in the presence of Ni and Co catalysts [17]. Moreover, in 1913 BASF already patented a process for the production of a liquid oil from synthesis gas over Co and Os catalysts. The first commercial plants running Fischer-Tropsch synthesis (FTS) were commissioned in Germany around 1936. At that time, much liquid fuel was desired to power vehicles in WWII. At peak production in 1944, 700,000 t/a was produced in 9 plants using a SiO_2-supported cobalt catalyst. A limited excess to crude oil drove the implementation of the FT process. Coal was an abundant raw material in Germany and the syngas from coal gas could be used as feed in the FT synthesis. This relation between crude oil availability and FT synthesis is still valid today. For example, Sasol in South Africa had limited excess to crude oil in the 1950s and therefore used coal gasification combined with Fischer-Tropsch to obtain liquid fuels to maintain a stable economy. More recently, renewable fuels are being developed that are produced via biomass gasification in combination with FTS to provide an alternative to fossil fuel. Biomass derived fuels are considered (nearly) carbon neutral as the carbon dioxide that is emitted during combustion will eventually be converted back into biomass via photosynthesis. In addition, FT fuels contain almost no sulphur and give lower NO_x emissions compared to conventional fuel [18].

In the Fischer-Tropsch synthesis, a mixture of $H_2$and CO react in the presence of a transition metal catalyst. The mixture of H_2 and CO is called synthesis gas or syngas. The transition metals Fe, Co, Ni, Ru, Rh and Os catalyze the FT synthesis [19]. The Fischer-Tropsch reaction provides mainly linear hydrocarbons with a carbon number of C_1 to C_{20+}. A H_2/CO ratio of around 2 is required for the FT reaction, which is described by the following reaction:

$$n\,CO + (2n+1)\,H_2 \rightarrow C_nH_{2n+2} + n\,H_2O \qquad \text{FT alkanes } (\Delta H/n = -154.1 \text{ kJ/mol})$$

Other products include olefins- and oxygen-containing compounds (oxygenates) via respectively the following reactions:

$n\,CO + 2n\,H_2 \rightarrow C_nH_{2n} + n\,H_2O$ FT alkenes

$n\,CO + 2n\,H_2 \rightarrow C_nH_{2n+1}OH + (n\text{-}1)\,H_2O$ FT alcohols (oxygenates) ($\Delta H/n = -147.0$ kJ/mol)

Water is the main by-product in FT synthesis and this inhibits the activity of the catalyst, therefore high conversions per pass cannot be achieved and a high recycle of syngas is required to get a reasonable conversion. The product distribution depends mainly on the process temperature and used catalyst. Fischer-Tropsch reactions are performed in 2 temperature regimes, the so-called High Temperature Fischer Tropsch (HTFT) operating in the range of 320-360°C and the Low Temperature Fischer Tropsch (LTFT) between 170 and 270°C. Fe catalysts, with metallic iron and iron carbide as active phase, are typically used in HTFT processes and Co is mostly used as catalyst in LTFT. Applying Co as catalyst in the HTFT regime leads to much methane formation, which is considered a by-product in FTS. Purification of the syngas feed is vital for prolonged activity (over months on stream), as the catalyst is sensitive to impurities such as sulphur-containing compounds. Especially when the syngas source contains a broad chemical composition (much S, N, O) as from coal or biomass gasification, extensive purification of syngas is required. FT catalysts typically have a low tolerance to S, N and halogen impurities in the syngas as reported in Table 2. Syngas is mostly obtained from natural gas via steam reforming or autothermal reforming in presence of O_2 or O_2/CO_2. For steam reforming, the reaction equation is as follows:

$CH_4 + H_2O \rightarrow 3\,H_2 + CO$ Steam Reforming ($\Delta H = 205.8$ kJ/mol)

Alternatively, syngas can be obtained from coal or biomass gasification in the presence of O_2/CO_2 or water. The obtained H_2/CO ratios are highly dependent on the feedstock and the type of reforming and varies typically in the range of 1 to 3. This ratio is also affected by the water gas shift reaction (WGS), an equilibrium reaction between CO and H_2O forming H_2 and CO_2:

$CO + H_2O \leftrightarrows H_2 + CO_2$ Water Gas Shift ($\Delta H = -41.0$ kJ/mol)

This reaction is catalysed by either Fe_2O_3 (310-450°C) or CuO (low T). The overall H_2/CO consumption in the FT reactor is the usage ratio and is slightly lower in Fe-catalysed reaction due to the WGS. When the usage ratio is fed into the reactor, the product H_2/CO ratio will not have changed. Fe-catalysed reactions have a H_2/CO usage ratio of approx. 1.7 whereas Co-catalysed systems have a usage ratio of 2.1, which is basically the stoichiometric value.

2.1.1 Fischer-Tropsch reaction conditions

In industry, the FT synthesis is applied using several technologies based on catalyst, temperature regime and reactor type. The mostly used and therefore most relevant are:

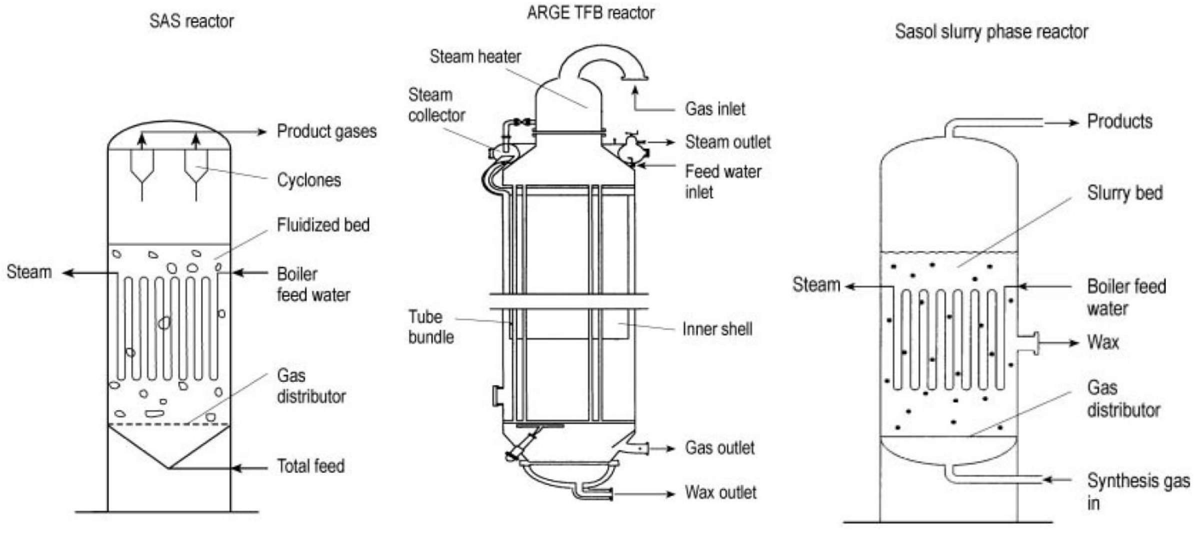
Fe-based HTFT in a fixed or circulating fluidized bed reactor
Co-based LTFT in a tubular fixed bed (TFB) reactor
Co-based LTFT in a slurry phase reactor (SPR)

Fe-HTFT – Fluidized bed

Sasol applies a reactor called the Sasol Advanced Synthol reactor (SAS), which is operated between 330 and 350°C at approximately 25 bar (see Figure 6) [20]. In this reactor, syngas is bubbled from the bottom of the reactor through the catalyst bed, thereby fluidizing the bed, and the product gas (syncrude) leaves the reactor at the top. In FTS operation at this high temperature produces hydrocarbon products with a lower carbon number compared to LTFT conditions. The product remains completely in the gas phase, because of the lower average boiling point of the products and the high reactor temperature [21]. As liquid products should be avoided in this fluidized catalyst system, this type of reactor can only be used in HTFT reactions. The catalysts particles, either precipitated or fused iron, are usually around 100 µm in diameter. In the reactor, internal cyclones prevent the solid particles from escaping along with the product gas. As the FT reaction is highly exothermic, cooling coils in the reactor produce steam from water.

In the early stages of Sasol's FT process development, from 1955 to 2000 the circulating fluidized bed (CFB) reactor was used, but this reactor has been replaced completely by the SAS reactor [22]. It was replaced by the SAS reactor, because the SAS reactor is easier to operate and therefore has lower operating costs, and it can run at higher conversion levels with higher gas loads. At the PetroSA Mossel Bay site in South Africa, the CFB reactor is still being used, however a transition to Co-LTFT is taking place replacing the Fe-HTFT and therefore the CFB reactors [23]. An overview of the different reactors used in industry can be found in Figure 6, excluding the CFB reactor. For Fe-HTFT processes, no exact numbers could be found on the CO conversion per pass, however conversion levels are normally kept low (<50% CO conv.) as the Fe catalyst's activity is highly affected by water.

Fe-HTFT	**Co-LTFT**	**Co-LTFT**
Fluidized Bed Reactor	Tubular Fixed Bed Reactor	Slurry Phase Reactor



T = 320-360°C	T = 170-270°C	T = 170-270°C
P = 25 bar	P = 20-25 bar	P = 20-25 bar
<50% conv. per pass	30-35% conv. per pass*	55-65% conv. per pass*
Catalyst: 50–200 µm	Catalyst: 1-3 mm pellets	Catalyst: 50–200 µm
α = 0.7-0.8	α = 0.8-0.9	α = 0.8-0.9

Figure 6: FTS reactor technology in industry. Generally Co is used in LTFT processes, however at Sasol I in Sasolburg Fe-LTFT is (still) applied. *Based on open literature and patents for Co-LTFT [36].

Co-LTFT – Fixed bed

The second type of technology involves the Co-LTFT in a tubular fixed bed reactor (TFB) shown in Figure 6. This type of reactor has been primarily developed and applied by Shell. Industrially applied reactors of 7-8 m in diameter holds many thousands of tubes containing the catalyst bed. Millimetre sized catalyst particles, typically cobalt supported by silica or alumina, are used to prevent major pressure drops. Cooling water flows around the tubes to cool the reaction mixture producing steam. Syngas flows through the catalyst bed from top to bottom to form gas and liquid products. The liquid product is collected and the gaseous product is passed through a condensation unit for separation. A first condensate contains the hot condensate (or oil). Then in a second condensation step, both water and a cold condensate are collected and can be separated through phase separation. The remaining tail gas contains syngas and light hydrocarbons. C_{3+} hydrocarbons can be separated through pressure distillation, but cryogenic separation is required to separate syngas from methane, ethane and ethene (if desired).

Co-LTFT – Slurry reactor

Co-LTFT synthesis can also be run in a slurry phase reactor, see Figure 6. This reactor is also referred to as a slurry bubble column reactor (SBCR) or slurry phase distillate (SPD, Sasol). In this reactor, the synthesis gas is fed from the bottom of the reactor, where it bubbles through a slurry of catalyst and liquid product to the top where the product gas is collected. The product gas contains the light hydrocarbons (naphtha), water and unreacted syngas. The liquid product in the reactor, containing product waxes and the catalyst, is continuously collected and separated from the catalyst. This separation can be done via e.g. filtration in the slurry bed reactor or downstream. An additional advantage of this system is that spent catalyst can be replaced by fresh catalyst when this is required. Much smaller catalyst particles can be used as compared to the TFB reactor as pressure drops in the reactor are very small. By reducing the particle size, naturally a higher (active) surface area can be achieved.

In Figure 6, the typical CO conversion per pass applied in the different reactors is also included. These are kept at an intermediate level as the productivity decreases at a higher conversion and deactivation of the catalyst becomes an issue.

2.1.2 FTS activity and product distribution

The FT synthesis gives a wide range of saturated and unsaturated hydrocarbons (C_1-C_{20+}) in the product syngas, the syncrude. This product mixture can be refined/upgraded in additional processes to a variety of products. As it is a type of (surface) polymerization reaction, weight fractions F_n of each hydrocarbon (with n carbon atoms) in the FT products distribution can be described by a mathematical function, the Anderson-Schulz-Flory (ASF) equation:

$$F_n = n\,(1-\alpha)^2\,\alpha^{(n-1)}$$

Where α represents the chain growth probability and n the number of carbon atoms. The product carbon number distribution in a FT synthesis with varying α values is shown in Figure 7. In this graph, the carbon numbers are linked to the type of liquid fuel product in which they are present i.e. gasoline typically contains hydrocarbons with a carbon number between 5 and 12. Clearly, for LPG (propane/butane) an α value of around 0.5 is desired and for diesel an α value of >0.8. In practice, the product distribution can be tuned via upgrading/refining so that high α values of >0.9 are desired. This high carbon number product is then processed by e.g. hydrocracking-isomerization to obtain a medium distillate product.

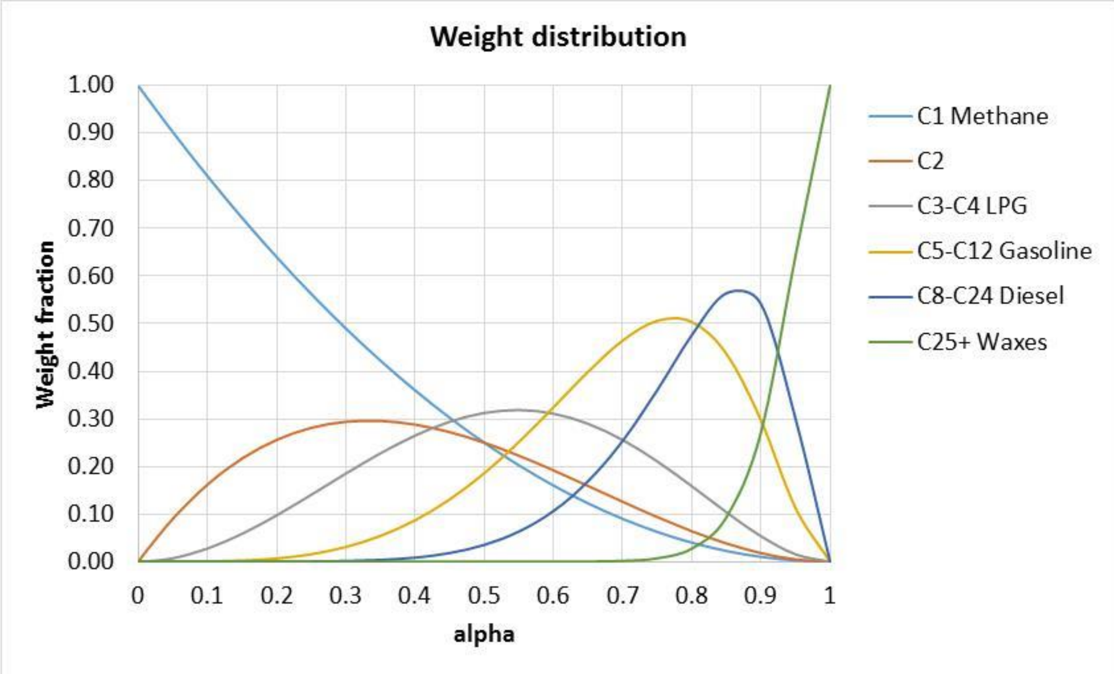


Figure 7: FTS product distribution as a function of the chain growth probability α described by the ASF model.

In the previous section, three types of reactor technologies used in FT are explained. However, for refining, only the LTFT and HTFT regimes matter. Namely, the LTFT product distributions from the TFB and SPR reactors are similar. Besides saturated hydrocarbons, FT products include olefins, oxygenates and aromatics. In Table 3, the syncrude composition for FTS at different conditions is listed. For comparison, data from two sources is included [24, 25]:

Table 3: Product distribution in Fe-LTFT, Co-LTFT and Fe-HTFT.

Product, % wt	Fe-LTFT	Co-LTFT	*Co-LTFT [25]*	Fe-HTFT	*Fe-HTFT [25]*
Alkanes	70	89	*85.8*	31	*25.8*
Alkenes	22	9	*12.4*	58	*59.0*
Oxygenates	8	2	*1.8*	6	*12.0*
Aromatic	0	0	*0*	5	*3.2*

Clearly, Fe-HTFT gives significantly more olefinic and oxygen-containing product compared to Co-LTFT or Fe-LTFT. In practice, an α value of around 0.7-0.8 is obtained in Fe-HTFT processes corresponding to around 50% C_1-C_4 products [26]. As a result, a much lower boiling product is obtained that also contains more oxygen-containing and unsaturated products compared to LTFT operation. One could argue that the selectivity towards long-chain, saturated hydrocarbons is low. A consequence of the much broader product distribution is a more tedious refining process. For Co-LTFT processes an α-value of around 0.9 is obtained providing 40-45% C_{22+} [27] i.e. a much better selectivity towards long-chain saturated hydrocarbons is obtained, which is especially desired when producing e.g. diesel and high quality waxes. Comparing Co-LTFT with Fe-LTFT shows that Fe, even at LTFT produces much more unsaturated and oxygenated hydrocarbons.

Selectivity; Effect of reaction conditions
The product formed and reaction rate in FTS depends on several parameters such as temperature, feed gas composition, pressure and catalyst. At higher temperature, a higher fraction of light hydrocarbons is obtained with a higher degree of unsaturation. Also, more secondary products are formed, such as oxygenates and aromatics. As Co is a better hydrogenation catalyst CH_4 concentrations increase sharply at higher temperatures [28].

One of the first studies on the relation between hydrocarbon number and reaction conditions was done by Matsumoto et al. [29]. The effect of temperature and pressure on the a-value, was studied over a K- and Ca-promoted Fe catalyst in a slurry bed reactor. A constant α-value of around 0.7 was found for a pressure increase between 1 and 10 bar. As expected, the production of waxes decreased at high temperature (310°C vs 225-263°C). In a recent literature overview by van der Laan [30], the effect of temperature and H_2/CO partial pressure on α in FTS over commercial catalysts was presented (see Figure 8 and Figure 9). These separate studies all show similar trends, namely that α decreases at higher temperature and decreases at higher feeding H_2/CO ratios.

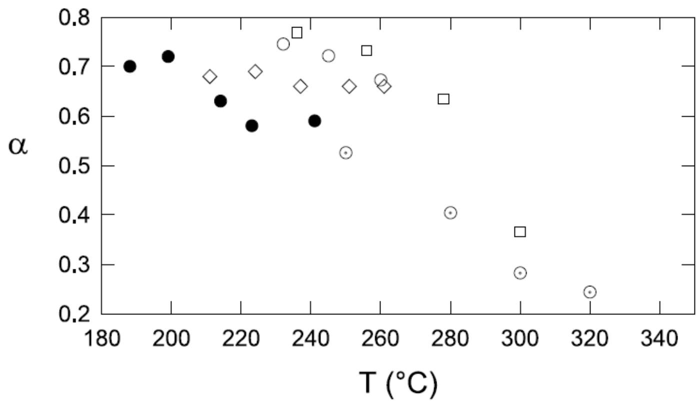


Figure 8: Chain growth probability factor α as a function of temperature, adopted from [30]. ○ : Fe/Cu/K commercial Ruhrchemie catalyst, gas-slurry system, (H_2/CO) feed= 0.7, 2.72 MPa, 0.33 10-4 Nm3 kg-1s-1; ● : Fe_2O_3 catalyst, gas-solid system, (H_2/CO) feed= 3, 0.8 MPa; ◇ : Fe_2O_3/K catalyst, gas-solid system, (H_2/CO) feed= 3, 0.8 MPa; □ : Ru catalyst, gas-solid system, (H_2/CO) feed= 3, 0.8 MPa; ⊙ : Fe/Cu/K commercial Ruhrchemie catalyst, gas-solid system, (H_2/CO) feed= 3, 2.0 MPa.

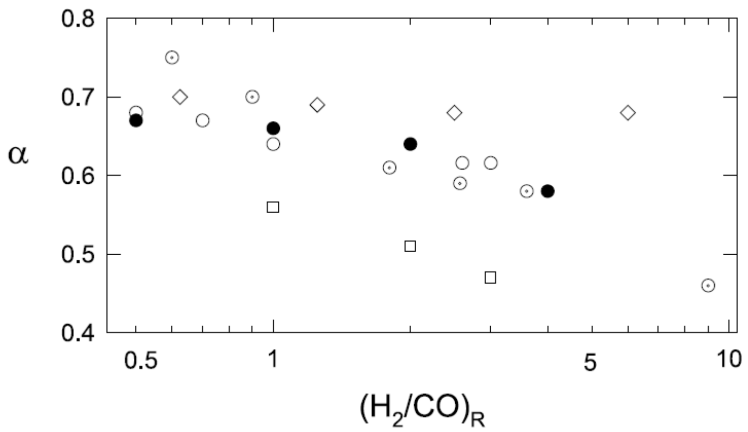


Figure 9: Chain growth probability factor α as a function of the H_2/CO ratio, adopted from [30]. ○ Fe/Cu/K catalyst, gas-slurry system, 1.48 MPa, 260°C; ● : Fe_2O_3 catalyst, 212°C , gas-solid system, 0.5 -1.2 MPa; ◇ : Fe_2O_3/K catalyst, 240°C, gas-solid system, 0.8 MPa; □: Ru catalyst, 275°C, gas-solid system, 0.8 MPa; ⊙ : Fe/Cu/K commercial Ruhrchemie catalyst, gas-solid system, 250°C, 1.0 - 2.5 MPa.

A similar relationship was found for FTS over a Co catalyst by Subiranas *et al*. In this study the H_2/CO was lowered from 3 to 1 at 230°C resulting in an increased α-value [31]. Moreover, low CO partial pressures led to much CH_4 formation. For this reason low CO concentrations are avoided. Although Co-LTFT has a H_2/CO usage ratio of 2.15 on average, in practice, a lower H_2/CO is chosen. The product gas has a ratio of 1.4-1.5, which is combined/recycled with a syngas ratio slightly below 2 resulting in an overall ratio of approx. 1.6-1.7. This is chosen to maximize C_{5+} selectivity at good activity. Fe-LTFT systems have a usage ratio of approx. 1.7 (WGS reactivity included). However, the exact H_2/CO feed composition used in practice varies strongly and depends on the water content (formed as by-product) and CO_2 concentrations in the gas phase. Gas composition, residence time and CO conversion are chosen based on the desired product range and whether or not flue gas recycling is applied.

Fe catalysts are normally promoted with alkali metals, in practice mostly K, as they can increase the chain growth probability factor and activity by increasing the basicity of the catalyst. Namely, the CO adsorption is facilitated as well as C-O bond dissociation. Co catalysts are less influenced by the addition of promoters/modifiers, although the addition of small amount of noble metals such as Ru, Re and Pt can enhance activity [28].

An overview on the effect of reaction conditions on selectivity is shown in Table 4 [32]. This summary is based on results obtained from academic and industry research.

Table 4: Selectivity control in FTS by optimization of process conditions and catalyst design, adopted from [32].

Parameter	Chain length	Chain branching	Olefin select.	Alcohol select.	Carbon deposition	Methane select.
Temperature	↓	↑	*	↓	↑	↑
Pressure	↑	↓	*	↑	*	↓
H_2/CO	↓	↑	↓	↓	↓	↑
Conversion	*	*	↓	↓	↑	↑
Space velocity	*	*	↑	↑	*	↓
Alkali content iron catalyst	↑	↓	↑	↑	↑	↓

Increase with increasing parameter: ↑
Decrease with increasing parameter: ↓
Complex relation: *

Reaction rate

The effect of hydrogen and carbon monoxide partial pressures on reaction rate was systematically studied by Dry et al. in 1971 [33]. They found that the rate of FTS was first order in H_2 and zero order in CO over a K-promoted Fe catalyst in a differential reactor at 240°C. The H_2/CO ratio was varied from 1 to 7. It was hypothesized that the Fe surface was saturated with CO due to its much stronger adsorption than H_2, with a zeroth order rate in CO as consequence. CO_2 formed during the reaction was almost exclusively formed via the WGS reaction, although its formation was low due to the low T of operation. Moreover, they stated that WGS equilibrium was reached at temperatures above 300°C using the Fe catalyst. The rate was determined by the production of H_2O and CO_2, no data on carbon number distribution was included.

The reaction rate as a function of the reactant partial pressures over an iron catalyst is expressed by [34]:

$$r = \frac{p_{H_2}\, p_{CO}}{p_{CO} + \, p_{H2O}}$$

For Co-catalysed FTS a similar relation was found in a separate study by Yates *et al.* [35]:

$$r = \frac{p_{H_2}\, p_{CO}}{(1 + p_{CO})^2}$$

Water has a strong negative impact on the Fe FT activity, but the influence of the CO_2 partial pressure is negligible. The rate increases with hydrogen partial pressure, especially at low CO conversion. The conversion was found independent of the overall pressure. For the Co-catalysed FTS reaction, the partial pressure of water is not included i.e. no negative rate dependence on the partial pressure of water was found. Using these relations for Fe and Co, a conversion profile was calculated for a once-through reaction at the H_2/CO usage ratios of Co- and Fe-based catalysts in a tubular fixed bed system, see Figure 10. Clearly, the effect of the increasing water concentration is apparent for Fe as conversion levels stabilize much faster. Cobalt catalysts have a clear advantage over Fe-based catalysts as high activity can be reached even at high conversion. Furthermore, a five times more active Fe catalyst is only more productive than a Co catalyst up to 50% conversion.

High conversions can be achieved also with iron, but sequential reactors are required with water knock-out or a single reactor with syngas recycling. Co-catalysed FT reactions are also run at intermediate conversion in practice, because small Co crystallites (cost related) are more easily oxidized especially at high conversion.

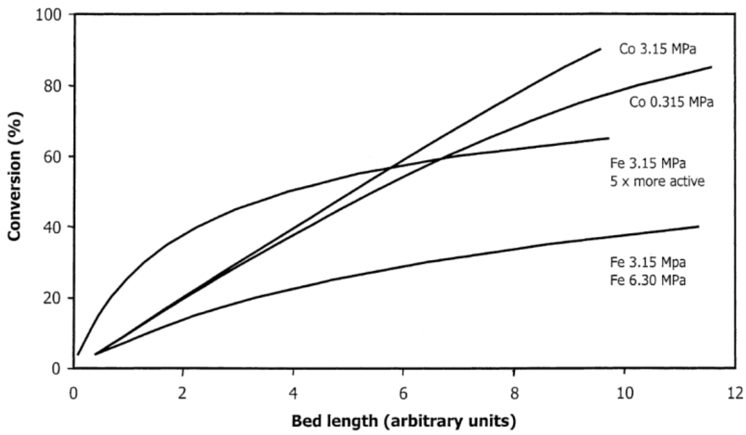


Figure 10: Conversion profiles in FTS for Co- and Fe-based catalysts, adopted from [28].

Mechanism

In industry, only Fe- or Co-based catalysts are used. During FT synthesis, Fe occurs in the carbide phase while Co remains mainly metallic [43]. Generally, Fe catalysts are promoted by alkali or S-compounds. Cobalt can be promoted by Pt, Re, Ru to enhance its reduction or by MnO to obtain larger α-values [36]. An experimental STM study by Wilson et al., showed that Co nanoparticles are converted into smaller nanoparticles under FT conditions [37]. Generally however, larger particles stabilize step-edge sites and are therefore more active than Co particles smaller than a few nanometres [38].

Although the FT reaction is almost 100 years old, the exact mechanism is still unknown as many different mechanisms are proposed. Fischer-Tropsch synthesis is a surface chain growth polymerization reaction with reaction initiation, chain growth and termination. Two main mechanisms of chain growth are described in the literature, these are the carbide mechanism [16] and the CO insertion mechanism [39] (see also Figure 11).

In the carbide mechanism, CH_x is formed via the dissociation of CO on the catalyst surface. CH_x can be considered the monomer to the polymer chain. Chain growth occurs by subsequent addition of CH_x species into the growing chain. The CH_x unit that provides the propagation, can be a CH_2 or a CH moiety. CH_2 is proposed as the inserting C1 species by Brady-Pettit [40] and Gaube [41], whereas a combined CH and CH_2 based growth is proposed by Maitlis [42].The growing chain can be alkyl, alkenyl or alkylidene in nature. After chain growth, the hydrocarbon chain is terminated and the hydrocarbon is liberated from the catalyst surface. This termination can proceed via three different scenarios. In a first scenario, CO instead of CH_x is added to the chain resulting in the formation of an aldehyde followed by liberation. A second possibility is that a hydride is abstracted from the C_nH_y alkyl at the beta carbon (a beta- hydride type elimination) leaving a metal hydride plus C_nH_{2n} alkene. Or finally, the metal-alkyl is protonated affording the saturated hydrocarbon, alkane.

In the CO insertion mechanism, a first CO dissociates to form a C1 species. Then a new CO molecule is inserted into CH_x followed by cleavage of the CO bond of the inserted CO giving the C_nH_y that can be attacked/inserted by another CO molecule. Liberation of the formed hydrocarbon can, similarly to the carbide mechanism, proceed in three different ways. These are protonation, hydride elimination or CO (+H) addition that give respectively alkenes, alkanes or aldehydes/alcohols. CO insertion mechanism is less structure sensitive than the carbide mechanism, because it’s the CO activation that is very structure sensitive and CO insertion tends to be slow so that this mechanism gives lower α values [43].

In general, the main competitive reaction to higher hydrocarbons is methane formation. General considerations are the relative rate of CH_x hydrogenation versus propagation and CO dissociation. In general, the CO dissociation should match the ‘demand’ for chain growth/propagation. CO activation relative to methane formation has to be fast so that chain propagation can occur. For instance Ni is a good methanation catalyst because the CO dissociation is very slow (high barrier) and the CHx hydrogenation rate is fast. Weak M-C bonds will also lead to much methane formation.

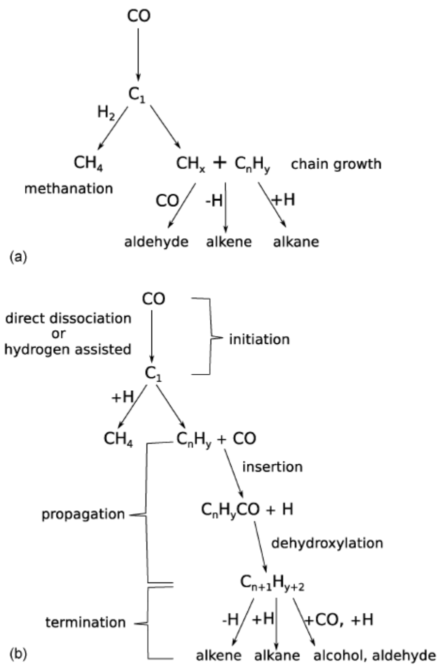


Figure 11: The carbide (a) and CO insertion (b) mechanisms, adopted from [44].

Diesel, gasoline and kerosene

In Table 5, the specifications of gasoline, kerosene and diesel are summarized. Gasoline typically is composed of saturated hydrocarbons (paraffins), olefins and aromatics [45]. Kerosene consists of mainly saturated hydrocarbons (linear, branch and cyclic) and diesel fuel consists mostly of linear saturated hydrocarbons [46].The exact compositions varies per region. Also the nomenclature depends on the region and can be confusing. Diesel is sometimes referred to as distillate or gas oil and gasoline is sometimes referred to as naphtha, but not all naphtha is gasoline depending on the octane number (RON). Clearly, much overlap exists between carbon numbers as the fractions are defined by their boiling ranges. Specific fractions with the right properties are obtained after multiple processing steps (refining) such as distillation, catalytic cracking and isomerization of crude oil.

Table 5: General properties and composition of gasoline, kerosene and diesel.

	Boiling range (°C)	Carbon number	Type of hydrocarbon
Gasoline	50-150°C	5-12	Sat. and unsat. linear/branched + aromatic
Kerosene	150-250°C	10-16	Sat. linear/branched/cyclic
Diesel	250-350°C	8-24	Sat. linear

From the FTS syncrude, without processing, the yields of ‘drop-in’ gasoline and also kerosene are basically zero as no branched hydrocarbons are formed. Only ‘drop-in’ diesel can be obtained directly via condensation or distillation of the FT syncrude with a boiling point between 200-350°C. The specifications and composition of liquid fuels in the EU are reported in Table 6. FT distillate has a cetane number higher than 70, which means it can be directly applied as FT diesel or it can be blended with conventional diesel to boost cetane numbers. But although the high cetane product can easily be blended, some blending advantages have been lost (for Shell), as crude oil diesel is also required to be free of sulphur. Traditionally, FT products would be promoted and sold as a basically sulphur-free product and overall concentrations could be lowered by blending. A

challenge for direct use of FT diesel can be its lower density. However, the EU for instance does not prescribe a minimum density (max. 845 g/L, see also Table 6).
For gasoline, a research octane number (RON) of 95 is required as minimum. This RON is a measure of the compression a fuel can take before ignition, which is important in an electrical sparked combustion engine as is the case for gasoline. It is related to the amount of branching in the hydrocarbons with n-heptane having an octane rating of 0 and iso-octane a rating of 100. FT products contain linear chains of hydrocarbons with almost no branched products. For this reason, unrefined FT naphta is not suited for direct application as gasoline. For instance, straight run Fe-HTFT naphtha has a RON of only 68 (US 1950s data). In a refinery, more branching can be obtained in the liquid product via e.g. oligomerization of light olefins over a solid acid catalyst. Also, hydrocracking-isomerization heavier FT fractions can provide a higher degree of hydrocarbon branching. Alternatively, RON numbers can be improved by addition of RON boosters. Typical RON boosters include MTBE, ETBE, isooctane and toluene. The alkene and aromatic content are less important (resp. max. 18% and 35%). FT gasoline as 'drop-in' transportation fuel is only produced in South Africa (SASOL Synfuels and PetroSA) after refining.

Table 6: Specifications of gasoline and diesel in the European Union [47].

	Gasoline	Diesel	Jet-A1 kerosene*
Combustion	RON: 95 min	Cetane: 51 min	LHV = 42.8 MJ/kg
Density (g/mL) at 20°C	0.720-0.775	0.845 max	0.775-840
Olefins (v.%)	18.0 max	N.A.	5.0 max
Aromatics (v.%)	35.0 max	Not reg.	25.0 max
Oxygen content (wt.%)	3.7 max	N.A.	N.A.
Sulphur content (ppm)	10 max	10 max	3000

N.A. Not applicable

Possible gasoline and diesel yields obtained from Fe-HTFT (FFB) and Co-LTFT (SPD) after refining are shown in Figure 12. These numbers were reported by PetroSA and are indicative as exact conditions are not included [48]. This data was published to show the Co-LTFT will result in much higher diesel yields than the more traditional Fe-HTFT process. Application of Co-LTFT conditions can yield up to 70% diesel and 25% naphtha (not gasoline grade). This yield is very high as the α-value of the Co catalyst is >0.9, which results in more than 50% C_{10+}. These long hydrocarbons are then treated in a hydrocracking-isomerization process to obtain hydrocarbons in the Diesel range. In the Fe-HTFT process, 48% of gasoline grade fuel was obtained with 39% diesel via a much more extensive (costly) refining.

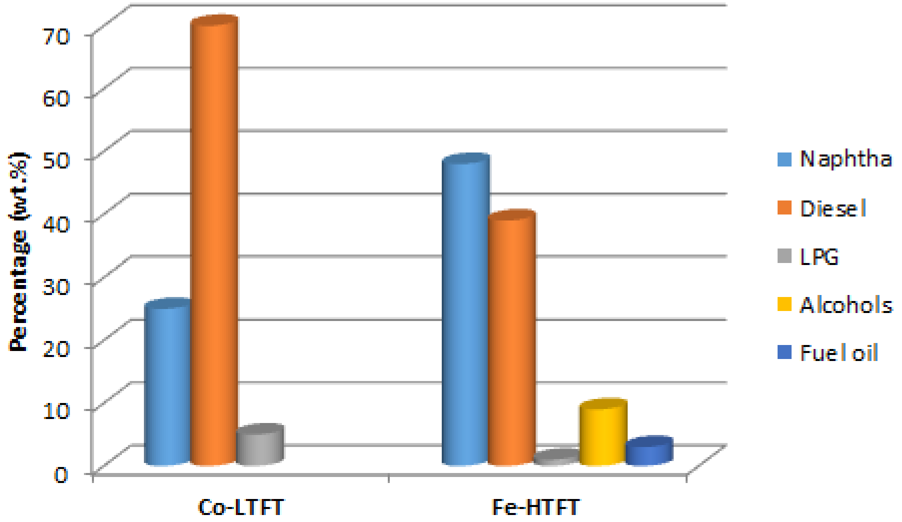


Figure 12: Realistic liquid fuel yields after FT syncrude refining from Co-LTFT and Fe-HTFT processes.

A better example that could serve as guideline for the production of liquid fuels can be found in the Shell Middle Distillate Synthesis (SMDS) process. This provides a better example as more details have been published on the FT syncrude composition and final product composition [49]. The term middle distillate already suggests that the desired products are kerosene and mostly diesel as both are part of the middle distillate by definition. In this process, a syncrude is obtained that contains 27% wax (C25+), 65% diesel/kerosene/gasoline (referred to as oil), 5% lpg and 3% C_1-C_2 in a Co-LTFT system that provides an α-value of 0.90. When the gaseous hydrocarbons are recycled to form syngas via intermediate reforming, hydrocracking-treatment of oil + wax over a metal-acid catalyst (only 1-step) can provide close to 100% **Naphtha/kerosene/distillate.** This so-called hydro processing catalyst (HPC), performs multiple tasks, namely hydrogenation of olefins, oxygen removal, hydro isomerization and hydrocracking. The final product ratio strongly depends on the cracking severity varying from **15/25/60** to **25/50/25**. Unfortunately, exact data could not be found in the literature, however, the cracking most likely takes place around medium temperature (500°C) over a zeolite with impregnated noble metal, e.g. 1% Pt/ZSM-5. More details on the SMDS can be found in section 2.2.3. In the current SMDS process part of the wax is not hydrocracked, but hydro treated to obtain high quality waxes (Sarawax).

2.2 Commercial FT processes

An overview of the currently running industrial/commercial facilities providing Fischer-Tropsch products is presented in this Section. This can be considered proven technology as most of the facilities run for more than 10 years. Two dominant players in FT technology are Shell and Sasol, with more than 50 years of experience in operating FT plants. For this reason, the Sasol and Shell production facilities will be discussed in more detail. Other companies with FT facilities are PetroSA and Chevron, however, the process technology that they use is based on the Sasol technology. At the end of the chapter an overview is presented with all currently operating FT processes. These commercial plants either run on synthesis gas from coal gasification, so-called coal to liquid (CTL) or from natural gas derived syngas, the gas to liquid processes (GTL). Details on the gasification process (formation of the FT feed) will not be discussed here. The emphasis will be on FT synthesis technology, the syncrude upgrading/refining and naturally the products that are obtained from these facilities after refining.

2.2.1 Sasol 1

The Sasol 1 site in Sasolburgh, South Africa is operational since 1956 with a production of 2,500 barrels of oil equivalent per day. Originally, two types of technology were used at Sasol 1. These were German Fe-LTFT and American Fe-HTFT technology, which syncrude fractions were partially combined in the refinery [50]. Coal gasification was used to produce the syngas. In the original refinery, stepwise condensation of syncrude was applied to obtain the different fractions. In this manner, an initial distillation is not required before refining. For Fe-HTFT the collected fractions were decanted oil, light oil separated from the aqueous layer and tail gas ($<C_4$). Oligomerization presented a key step in the refining as C_3-C_4 olefins were oligomerized over a copper-pyrophosphate (historically SPA) to produce an olefinic motor gasoline hereby improving the liquid yield. Bauxite treatment (commercial Perco process), an acidic isomerization of syncrude removed oxygenates and sulphur (in oil refineries) and at the same time improves the octane number of the gasoline fraction. Similarly, hydro treatment over clay-type catalysts was done to produce motor gasoline. Chemicals were mainly obtained from the Fe-LTFT such as waxes and combined oxygenates.

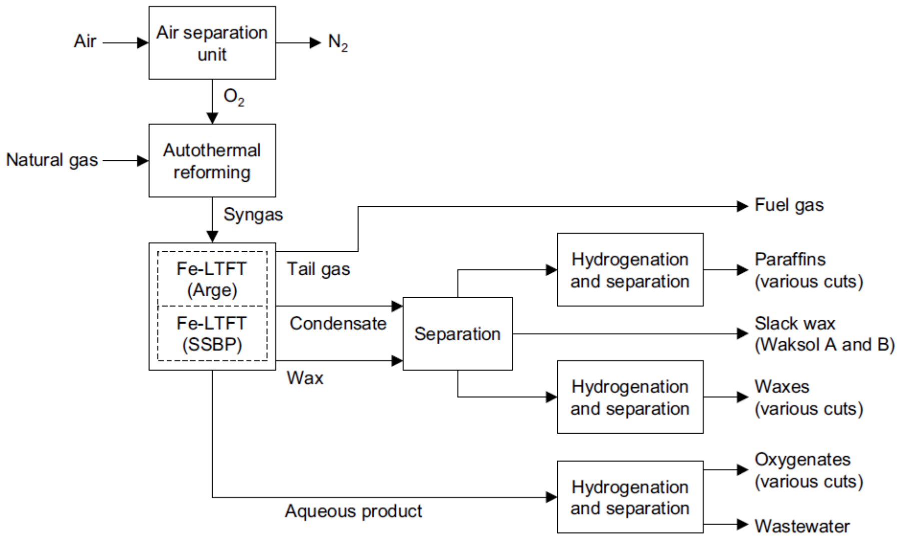


Figure 13: Sasol I GTL facility after 2004, adopted from [51].

In 2004, the Sasol I coal to liquid plant was converted into a gas to liquid (GTL) facility via connection to a natural gas pipeline. An advantage of using natural gas instead of coal is that it can be freed from sulphur before reforming which makes it much easier to process and at the same time reduces the H_2S output of the facility. Together with the switch from coal to natural gas, the Fe-HTFT was exchanged for a Fe-LTFT SPD reactor as the target product were chemicals instead of fuels. The current flow scheme is shown in Figure 13. The liquid FT product is processed into a variety of specialty waxes and the gaseous product provides pipeline gas (mostly methane). Unreacted hydrogen is used to produce ammonia that can be upgraded to fertilizer or explosives. Side-streams from the methane reformer are used to produce other valuable chemicals such as n-butanol and methanol (from syngas). In short, the production of chemicals from high molecular weight products relies mostly on hydro processing and separation [51].

2.2.2 Sasol Synfuels

Sasol is also operating the second oldest FT facility, namely the Sasol Synfuels site (originally Sasol 2&3) at Secunda, South Africa. To the best of our knowledge it’s the only FT process that still runs on coal-derived syngas and it’s one of two (with PetroSA) plants that still produces ‘drop-in’ fuels. The facility makes use of a Lurgi gasifier for the generation of syngas from coal. The gasification and FTS facility is shown in Figure 14. An overview of the extensive syncrude refinery process is included in Appendix A.

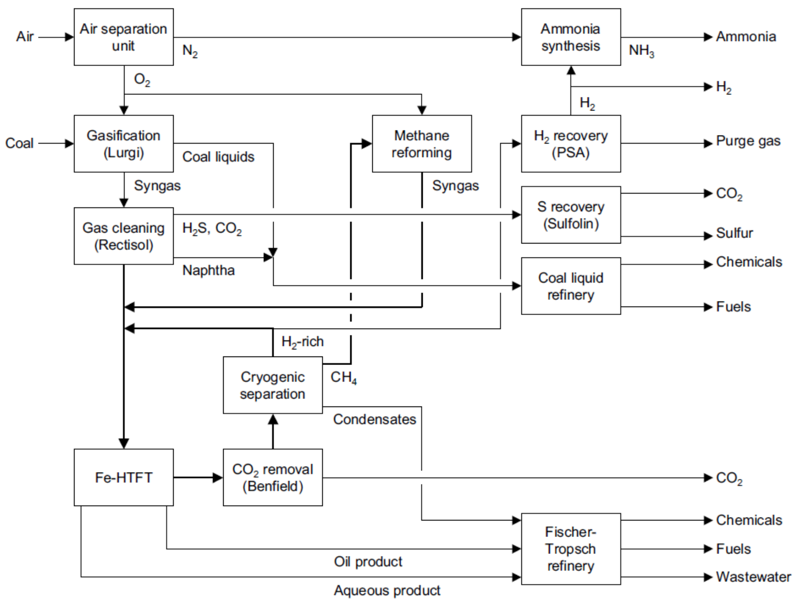


Figure 14: Sasol Synfuels coal to liquid facility, adopted from [51].

Iron is used traditionally in combination with coal derived syngas, as the hydrogen ratios are somewhat lower and Fe also has WGS activity. A condensation train provides respectively decanted oil (atmospheric residue and distillate range) then light oil (distillate and naphtha) and water after phase separation containing most of the oxygenates. C_3 and heavier gases (condensates) can be recovered from the tail gas by pressure distillation. The tail gas ($<C_4$) is first freed from CO_2 using a Benfield unit after which cryogenic separation is required to separate methane from hydrogen, ethylene and C_3-C_4. Hydrogen-rich gas can be fed back into the Fe-HTFT Synthol reactor. Methane is sent to a reformer, transformed into syngas and sent back into the FT reactor. Isolated ethylene is a valuable chemical feedstock and can be sold as such. Olefinic C_3-C_4 can be polymerized into gasoline (with good RON values). The heavier hydrocarbons, formed in lower concentrations in Fe-HTFT (α~0.7), are present in the light oil and decanted oil fractions. These are upgraded using isomerization and hydro treatment (isomerization, cracking, hydrogenation). The overall production of Secunda Synfuels is with an estimated 160,000 bbl/d much higher than Sasol 1.

2.2.3 Shell, Bintulu

Shell has two operational GTL facilities, one in Malaysia and one in Qatar. The shell process is referred to as the Shell Middle Distillate Synthesis (SMDS) and the FTS process is run at low temperature in the presence of a Co-catalyst (Co-LTFT) in tubular fixed bed reactors. Its development began at the Shell Research and Technology Centre in Amsterdam where a pilot plant was built in 1983. This eventually resulted in the Bintulu GTL plant in Malaysia (see Figure 15).

Shell runs a GTL plant at the Bintulu site in Malaysia since 1993 [52]. The other Shell GTL production facility in Qatar runs on similar SMDS technology, hence only the Malaysia plant will be discussed. In general, the syngas from the natural gas reformer contains a H_2/CO ratio of approximately 1.8. Interestingly, Shell started using cobalt catalysts instead of Fe, which was mostly used at that time. With Co-LTFT (α >0.9) a higher carbon number product is obtained with little LPG/light naphtha. Part of the heaviest hydrocarbon fraction, the waxes could be further upgraded and sold as high quality paraffins and waxes and the lighter oil fraction is hydro-cracked/isomerized to mostly distillate that can be sold as diesel blend. On-specification gasoline was not desired as the best market conditions for diesel were foreseen [27]. And the high quality distillate from the FT synthesis has excellent properties for blending with conventional diesel. Another benefit of Co-LTFT was the low amount of light naphtha or LPG that would be difficult to transport from remote locations. The accompanied refinery could be kept relatively simple compared to e.g. Sasol Synfuels were on-specification gasoline is produced. The SMDS flow scheme is shown in Figure 16.

For the Co-LTFT, tubular fixed bed (TFB) reactors are used at 200-230°C and 30 bar. Thousands of tubes hold the solid catalyst bed. Multiple TFB reactors are placed in series to increase the syngas conversion. Gas flows through the reactor from top to bottom. As expected with LTFT, mostly liquid products are formed. After Co-LTFT, wax is obtained directly as a liquid from the reaction mixture. Then, a lighter oil fraction is obtained in a condensation step. Tail gas containing methane and C_2-C_4 is send directly to the reformer producing more syngas. The waxes are hydro treated and separated to give waxes and paraffins. Oil is hydrocracked to produce distillate, kerosene and naphtha that are not further refined. They are either used for blending (diesel) or are sent to a conventional crude oil refinery for further processing. The H_2/CO ratio is adjusted by the steam methane reformer (not the natural gas gasifier that uses non-catalytic partial oxidation).

The total production at the Bintulu, Malaysia site is approx. 14,700 bbl/d. The pearl GTL plant in Qatar produced up to 140,000 bbl/d.

Figure 15: Image of the Bintulu site, with the SMDS facility within the black lines.

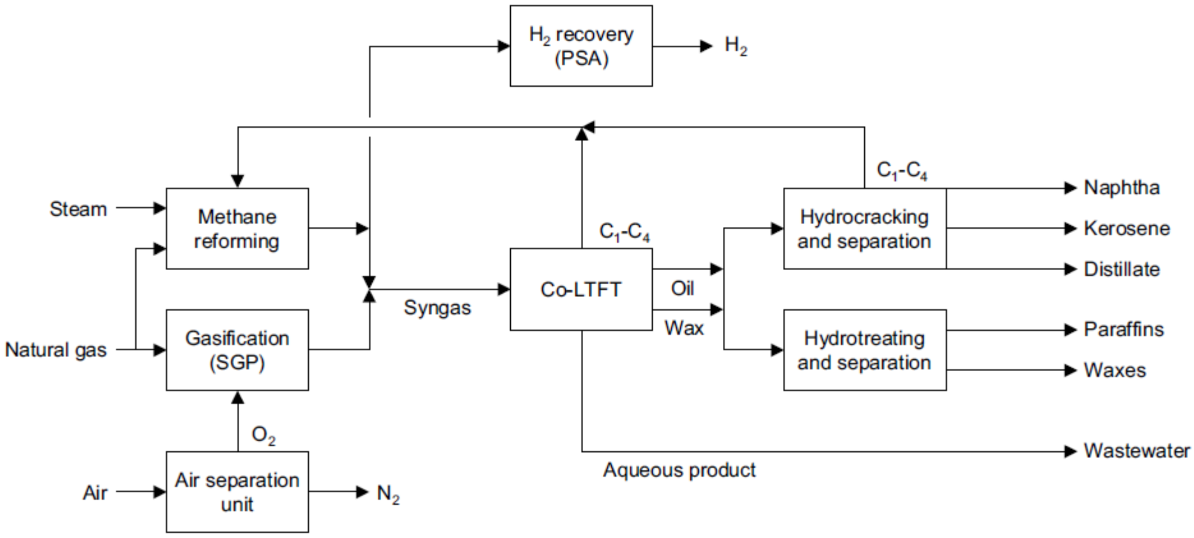


Figure 16: Flow scheme of the Shell Middle Distillate Synthesis (SMDS) at the Bintulu site [60].

2.2.4 Overview I: LTFT in industry

Table 7: Most important FTS facilities running LTFT conditions [13][53][54][55][56].

Company	Plant, Location, Date	Syngas source	Reactor type	Catalyst	T, P	Current production + capacity
Sasol	SASOL I Sasolburg, South Africa 1955	Natural gas	Slurry Phase Distillate + Multi-tubular fixed bed.	Prec. Fe/K	220-250°C	5,000 bbl/d Paraffin, waxes, oxygenates and fuel gas.
Shell	Bintulu site Bintulu, Malaysia 1993	Natural gas	Multi-tubular fixed bed	Co/SiO_2	220°C, 25 bar	SMDS 14,700 bbl/d LPG (0-5%), naphtha (30-40%), distillate (40-70%) and oils (0-30%)
Sasol	Oryx GTL Ras Laffan Industrial City, Qatar 2007	Natural gas	Slurry phase distillate	Co/Pt/Al_2O_3 (BASF)	230°C, 25 bar	34,000 bbl/d LPG, naphtha and distillate (diesel blend).
Shell	Pearl GTL Qatar 2009	Natural gas	Multi-tubular fixed bed	Co/SiO_2	220°C, 25 bar	SMDS 140,000 barrels/d LPG (0-5%), naphtha (30-40%), distillate (40-70%) and oils (0-30%)
Chevron	Escravos GTL Escravos, Nigeria 2014	Natural gas	Sasol technology, Oryx plant clone	Co/Pt/Al_2O_3	230°C, 25 bar	34,000 bbl/d LPG, naphtha and distillate (diesel blend).

2.2.5 Overview II: HTFT in industry

Table 8: Most important FTS facilities running HTFT conditions [53][54].

Company	Plant, Location, Date	Syngas source	Reactor type	Catalyst	T, P	Current production + capacity
SASOL	SASOL 2&3 (Synfuels) Secunda, South Africa 1980	Coal	Fixed Fluidized Bed (SAS)	Fused Fe/K	350°C, 24 bar	160,000 bbl/d. Fuel gas, oils, alpha-olefins, ammonia, gasoline, jet fuel, diesel.
PetroSA	Mossgas Mossel Bay, South Africa 1993	Natural gas	Circulating fluidized bed	Fused Fe/K	330-360°C, 25 bar	30,000 bbl/d LPG, gasoline, Diesel, fuel oil, kerosene, aromatics, alcohols.

2.2.6 FT catalyst formulations

As reported in the previous sections, Co catalysts are now mostly applied under LTFT conditions. The exact catalyst formulations are highly confidential and therefore hard to find in the literature. However, in the patent literature examples of catalysts that are most likely used in the current processes can be found. The values shown in Table 9 are indicated.

Table 9 Commercial FT synthesis catalyst formulations

Manufacturer	Active metal	Additive	Support	α-value
Shell 1st generation [57]	15 wt.% Co	14 wt.% Zr	SiO_2	0.90
Shell 2nd generation [58]	10-15 wt.% Co	Mn or V	TiO_2	0.95
Sasol [59]	15 wt.% Co	60 ppm Pt	SiO_2-Al_2O_3	0.8-0.9

2.2.7 Trends in commercial Fischer-Tropsch application

Only two High Temperature Fischer-Tropsch plants are currently running production, these are PetroSA and Sasol Synfuels. Not coincidently, both are producing ‘drop-in’ liquid fuels as main products. The formation of a higher fraction of lighter hydrocarbons in HTFT gives a higher fraction of hydrocarbons in the gasoline range (that still need processing). Moreover, the large fraction of C_2-C_4 olefins can be oligomerized to obtain a better overall quality of gasoline. For this reason HTFT syncrude is easier to refine to on-specification transportation fuel with a high fraction of gasoline/naphtha when compared to LTFT.

However, from sections 2.3 and 2.4, it becomes clear that most processes run Co-LTFT (or Fe-LTFT) and focus on the production of chemicals and fuel blends. The facilities that were built and operated since the 2000s are all Co-LTFT, both with Shell or Sasol technology. Moreover, PetroSA has started to introduce Co-LTFT in 2005 with a 1000 bbl/d Co-LTFT reactor, resulting in a LTFT-HTFT facility [60]. As in the SMDS case, the C_1-C_2 tail gas is recycled to the autothermal reformer, not requiring cryogenic distillation. The most important reason for the Co-LTFT choice seems to be the simpler refinery and the high activity and saturated hydrocarbon selectivity of cobalt.

Interestingly, Sasol is now employing the slurry phase reactors for Co-LTFT, for instance in the Oryx plant that is operational since 2007. Shell on the other hand is only using tubular fixed bed (TFB) reactors in their Co-LTFT processes (Malaysia and Qatar). Advantages of the slurry phase reactor include isothermal conditions, lower pressure drop and lower capital costs. Also, addition and removal of (spent) catalyst during operation is possible in a slurry bed reactor. Advantages of a TFB reactor are that no solid/liquid separator is required and the lower catalyst attrition of the fixed catalyst particles.

Strikingly, only one plant is still operating FT synthesis on syngas from coal (CTL) technology, namely the Sasol Synfuels site. All others are now operating GTL with natural gas reformers as the gas cleaning of methane for syngas production is much easier than removal of impurities from coal-derived syngas. Moreover, as the H_2/CO ratios from natural gas reforming are high, WGS activity is not required i.e. it is no longer an incentive for using a Fe catalyst.

2.3 Integration of FTS with bio-syngas

Several pilot and demo BTL plants are operational today. As the BTL-FT consists of multiple processing steps, companies combine their expertise in gasification, gas purification and FT synthesis in a collaborative effort. The individual technologies are typically already proven at different scales, but the integration with biomass gasification has never been operational on a commercial scale. An overview of the running, planned and cancelled pilot and demo plants is listed in Table 11. The BioTfuel and Güssing plants are discussed in detail in the following paragraphs.

2.3.1 Güssing Pilot Plant

An example of a FT plant integrated with biomass gasification is the pilot-scale BTL-FT facility in Güssing, Austria. It is part of BIOENERGY 2020+, a competence centre founded by the Austrian federal government including among other the Vienna University of Technology. This plant is currently not operational as the first funded program has been completed. Nevertheless, this example is discussed here, because the project is public and explains the process of upgrading low temperature producer gas for FT application. Details of process conditions and gas cleaning can be found in open literature [61].

A combined heat and power plant (CHP) produces the syngas for the lab-scale Fischer-Tropsch synthesis. The CHP plant uses a FICFB-indirect gasification system (Fast Internal Circulation Fluidised Bed) where biomass is converted into CO, CO_2, CH_4, H_2, H_2O and char in the presence of steam at 850-900°C. Only a slipstream of the produced gas is used for Fischer-Tropsch synthesis. As the gasified biomass contains many by-products, multiple processing steps are required to achieve the syngas quality required for FT synthesis. A flow scheme of the FT process, including all the gas processing steps, is shown in Figure 17.

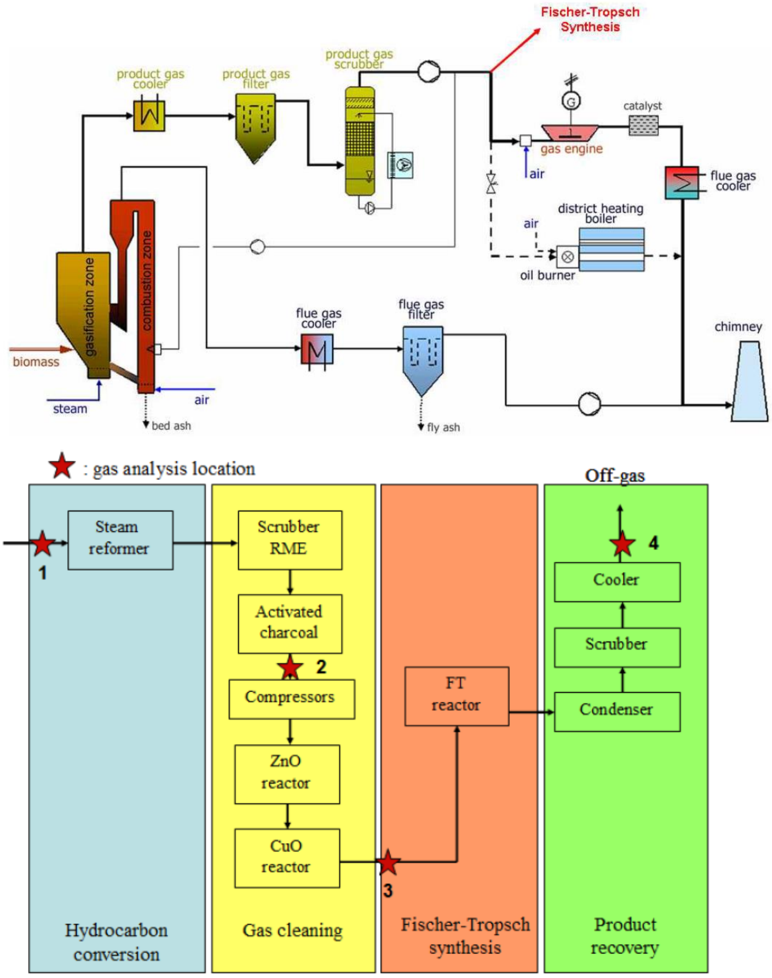


Figure 17: Flow scheme of the CHP pilot plant (top) and the lab-scale FT setup (bottom). The stars in the FT flow scheme represent the sampling points for gas analysis.

Already in the CHP plant, tars are removed from the syngas in two stages. In the first stage, the gas is cooled from 850-900°C to 160-180°C and passed through a fabric filter. In a second stage, it is passed through a rapeseed methyl ester (RME) solvent scrubber at 40°C. Here the water content is lowered to 10vol%. Specs of the CHP plant using gasification for power generation (excluding FT):

- Fuel power – 8000 kW
- Electrical output – 2000 kW
- Thermal output – 4500 kW
- Electrical efficiency – 25%
- Thermal efficiency – 56.3%
- Total efficiency – 81.3%

Part of this gas is used in a lab-scale FT plant, basically for proof-of-principle liquid fuel production. First, the gas from the gasifier passes through a steam reformer to enhance the H_2/CO ratio. Steam was added before the steam reformer and the syngas was heated to 850-950°C. It passed through 2 heated reforming reactors after which the gas was cooled down. Here, the syngas ratio was increased from 1.9 to 2.2. This gas then passes again through a RME scrubber used for gas cleaning and drying. Drying is important as the syngas contains much water after the reformer. After the scrubber, the gas is cooled down to 3°C, which removes most water and some aromatic components such as naphthalene. In the next step, sulphur was removed from the syngas. For this purpose, activated charcoal coated with KI was used to catalytically convert H_2S into elementary sulphur which is adsorbed. Further purification is accomplished over ZnO and CuO. Then, the cleaned gas was led to the FT reactor.

The FT reactor that was used is a three-phase slurry reactor with a 0.1 m tube diameter, 2.5 m high and 20 L of volume. It was filled with a commercially available Co catalyst obtained from Albemarle suited for operation under Co-LTFT conditions. 2.5 kg of reduced catalyst was suspended in 10 kg FT-wax. The reactor was operated under the following conditions: T = 230°C, P = 20 bar, Gas flow = 83 L/min (5-6 m^3/h), H_2/CO = 2.3. After FTS, a first fraction of waxes was collected in a condenser at the same pressure, but a lower temperature. The remaining gas is expanded to 80 mbar and transferred to an off-gas scrubber (OGS, H_2O, 80°C). Also the condensed waxes pass through the OGS, through a separate needle valve. Thus both fractions are collected from the OGS together, containing mostly the solid hydrocarbons (C_9-C_{64}). Lower hydrocarbons (~C_7-C_{20}) are collected from the off-gas cooler (OGC) at 5°C.

Gas analysis data from different sampling points in the FT process provides valuable information about the gas compositions and the reactions that occur, see Table 10.

Table 10: Gas analysis data from the Güssing Pilot BTL-FT plant.

Gas composition, Vol.%	Before Steam reformer 1	After activated charcoal 2	After CuO reactor 3	After Off-gas cooler 4
H_2	39.8	48.7	48.3	37.06
CO	20.9	21.4	21.2	16.5
CO_2	21.8	19.3	20.0	29.5
N	2.43	2.7	2.34	3.14
CH_4	10.5	6.9	7.4	12.4
C_2H_4	3.4	0.5	0	0.02
C_2H_6	0.2	0.05	0.6	1.06
C_3H_6	0.2	0.002	0	0
C_3H_8	0.02	0.001	0.002	0.1
H_2/CO [-]	1.9	2.2	2.3	2.2
Total S [ppm]	110	3	0.003	-

The steam reformer lowered the methane concentration and also reformed ethylene and higher hydrocarbons. As expected, CuO also provides some hydrogenation activity as can be seen from the increased C_2H_6 concentration. Furthermore, sulphur levels were reduced successfully to below 0.003 ppm. Interestingly, CO_2 was not removed prior to FT synthesis and its overall concentration increased from 20% to 29.5% after FTS. The high CO_2 concentration could have motivated the choice of Co as FTS catalyst, as much CO_2 can be formed over Fe through the reverse-WGS reaction. Finally, the syngas ratio entering the FTS slurry reactor was around 2.3. Unfortunately, the overall CO conversion in the slurry reactor (HC selectivity/yield) was not published. However, the combined solid, liquid and gaseous hydrocarbon product distribution (C_1-C_{64}) was used to determine an α-value of 0.89, typical for a Co-LTFT system. The overall carbon number distribution is shown in Figure 18. The mass distribution has the highest concentration of C_9, which seems to be somewhat low if diesel is the desired product. Namely, diesel typically contains hydrocarbons with a carbon number between C_8 and C_{24}. A maximum at C_{12}-C_{15} would therefore be preferential. After removal of the light hydrocarbons in the gas cooler, no further refining was performed. The off-gas could be transferred to the CHP plant.

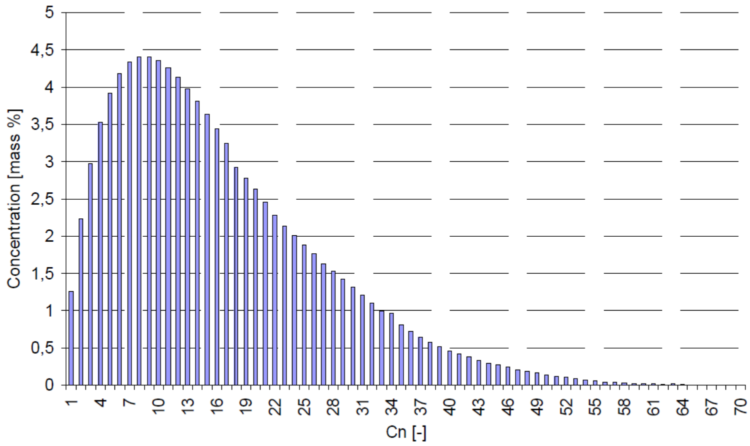


Figure 18: Carbon number distribution of combined gaseous, liquid and solid hydrocarbons after FTS.

In summary, a simplified flow scheme of the Guessing facility is shown in Figure 19. It is unclear whether a RME scrubber is place also before the steam reformer, certainly one is placed after steam reforming to remove the excess of water and traces of aromatics. In this system, the gasifier supplied gas at a H_2/CO ratio of 1.9. Steam reforming, at 850-950°C, is applied to increase the ratio to 2.2 by converting higher hydrocarbons and part of the methane to syngas. An α-value of 0.89 was established, which corresponds to a liquid selectivity of approx. 90 wt%.

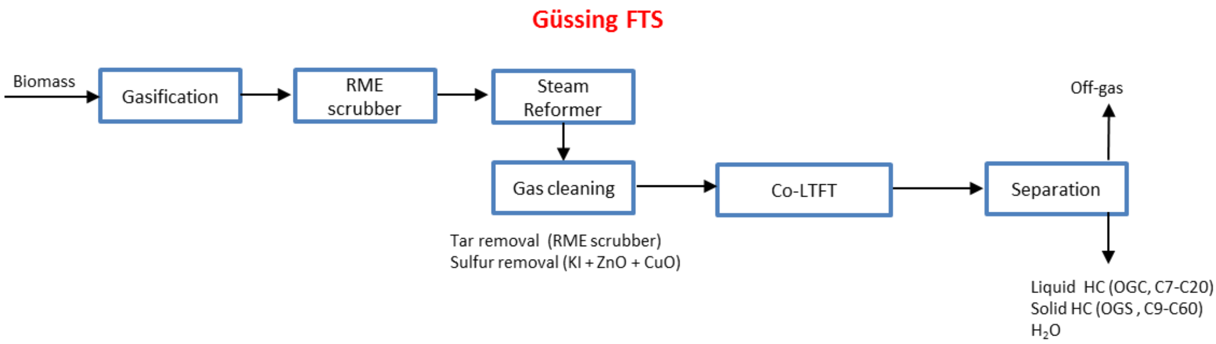


Figure 19: Flow scheme of the lab-scale FT plant at Güssing, Austria.

2.3.2 BioTfuel

BioTFuel project is run by Bionext. Bionext is a dedicated partnership consisting of Axens, CEA, IFP Energies nouvelles, Sofiproteol, ThyssenKrupp Uhde and Total [6]. They operate a pilot-scale setup and a demo-scale plant is under construction at the Total site in Dunkirk, France. The process is referred to as XTL (x=biomass, coal or msw). The concept involves development of a process that can handle biomass as well as pure fossil fuel feedstock. Seasonal changes in biomass content and quantity can be anticipated by coal. The demo plant is constructed in such a way that the torrefaction and gasification takes place at demonstration plant level (gasifier is appr. 15 MWth). Pre-treatment and torrefaction technology is provided by Sofiproteol (in Venette). Gasification is done in a Prenflow^{TM} PDQ (pressurized direct quench) multipurpose EF-type gasifier (15MW, 35 bar). This reactor is able to process pre-treated coal as well as pre-treated biomass. Only 10-15% of the producer gas is used in the FTS pilot plant [62]. In a WGS reaction, the H_2/CO ratio is increased from 0.5-0.7 to values appropriative for FT (probably 1.5-2). After acid gas removal (AGR) of H_2S and CO_2 the gas is passed through a guard bed. Finally, Fischer-Tropsch synthesis provides the syncrude. However, the FTS is currently only performed in a 1 L reactor to show its feasibility. After refining of the syncrude, the produced diesel should be considered drop-in, which means that the fuel can be used as such and does not require blending or modification of the vehicle. A schematic representation of the overall process is depicted in Figure 20.

Axens

FT technology provided by Axens, called Gasel, includes the FT and hydroisomerization-cracking technology. The Gasel® Technology Suite is the fruit of a process and catalyst development program started in 1996 by IFP Energies nouvelles, Eni and Axens [63, 64]. In BioTfuel, Axens has been responsible for the pilot plant design and catalyst preparation and production development. It seems that at the Dunkirk plant, the initial built does not include any FT reactor. The syngas composition was imitated and used in Axens demoplant in Eni's Sannazzaro plant [65] (Eni & IFP Energies nouvelles development since 1996) in Italy for the development testing and validation of the catalyst systems (FT + hydroisomerization-hydrocracking). The Sannazzaro Fischer-Tropsch pilot plant (20 bbl/d) was operated in campaigns between 2001 and 2010, testing, proving and improving the technology and the catalyst. In total it has been operational for 20,000 hours since 2001. The FTS is performed in a slurry-bubble column with a Co-based catalyst (Co-LTFT). The catalyst consists of a Co on a γ-alumina support with silica/TEOS to prevent dissolution of the support by the acidic water [66]. After hydrocracking-isomerization three product fractions are obtained. A lighter paraffinic naphtha (25%), which can be used as petrochemical feedstock. 25% kerosene which can be incorporated into jet-A1 pool and 50% high cetane (>75), zero-sulphur diesel. Axens technology will also be used in Ajos BTL Finland (with Kaidi).

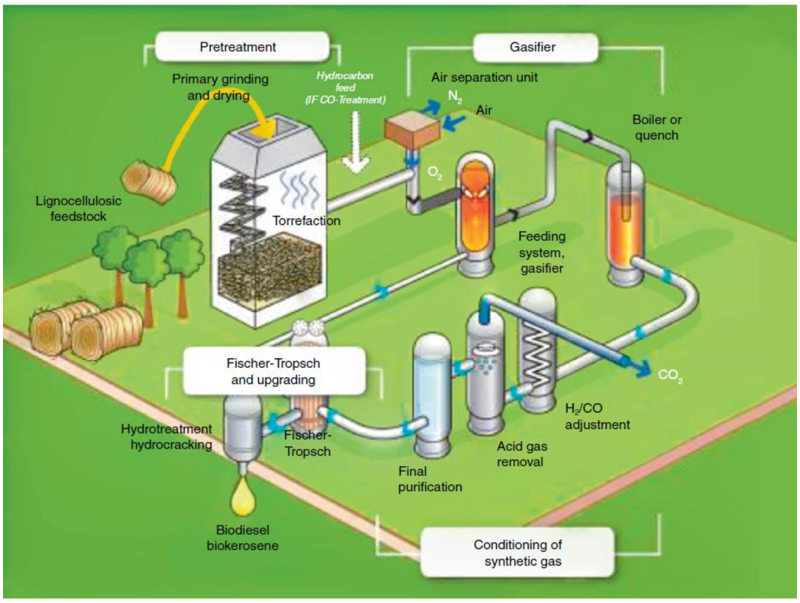


Figure 20 The BioTfuel process, production of second generation bio jet fuel and diesel [62].

2.3.3 Overview pilot- and demo-scale facilities

Table 11: Operational, planned and cancelled pilot and demonstration plants in BTL-FT, adopted from [67]

Project	Location	Year	Input	Product(s)	Scale	Project owner/Partners	Status
BioTfueL pilot	France, Dunkirk	2012	Forest waste, straw, green waste, dedicated crops.	FT liquids (60 t/y diesel and jet fuel)	TRL 4-5	BioTfueL-consortium: Axens (FT); CEA; IFP Energies Nouvelles; Sofiprotéol (biomass pretreatment); ThyssenKrupp Uhde (Gasification); Total	Operational
FT pilot Guessing	Austria, Guessing		Syngas from FICFB gasifier (5 m3/h)	FT liquids (5 kg/d)	TRL 4-5	Vienna University of Technology	Stopped
Sunshine Kaidi New Energy Group pilot	Finland	2013	Biomass with 85% dryness	FT liquids	Pilot	Sunshine Kaidi (Finland) New Energy Co. Ltd	Operational
Red Rock Biofuels	USA, Oregon, Lakeview		525 ton/d wood	FT liquids (850 bbl/d)	TRL 8	Velocys (FT), FedEx Express (3m gallons jet fuel), Southwest Airlines	Planned
BioTfueL demo	France, Dunkirk	2016	straw, forest waste, dedicated energy crops	FT liquids (200,000 t/y)	Pilot	Total (owner), Axens (FT), CEA, IFP Energies Nouvelles, Avril, ThyssenKrupp Industrial (gasification)	Planned
Sierra	USA, McCarran		MSW 600 t/d	FT liquids (850 bbl/d)		Fulcrum Bioenergy, Abengoa	Planned

2.4 Recent developments in academia (novel catalysts)

In this section, trends and highlights on the development of novel FT catalysts will be presented. These possible improvements over more conventional commercial catalysts is mostly related to activity and selectivity. New valuable chemical routes e.g. in the case of Fischer-Tropsch to olefins or improved liquid (C_{5+}) yield at much higher activity can lead to lower CAPEX and OPEX in a BTL-FT plant. Although the same is true for integration in a coal to liquid or gas to liquid facility.

Unfortunately little is reported on the effect of inert gases, i.e. CO_2, CH_4 and to a lesser extent the effect of HCl, NH_3 and S-containing impurities. Syngas purification accounts for most of the CAPEX for natural gas and biomass derived syngas. Development or at least extensive testing of catalysts that are more sturdy and do not require complete cleaning (S-removal will be required anyhow) would be helpful.

2.4.1 Mesoporous FT catalysts

Mesoporous silica such as MCM-41, SBA-15 and SHS have received much attention for application in FTS since their first synthesis (1990s). Namely, they have a relative large surface area, a

controllable pore size and narrow pore size distributions. The most studied are MCM-41 and SBA-15.
MCM-41 (mobile composition of matter -1992) has one-dimensional cylindrical pores with a sharp pore size distribution within 2 and 7 nm [68]. MCM-41 has a wall thickness between 0.6 and 1.2 nm, which makes it hydrothermally not very stable. To achieve this pore distribution, tertiary ammonium surfactant are used as template during the synthesis under alkaline conditions

SBA-15 (Santa Barbara No 15 - 1998), consists of uniform hexagonal pores tunable between 4 and 30 nm [69]. This material has a higher wall thickness of 3.1-6.4 nm with a higher hydrothermal stability than MCM-41. The triblock copolymer Pluronic 123 is used as template for its synthesis. Its total surface area is typically lower than for MCM-41. SBA-15 also has some micropores connecting the mesopores.

A promising example of mesoporous supported FTS catalysts was reported by Jung et al. in 2012. They prepared several Co catalysts on commercially available SiO_2, MCM-41 and SHS (spherical hollow silica) [70]. The catalysts were all prepared via incipient wetness to obtain a metal loading of 20 wt.%. After impregnation, the catalysts were dried at 120°C for 12 h followed by calcination at 450°C. Prior to FTS , a H_2 pre-treatment was done in the fixed bed reactor at 450°C for 4 h. A particle size of 35-75 µm was used (surprisingly small, but very common size for academic fixed bed). The Co/SHS performed best with the highest activity and C_{5+} selectivity. A 75.5% CO conversion was achieved with 70 wt.% C_{5+} selectivity versus a 60.1% CO conversion and 55 wt.% C_{5+} selectivity over Co/SiO_2. For Co/MCM relatively 63.8 % and 59 wt.% was obtained. The results clearly showed an improvement in activity and hydrocarbon selectivity (less CO_2 formation) when ordered mesoporous silica was used as Co support.

Another study on the effect of the mesoporous support was performed by Peng et al. [71]. They showed that Co/HMS performed even better than Co/MCM-41 prepared in a similar way. HMS is a hexagonal mesoporous material prepared from alkyl amine surfactants with an average pore size of 3 nm. A higher CO conversion was achieved at 503 K (87.8% vs 53.1%) as well as a higher C_{5+} selectivity (79.4 vs 60.0 wt.%). Further improvements were obtained by ZrO_2 modification of Co/HMS leading to an even better C_{5+} selectivity of 86.1 wt.%.
Another study on the pore-size effect in Co-catalysed FTS has been reported by Khodakov et al. [72]. Three types of catalysts were tested consisting of mesoporous silica at different pore sizes. These were three Co/MCM-41 (pore size: 2nm), two Co/SBA-15 (pore size: 4 and 9 nm) and two Co/SiO_2 with fumed silica (pore size 28 and 33 nm). Tests were performed in a fixed bed microreactor at 190°C and atmospheric pressure at <5% conversion. All catalysts were loaded with 5 wt.% Co. The Co/SiO_2 showed the highest reaction rate of 2.68 * 10-4 s-1 with a 60% C_{5+} selectivity. The Co/SBA-15 was less active, but the highest C_{5+} selectivity of 68.4% was achieved. In general they found that smaller Co particles were formed on the mesoporous silica with average pore sizes under 20 nm and these smaller crystallites (0.6-12 nm Co_3O_4 crystallites) are more difficult to reduce leading to lower FTS activity compared to the 14-23 nm crystallites found on fumed silica. Naturally, the type of support can also effect the metal reducibility as a Co/Al_2O_3 is harder to reduce than a Co/SiO_2 catalyst, as the Co-SiO_2 interaction is much weaker and a higher activity is obtained in FTS [73]. In general, CO conversion can be correlated with metal dispersion and selectivity with porosity.

2.4.2 Fischer-Tropsch to Olefins (FTO)

In recent years, the use of syngas for the production of light olefins has gained considerable attention. Production of olefins from syngas can proceed indirectly via methanol or DME (MTO process) or directly by using FT-type catalysts. The latter is known as the Fischer-Tropsch to olefins

(FTO) process. It has been shown that addition of Na and S promoters to Fe catalysts promote the production of olefins, suppress the formation of methane and increase the FTO activity. A recent example involves the use of iron carbide at high temperature (340°C) supported by mesoporous carbon [74]. Mesoporous supports were chosen as they potentially slow down particle growth and stabilize the active phase. Here, carbon was chosen as it is more inert towards Fe than silica or alumina. An ordered mesoporous carbon CMK-3 was functionalized and used as support for Fe. This catalyst was tested with and without promotion by Na or S. An O-enriched mesoporous support was prepared by heating in air and a N-functionalized mesoporous carbon was prepared by ammonia treatment of the O-enriched CMK-3. TEM and HAADF-TEM revealed the presence of 3-5 nm Fe particles within the hexagonally ordered CMK-3 pore system. Under FTO conditions (340°C, 10 bar, H_2/CO = 2) the highest selectivity of 55% to C_2-C_4 olefins was obtained with Fe/Na/S-CMK-3-N after 100 h TOS at 20% conversion. This Fe/Na/S-CMK-3-N catalyst represents a S-and N-promoted Fe catalyst on a N-enriched mesoporous carbon. TEM investigations showed that the Fe particles in the spent catalyst had grown to 18-26 nm after each run in all catalysts. In absence of S/Na promotion, as much paraffins as olefins were obtained, but even more methane (25-25-40%).

2.4.3 Syngas to olefins (OX-ZEO)

In a perspective article in Science in 2016, K. P. de Jong identified a publication on the conversion of syngas to olefins by Jiao et al. as a potential alternative to FTO and methanol to olefins (MTO) [75, 76]. In this work, light olefins were obtained in one step from syngas over a $ZnCrO_x$/MSAPO catalyst. A selectivity of up to 74% C_2-C_4 olefins was obtained over a ZnCrOx/MSAPO catalyst (25 bar H_2/CO = 2.5, 400°C, 17% CO conversion). This is higher than the highest 61% reported for FTO, as summarized in Figure 21B. Although the mechanism has not yet been elucidated, it must be different from the FTS mechanism as CO_2 is formed as the major by-product instead of H_2O. Moreover, the product distribution from FTS follows the ASF model that predicts a maximum C_2-C_4 selectivity of 58%.

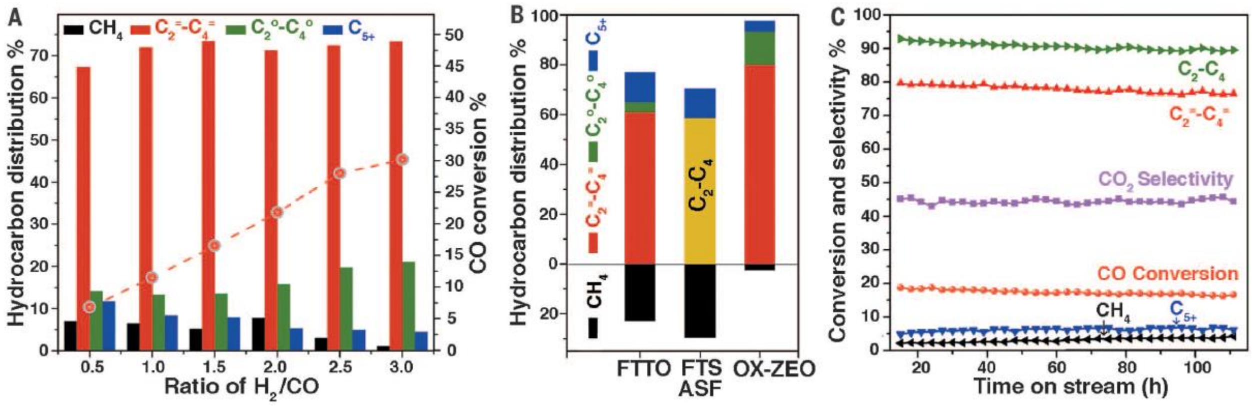


Figure 21 Catalytic performance of OX-ZEO at varying syngas ratios (A), its selectivity compared with FTO processes (B) and a stability test with more than 100 h on stream (C).

2.4.4 Fischer-Tropsch to Aldehydes (FTA)

A paper published in Nature communications in 2016 by Xiang and Kruse described the tuning of the CO hydrogenation to aldehydes/alcohols or olefins/paraffins [77]. Several K-promoted CoMn catalysts were used. Typical conditions were H_2/CO ratio of 1.5 at 40 bar and 220°C (LTFT conditions). CO conversion, but also CO_2 formation was directly proportional to the reaction temperature. In the best case a 50 % selectivity towards oxygenates was obtained of which 90% aldehydes. Methane formation is as low as 6 wt.%. Again a linear relation between activity and the partial pressure of hydrogen was found. When the H_2/CO was lowered to 0.5, a 60% aldehyde selectivity was achieved. However, the CO conversion was less than 5% due to the low partial pressure of hydrogen. At an acceptable 20% CO conversion, with a H_2/CO of 5, the selectivity dropped to approx. 25%. With a H_2/CO of 9 mostly paraffins were formed (65% paraffins 35% alcohols). Remarkably, the α-value did not change when the H_2/CO partial pressure ratio was varied. Although highly interesting, the activity and aldehyde selectivity are not high enough to be applicable as catalyst in BTL-FT.

3. Methanol synthesis

3.1 Methanol synthesis chemistry

Methanol is one of the most important and versatile platform chemicals for chemical industry. It is used to produce other chemicals such as formaldehyde, acetic acid, acetic anhydride. In recent years methanol has also been used for other markets such as production of DME (Dimethyl-ether) and olefins by the so-called methanol-to-olefins process (MTO) or as blendstock for motor fuels. Methanol can also be directly used in dedicated internal combustion engines as a high-energy fuel, due to its low cost, high octane number and low well-to-wheel GHG emissions. However, there are questions concerning the compatibility of methanol with vehicle applications. Some people have thus rejected methanol as a transport fuel in favor of more suitable alternatives [78]. Low energy density and poor cold-start properties (avoided by blending with fossil fuels) are two concerns. Methanol is corrosive, and this affects pipeline transport and storage. It is highly soluble in water, which raises contamination concerns similar to ethanol. Both are blended at terminals before being distributed to forecourts to avoid pipeline problems. Nevertheless, particular standards allow and govern methanol blending in Europe, the US and China.

On an industrial scale, methanol is predominantly produced from natural gas. Several new plants have been constructed in areas where natural gas is available and cheap such as in USA and the Middle East. There is little doubt that (cheap) natural gas will remain the predominant feed for methanol production for many years to come. The production of methanol from coal is increasing in locations where natural gas is not available or expensive such as in China. Some of the biggest coal-to-methanol plants, worldwide, including details about performance and cost data, can be found in a previous ECN report [79].

Catalytic methanol synthesis from syngas is a classic high-temperature, high-pressure, exothermic and equilibrium limited synthesis reaction that is well-developed and industrially practiced process. In a typical plant, methanol is made from syngas produced from natural gas in a steam reformer. The synthesis gas, a mixture of CO and H_2, is then pressurized and converted to crude methanol in the presence of a Cu-ZnO-Al_2O_3 or ZnO-Cr_2O_3 catalyst at 60-100 bar and about 260 °C. The crude methanol contains up to 18% water with traces of ethanol, higher alcohols, ketones, and ethers, and is purified in a distillation plant that consists of a unit that removes the volatiles and a unit that removes the water and higher alcohols. The unreacted syngas is recirculated back to the methanol converter resulting in an overall conversion efficiency of 99%. A generic methanol synthesis process flow diagram from natural gas reforming, is shown in Figure 22.

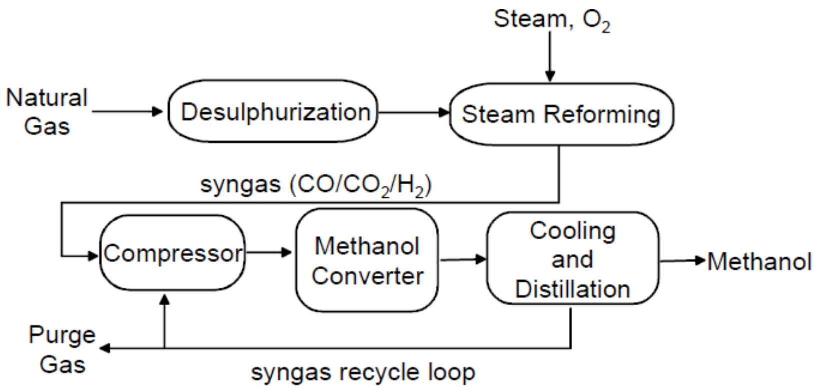


Figure 22: Simplified Flow Diagram for the Methanol Synthesis from Natural Gas [12].

The chemistry of methanol synthesis is defined by three equilibrium reactions [12]:

$CO + 2H_2 \rightleftharpoons CH_3OH$, ΔH = -91 kJ/mol (1)

$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$, ΔH = - 49 kJ/mol (2)

$CO + H_2O \rightleftharpoons CO_2 + H_2$, ΔH = - 41 kJ/mol (3)

The synthesis of methanol from CO (reaction 1) and CO_2 (reaction 2) is exothermic and involves a decrease in the number of moles, so according to *Le Chatelier's principle*, the equilibrium is favoured by low temperature and high pressure conditions. However, the catalyst used for methanol synthesis is not active at temperatures much lower than 220°C and a compromise between reaction kinetics and equilibrium considerations is required. The slightly exothermic water-gas shift (WGS) reaction (reaction 3) occurs as a side reaction to methanol synthesis. The synthesis gas composition also determines the maximum achievable conversion. Inert compounds, such as CH_4, N_2 and Ar, lower the conversion [80]. The stoichiometric amount of hydrogen required for methanol synthesis is [81]:

$(H_2\text{-}CO_2)/(CO+CO_2) = 2$

The kinetics and mechanisms of the methanol synthesis is still debated and controversial. The main point in the debate is whether the formation of methanol proceeds primarily via CO or CO_2 hydrogenation. Some authors have reported maximum methanol production rates with CO_2 concentrations in the feed in the range of 2–5%, while others reported a constant increase with increasing CO_2 concentrations [82, 83]. Additionally, it has been shown that Cu-based catalysts with carefully purified CO/H_2 mixtures did not show any activity [12,80]. In addition, isotopic labelling proved that CO_2 is the source of C in methanol, since its hydrogenation is much faster than that of CO. CO_2 is also believed to keep the catalysts in an intermediate oxidation state (Cu^0/Cu^+), preventing ZnO reduction followed by brass formation. However, a high CO to CO_2 ratio will increase the reaction rate and the achievable per pass conversion. In addition, the formation of water will decrease, reducing the catalyst deactivation rate [12]. Today there are only a few proponents left who believe that methanol is formed in any substantial quantities from CO, at least with industrially used catalysts and under industrial conditions.

Although abundant literature exists on the intentional formation of higher alcohols by modified low-temperature methanol synthesis catalysts, studies of selectivity in proper methanol synthesis are relatively scarce. Modern copper-based methanol catalysts are very selective. In fact, selectivities above 99.9% are not uncommon. This is truly remarkable, because all of the by-products (e.g. higher alcohols, esthers, ethers) are thermodynamically more favored than methanol with formaldehyde and formic acid as exceptions [80]:

3.2 Methanol Synthesis Catalysts

Currently, the production of methanol from synthesis gas is based on Cu-based catalysts and is the product of years of research. Methanol was first produced at commercial scale in the 1920s by *BASF*. The process used ZnO/Cr_2O_3 catalysts at high temperature (320–380°C) and high pressure (250-350 bar). The catalyst was relatively poison-resistant, allowing to be used for syngas from feedstocks containing chlorine and sulphur impurities, as commonly found in gas from low-grade German coal (lignite) [14]. However, methane formation was one of the major problems with these catalysts. Later, with advancements in gas cleaning technology, efforts were directed toward synthesis of more active, selective, and stable catalysts with higher yields. In 1996, *Imperial Chemical Industries (ICI)* patented a highly active $Cu/ZnO/Al_2O_3$ catalyst synthesized by co-precipitation methods for conversion of syngas to methanol. The operating temperature and pressure were 220-275°C and 50-100 bar, respectively. The use of new catalysts resulted in significant energy savings and allowed milder operating conditions and became known as the 'low pressure' process. The catalyst performance depends on many factors, including the particle size of copper and its dispersion, preparation method, Cu/Zn molar ratio, and calcination temperature. Particle-size distributions should be in a narrow range for optimum performance, and therefore, many synthesis methods, including sol–gel and sonochemical methods, have been tested. The last high temperature methanol synthesis plant closed in the mid-1980s and, at present, low-temperature and low-pressure processes based on Cu catalysts are used for all commercial production of methanol from syngas. The synthesis process has been optimized to the point that modern methanol plants yield 1 kg of MeOH /L_{cat}/hr with >99.5% selectivity for methanol. Commercial methanol synthesis catalysts have lifetimes in the order of 3-5 years under normal operating conditions [12].

The Cu crystallites in methanol synthesis catalysts have been identified as the active catalytic sites although the actual state (oxide, metallic...) of the active Cu site is still being debated. Most active catalysts have a high Cu content, with an optimum at approx. 60 wt% Cu, that is limited by the need to have enough refractory oxide to prevent sintering of the Cu crystallites. Hindering agglomeration is why ZnO creates a high Cu metal surface area. ZnO also interacts with Al_2O_3 to form a spinel that provides a robust catalyst support. Acidic materials like alumina, are also known to catalyze methanol dehydration reactions to produce DME. By interacting with the Al_2O_3 support material, the ZnO effectively improves methanol selectivity by reducing the potential for DME formation. Catalysts are typically prepared by co-precipitation of metal salts with a variety of precipitation agents. It is important to avoid contaminating methanol catalysts with metals that have hydrogenation activity (Fe or Ni) during the synthesis. Incorporation of alkali metal in the catalyst formulation should also be avoided for methanol synthesis, because they increase higher alcohols production. Table 12 shows catalyst formulations from several commercial manufacturers.

Table 12: Commercial Methanol synthesis catalyst formulations [12]

Manufacturer	Cu, wt%	Zn, wt%	Al, wt%	Other, wt%
IFP	45-70	15-65	4-20	Zr: 2-18
ICI	20-35	15-50	4-20	Mg
BASF	38.5	48.8	12.9	-
Shell	71	24	-	Rare Earth Oxide: 5
Sud Chemie	65	22	12	-
Dupont	50	19	31	-
Haldor Topsoe	>55	21-25	8-10	-

Additional catalyst formulations have been presented in the literature with the purpose of improving per-pass methanol yields [12]. The addition of Cs to Cu/ZnO mixtures has shown improved methanol synthesis yields. This only holds true for the heavier alkali metals, as the addition of K to methanol synthesis catalysts tends to enhance higher alcohols yields. The Cu/ThO_2 intermetallic catalysts have also been investigated for methanol. These catalysts have demonstrated high activity for forming methanol from CO_2-free syngas. Cu/Zr catalysts have proven active for methanol synthesis in CO-free syngas at 5 bar and 160-300°C. Supported Pd catalysts have also demonstrated methanol synthesis activity in CO_2-free syngas at 5-110 bar and 260-350°C [12].

Cu/ZnO/Al_2O_3 catalyst can deactivate due to various impurities in the feed. Small amounts of chlorine are found to deactivate the catalyst very rapidly and therefore should be completely excluded from the feed. HCl can react with active copper metal to produce copper chloride, which can cause sintering. Other impurities include phosphine (PH_3) or any sulphur-containing contaminant (H_2S, COS, CS_2, thiophene, and CH_3SCN), which can poison the active sites. Gas-phase sulphur impurities should be limited to <1 ppm and preferably <0.1 ppm to maintain the high yield of catalyst over a long period of time. The synthesis gas specifications for the CO hydrogenation reaction to MeOH, over Cu-based catalyst, are demonstrated in Table 2.

It is important to note that methanol synthesis catalysts undergo relatively fast deactivation even in the absence of poisons. More than one-third of the activity is lost during the first 1000 h of operation [80]. Despite this fact, which often determines the economic lifetime of an industrial catalyst charge, relatively little has been published on the subject.

Irreversible deactivation was observed when Cu/ZnO was operated in CO/H_2 gases without CO_2 or H_2O [80], which has been interpreted as reduction of Cu^+ from the ZnO matrix. Other explanations could be evaporation of Zn or formation of brass (Cu_nZn metal alloy). The latter has been observed in low-temperature shift catalysts above 260°C. Rapid formation of brass has been observed in methanol synthesis catalysts using H_2/CO mixtures above 300°C, leading to rapid deactivation [80]. The beneficial effect of adding alumina (or chromia) and ZnO to the catalysts has been explained by rather crude models invoking a mechanical spacing effect, which prevents sintering [80]. In very CO_2-rich synthesis gases (leading also to high water contents), accelerated aging can also be observed, perhaps related to failure of the alumina phase to stabilize the Cu/ZnO constituent of the catalyst. It was indicated by the results reported from stability tests with a commercial

$Cu/ZnO/Al_2O_3$ catalyst in slurry phase that high CO_2 content in itself does not necessarily induce rapid aging, but it is rather the resulting water which is responsible [80].

3.3 Commercial Methanol Production

Methanol production from syngas is a commercially demonstrated technology, using both natural gas and coal as feedstock. The current methanol plants are typically in the order of 2000 to 2500 tons/d, but also larger-scale (5000 tons/d) single train methanol process technologies are being offered [12].

The methanol industry spans the entire globe, with production in Asia, North and South America, Europe, Africa and the Middle East. Worldwide, over 90 methanol plants have a combined production capacity of about 110 million tons (almost 36.6 billion gallons or 138 billion liters). According to IHS, global methanol demand reached 70 million tons in 2015 (87 billion liters), driven in large part emerging energy applications for methanol which now account for 40% of methanol consumption. Each day, nearly 200,000 tons of methanol is used as a chemical feedstock or as a transportation fuel (254 million liters) [79].

A major challenge for commercial MeOH generation is to overcome thermodynamic limitations. Around 25% of syngas is converted to MeOH per-pass, which is quite low [81]. This conversion efficiency could be enhanced by lowering the operational temperature, shifting the equilibrium toward the products. However, a decrease in temperature reduces catalyst activity. This issue can be handled by removing MeOH as soon as it is produced, after every pass. Methanol can either be removed via condensation, physisorption or can be converted to some useful derivative such as DME, acetic acid, etc.

In the 1920s, the first commercial methanol synthesis plants operated at high pressures, until low pressure routes were developed and by the early 1980s the majority of the producers had switched from the high-pressure process to a low pressure one. This happened because the low-pressure process is more efficient, has lower capital costs due to reduced thickness of steel piping and reactors and is less expensive to operate (reduced syngas compression). However, a higher pressure is favored in the equilibrium reaction which also reduces the required unit volume. A reduced temperature enables higher conversions, but also yields lower catalytic activity and larger reactors. Higher temperatures negatively affect product distribution (by-products as CH_4, dimethyl ether (DME), methylformate, higher alcohols and acetones) and catalyst lifetime due to e.g. catalyst sintering.

For the 'low pressure' technology, the pressure in the reactor system generally is 50 - 100 bar (*ICI, Lurgi*), with recycle ratios of 3 to 7. The largest plants have methanol reactors with individual production capacities of 1,800 to 2,500 tpd. *Mitsubishi Gas Chemicals (MGC)* originally designed their system for 150 bar, but it also operated successfully at 100 bar or less. The process is offered in the pressure range of 50 to 200 bar, and temperatures between 235 and 270°C. *Haldor Topsoe* provides a design for pressures up to 150 bar, and temperatures of 200 up to 310°C. For *Linde AG* process pressures of 50 to 150 bar are stated but at lower temperatures of 240 to 270°C [12]. Table 13 shows the reaction conditions used by several suppliers in the low-pressure methanol synthesis.

Table 13: Low-Pressure methanol synthesis process conditions [12]

Technology Supplier	T (°C)	P (bar)
ICI (Synetix)	210 – 290	50 – 100
Lurgi	230 – 260	50 – 100
Mitsubishi	235-270	50-150
Linde AG	240-270	50-150
Haldor-Topsoe & Nihon	200-310	48-300

3.4 Reactor Technology

As is the case with Fischer-Tropsch synthesis, one of the challenges associated with commercial methanol synthesis is removing the large excess of reaction heat. Controlling and dissipating the heat of reaction and overcoming the equilibrium constraint to maximize the per-pass conversion are the two main process features that are considered when designing the methanol synthesis reactor, commonly referred to as a methanol converter. Numerous methanol converter designs have been commercialized over the years and these can be roughly separated into two categories: adiabatic or isothermal reactors. *Adiabatic reactors* often imply multiple catalysts beds separated by gas cooling devices, either direct heat exchange or injection of cooled, fresh or recycled syngas. The *isothermal reactors* are designed to continuously remove the heat of the reaction so they operate essentially like a heat exchanger.

One of the more widely used commercial isothermal methanol converters is the *Lurgi Methanol Converter* (Figure 23). It is a shell and tube design similar to their Fischer Tropsch (FT) reactor. The tubes contain a proprietary *Lurgi* methanol catalyst ($Cu/ZnO/Cr_2O_3$ + promoters) and are surrounded by boiling water for reaction heat removal. These units operate at 50-100 bar and 230-265°C. Varying the pressure of the boiling water controls the reactor temperature. By-product steam is produced at 40-50 bar and can be used to run the compressor or to provide heat for the distillation process [12].

Based on the Lurgi Methanol Converter and the highly active methanol catalyst with its capability to operate at high space velocities, Lurgi has recently developed a dual reactor system featuring higher efficiency, the *Combined Methanol Converter*. The isothermal reactor is combined in series with a gas-cooled reactor. The first reactor, the isothermal reactor, accomplishes partial conversion of the syngas to methanol at higher space velocities and higher temperatures compares with single-stage synthesis reactors. This results in a significant size reduction of the water-cooled reactor compared to conventional processes, while the steam raised is available at a higher pressure. The methanol-containing gas leaving the first reactor is routed to a second downstream reactor without prior cooling. In this reactor, cold feed gas for the first reactor is routed through tubes in a counter current flow with the reacting gas. Thus, the reaction temperature is continuously reduced over the reaction path in the second reactor and the equilibrium driving force for methanol synthesis maintained over the entire catalyst bed. The large inlet gas preheater normally required for synthesis by a single water-cooled reactor is replace by a relatively small trim preheater. After synthesis, methanol undergoes energy-integrated distillation to produce high-purity methanol (e.g. grade AA and IMPCA grade). The crude methanol is purified in a cost-saving 2-column or an energy-saving 3-column distillation unit. The low boiling compounds are removed in the pre-run column and the higher boiling components are separated in either one or two pure methanol columns [84].

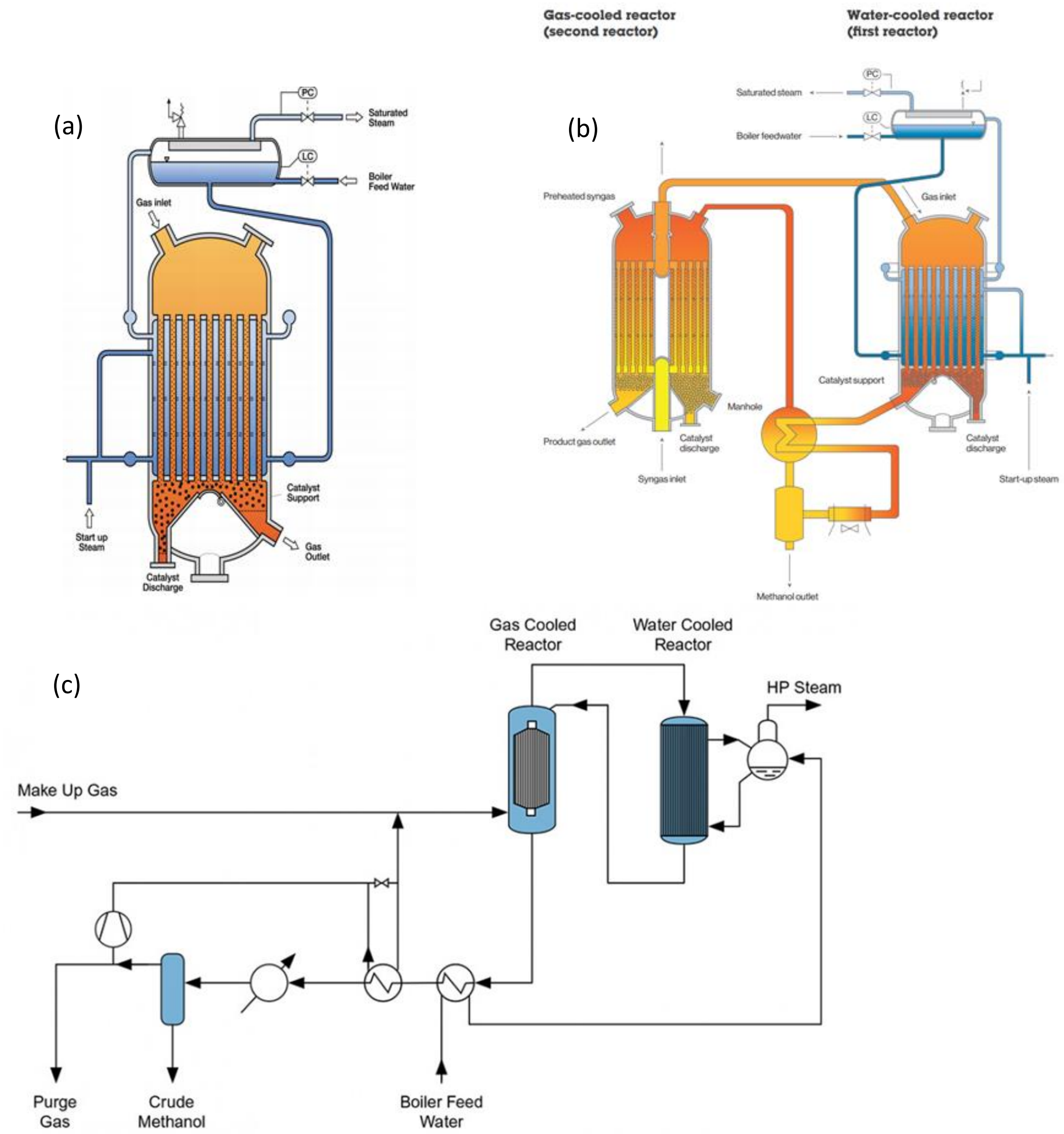


Figure 23: Lurgi Methanol Converter (a), Combined Methanol Converter (b) and Methanol Synthesis Unit (c) [84]

The Low Pressure (LP) Methanol synthesis is a proven technology, provided by *Air Liquide Engineering & Construction*, that is used to produce methanol from any syngas derived from carbonaceous material. The syngas is converted to methanol in a water cooled reactor filled with a highly active and selective synthesis catalyst provided by Clariant. Due to quasi-isothermal operation, high per pass yields are achieved. Any unconverted syngas is then recycled back into the synthesis loop to improve both yield and carbon efficiency. The raw methanol exits the synthesis loop and is further distilled to meet client requirements in terms of methanol specifications. LP Methanol is an ideal technology for medium-scale methanol production of <1 million tons/d (Figure 24) [85].

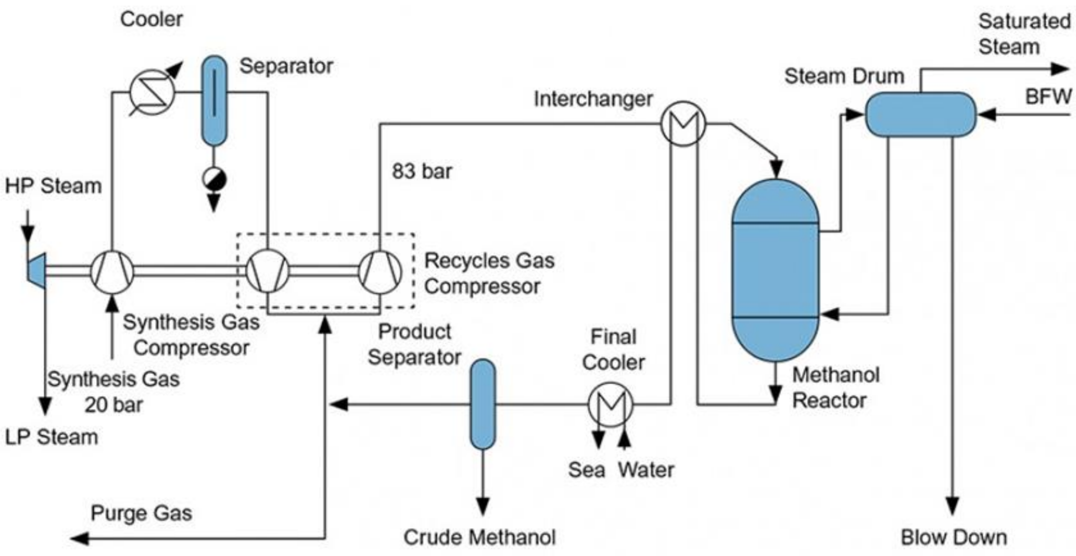


Figure 24: *Air Liquide* Low Pressure (LP) Methanol Synthesis unit [85]

The *ICI Low pressure Quench Converter* is the most widely used *adiabatic* methanol converter (Figure 25). It is operated at 50-100 bar and 270°C. The $Cu/ZnO/Al_2O_3$ catalyst is contained in a single bed supported by an inert material. Adding cold fresh and recycled syngas quenches the synthesis reaction and controls the reaction temperature. The gas is injected at appropriate depths within the reactor through spargers called lozenges. There are horizontal layers of these lozenges that run across the converter from side to side and each has an outer surface covered with wire mesh and a central pipe that delivers the cold gas. ICI has an improved version of this reactor known as an *ARC converter* (Figure 25). The main technical difference is that instead of a single continuous catalyst bed, the bed is separated by distribution plates to form multiple consecutive catalyst domains [12].

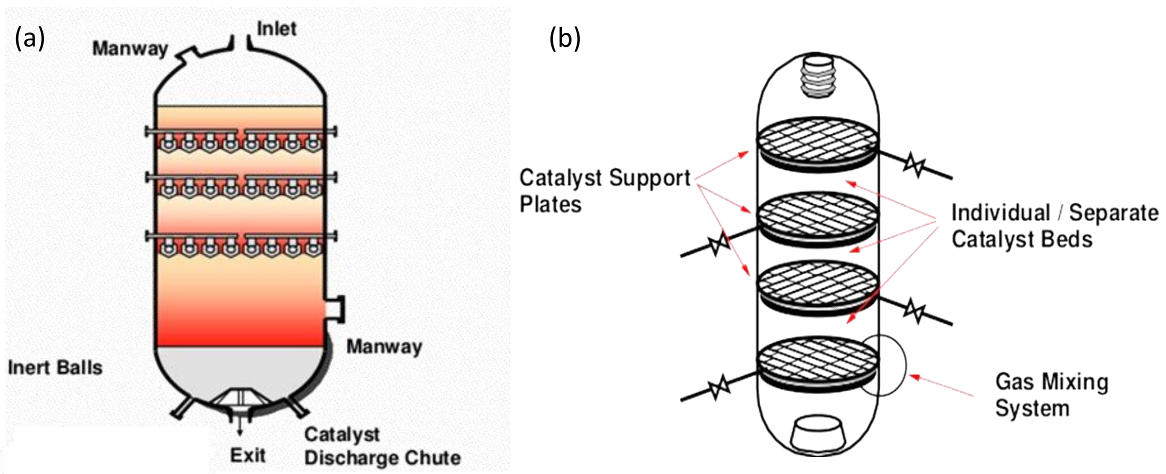


Figure 25: ICI Low pressure Quench Converter (a) and ARC Converter (b)

Kellogg, Brown, and Root (now Halliburton) has developed an *adiabatic* methanol converter that has multiple fixed bed reactors arranged in series and separated by heat exchangers. All of the recycled syngas is fed directly into the first reactor stage. The reactors have a spherical geometry to reduce construction costs and they also use less catalyst compared to the ICI Quench Converter. The *Haldor-Topsoe Collect, Mix, Distribute (CMD) converter* operates on a similar principle. Vertical support beams separate catalyst beds. The gas inlet at the bottom of the reactor provides fresh syngas that flows radially up through the first catalyst bed. At the top of the reactor, this first pass through gas is mixed with quench gas and distributed evenly so that it flows radially down through the second catalyst bed. The cited benefit of this design is an increase in per-pass conversion. *Toyo Engineering Corporation* has designed another version of a multistage radial flow methanol converter (*MRF-Z™*) that uses bayonet boiler tubes for intermediate cooling. The tubes divide the catalyst into concentric beds (Figure 26) [12].

The *Tube Cooled Converter* (Figure 26) is a reactor design that is simple to operate. Methanol synthesis proceeds exothermically in the gas phase, and is cooled by counter-current heat exchange with the feed stream. Syngas, following compression, passes to the TCC. Entering the bottom of the reactor, the feed gas flows upwards through axial tubes which are embedded in catalyst. As the syngas flows upwards, it absorbs heat from the exothermic reaction taking place shell-side in the catalyst bed. The heated syngas leaves the top of the tubes, then passes down through the catalyst bed where it reacts to form methanol. At the same time, heat from this exothermic reaction transfers to the fresh feed flowing up through the tubes. The crude product exits the bottom of the vessel, and a simple loop arrangement adjoining the TCC separates the methanol by condensation. The loop then purges small quantities of inerts from the unreacted syngas before circulating it back to the TCC for further conversion. The crude liquid methanol product passes to distillation for purification.

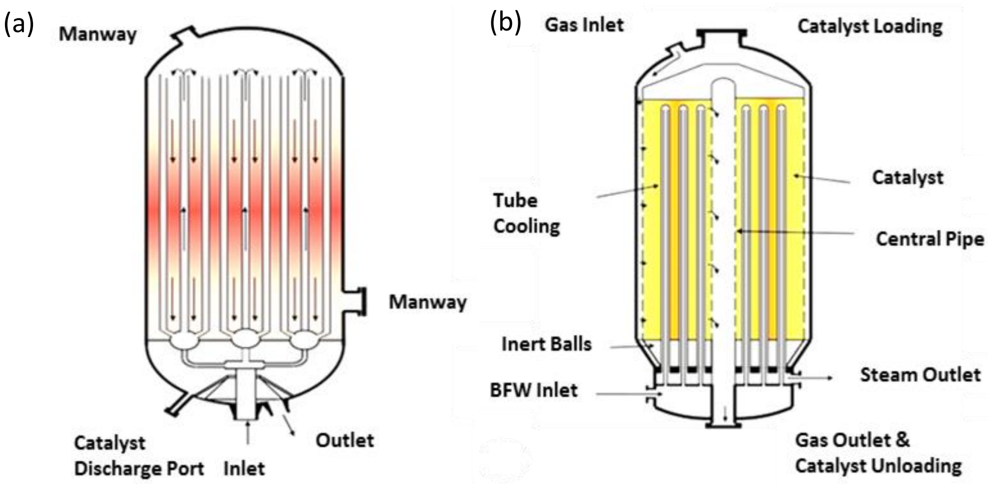


Figure 26: Tube Cooled Converter (a) and Toyo MRF-Z ™ Converter (b)

The *Linde isothermal reactor*, known as the *Variobar converter*, is a fixed bed reactor with indirect heat exchange suitable for endothermic and exothermic catalytic reactions. This reactor (Figure 27) provides the benefits of a tube reactor while simultaneously avoiding the heat tension problems of a straight tube reactor. Isotherm Reactor Gas/gas, gas/liquid and liquid/liquid reactions can be carried out. The palpable head of gases and liquids as well as the latent evaporation heat can be used for cooling or heating operations. The heating or cooling tube bundle embedded in the catalyst transfers the reaction heat in such a way that the catalyst can work at an optimum temperature. This results in higher outputs, a longer catalyst lifetime, fewer by-products as well as efficient recovery of the reaction heat and lower reaction costs. The development of the Linde reactor was carried out with a particular view toward exothermic reaction and steam generation [86].

Mitsubishi Gas Chemical in collaboration with *Mitsubishi Heavy Industry* has developed an isothermal reactor known as the *MGC/MHI Superconverter*. This reactor design (Figure 27) uses double-walled tubes that are filled with catalyst in the annular space between the inner and outer tubes. The feed syngas enters the inner tubes and is heated as it progresses through the tube. The gas then passes downward through the catalyst bed in the annular space. Heat is removed on both sides of the catalyst bed by the boiling water surrounding the tubes as well as by the feed gas introduced into the inner tube. A high conversion rate (about 14 % methanol in the reactor outlet) is cited for this reactor [12].

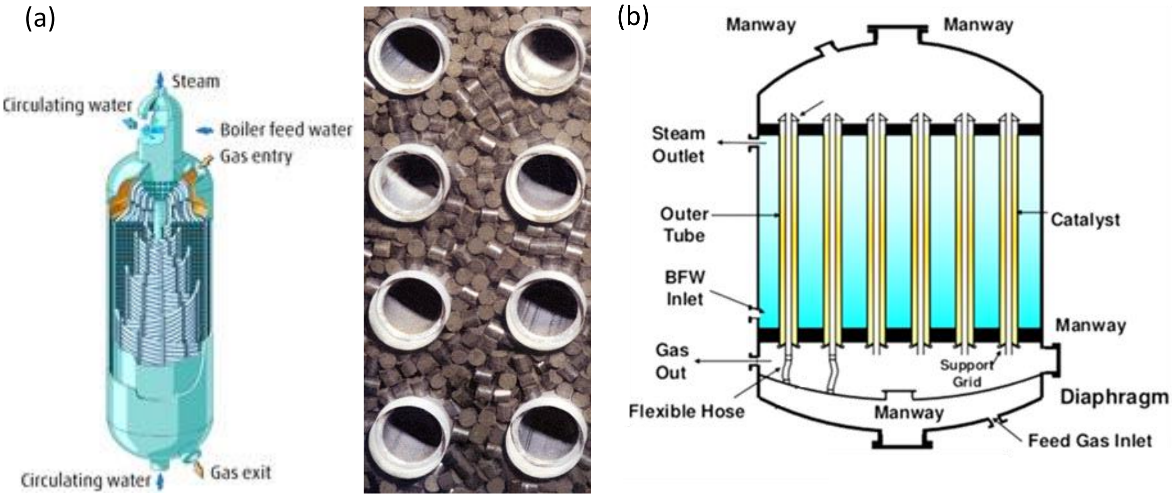


Figure 27: Linde Isothermal Reactor (a) and MGC/MHI Superconverter (b)

Additional methanol converter designs include technologies using three phase systems similar in principle to the slurry reactors used for Fischer Tropsch synthesis (FTS). These technologies are collectively known as *Liquid Phase Methanol Synthesis*. *ChemSystems, Inc.* and *Air Products and Chemicals, Inc.* with US Department of Energy (DOE) funding developed a *liquid-entrained catalytic reactor* for converting low $H_2/(CO + CO_2)$ ratio syngas into methanol known as *LPMEOH™* (Figure 28). The ability to convert low stoichiometric ratio (CO rich) syngas lends itself to using syngas from coal or biomass gasification for methanol production. The three-phase slurry reactor provides better temperature control by uniformly dissipating the heat of reaction into the high heat capacity liquid. The LPMEOH™ process uses a supported Cu/ZnO catalyst (20-45 wt%) dispersed in circulating mineral oil with reactor temperatures of 225-265°C and a pressure of 50 bar [12].

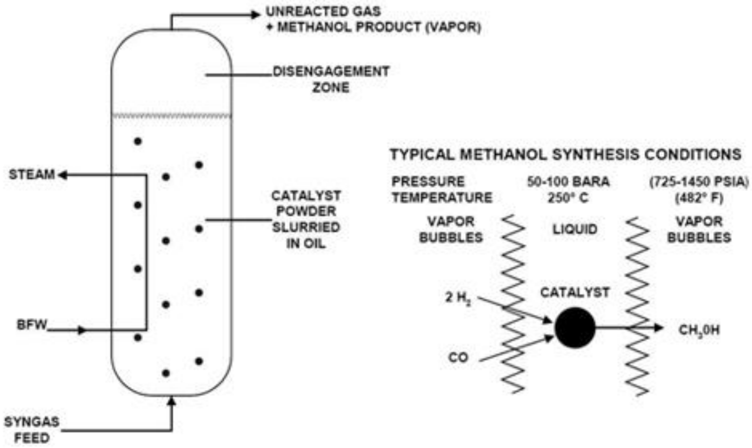


Figure 28: LPMEOH™ Converter and reaction schematics

Two other methanol conversion processes are based on systems in which the product methanol is continuously removed from the gas phase by selective adsorption on a solid or in a liquid. The *Gas-Solid-Solid Trickle Flow Reactor (GSSTFR)* utilizes an adsorbent such as SiO_2/Al_2O_3 to trap the product methanol. The solid adsorbent is collected in holding tanks and the methanol is desorbed. In the *Reactor System with Interstage Product Removal (RSIPR),* a liquid solvent is used to adsorb the product methanol [12].

3.5 Methanol Recovery

Depending on the desired quality of the final methanol product (Table 14), the purification section consists of a number of distillation towers. To produce DME or MTO-grade methanol, only a single column is required to remove the dissolved gases and some of the light by-products. To produce refined methanol for chemical or fuel usage, for example Grade AA and IMPCA (International methanol producers and consumers association) methanol, a two or three column refining system is used. In the first stabilizer column, dissolved gases and very light by-products such as DME and ketones are stripped off. In the subsequent columns, methanol is separated from water and higher alcohols. Especially the separation of ethanol and methanol requires a substantial number of trays. If a three-column layout is used, the first concentration column operates at a slightly elevated pressure, permitting the use of the condensation duty as reboiler duty for the second concentration column. This layout reduces the energy consumption for purification of the methanol [80]. Typically, a 3-column system has a recovery efficiency of 99%, while the 2-colomn system has a recovery efficiency of 98.5%.

Table 14: Quality of methanol products [80].

Methanol quality	Grade A	Grade AA	IMPCA
Acid (ppm max)	30	30	30
Acetone (ppm max)	30	20	-
Ethanol (ppm max)	-	10	50
Water (ppm max)	1500	1000	1000
Non-volatile substances (mg/L)	100	100	8
Density (20°C, g/ml)	0.7928	0.7928	0.791-0.793

3.6 Existing bio-MeOH Plants

Natural gas reforming is the primary source of syngas for MeOH synthesis. However, methanol can also be produced from other carbon-containing feedstock, including biogas, biomass, waste streams and CO_2. Bio-methanol (also called renewable methanol) is chemically identical to conventional methanol. The main advantage of bio-methanol is the reduction of fossil fuel use and greenhouse gas emissions compared to conventional methanol production, and the possibility to use a broad range of renewable feedstocks (virgin or waste biomass, non-biogenic waste streams, or even CO_2 from flue gases). These feedstocks are converted (typically through gasification) into syngas that is conditioned through several steps to reach the optimal composition for methanol synthesis. At present, about 200 thousand tons of bio-methanol are produced per year. However, the production cost of bio-methanol is estimated between 1.5 and 4 times higher than the cost of natural gas-based methanol, which, at current fossil fuel prices, ranges from €100/ton to €200/ton. Bio-methanol production costs also depend significantly on feedstock prices, plant set-up and local conditions [87].

Current bio-methanol demonstration projects focus mainly on using waste and by-product streams from other industrial processes as feedstock, which offer the best economics. In Iceland, renewable methanol (*Vulcanol*™) is produced by combing hydrogen and CO_2 by *Carbon Recycling International*. Other potential feedstock includes biogas from landfills or solid organic waste, and bagasse (i.e. milled sugarcane fiber). The current demonstration projects benefit from favorable conditions such as low feedstock prices (glycerin), strong integration with conventional industrial

processes (pulp and paper) or very inexpensive renewable electricity (Iceland). Depending on the presence of such resources, other early or niche opportunities for bio-methanol production exist, e.g. integrated production with bio-ethanol from sugarcane, co-feeding biomass feedstock and fossil fuels, and co-production of heat, electricity and other chemicals [87].
The use of locally grown biomass for methanol production can make countries less dependent on fossil energy imports, reduce greenhouse gas emissions compared to methanol production from fossil fuels, and could stimulate local economies and employment. Co-feeding of renewable feedstock in natural gas or coal-based methanol production facilities can be used to gradually introduce bio-methanol production and reduce the environmental impact of the conventional methanol production [87].

Existing and planned methanol, ethanol and DME generation plants, from syngas originated from biomass are illustrated in Table 15 and some of them are discussed below.

BioMCN in the Netherlands used an innovative process to synthesize MeOH employing the gasification of crude glycerin for more than ten years. The crude glycerin from biodiesel plants is transported to the *BioMCN* plant. This was then purified, evaporated and cracked to obtain syngas, which was further employed to generate MeOH. The production capacity of *BioMCN* in Farmsum, was about 450,000 tons of bio-methanol annually. However, this process is not currently in operation. The company recently invested in a new method for the production of bio-methanol from biogas that will lead to a substantial reduction in CO_2 emissions [81].

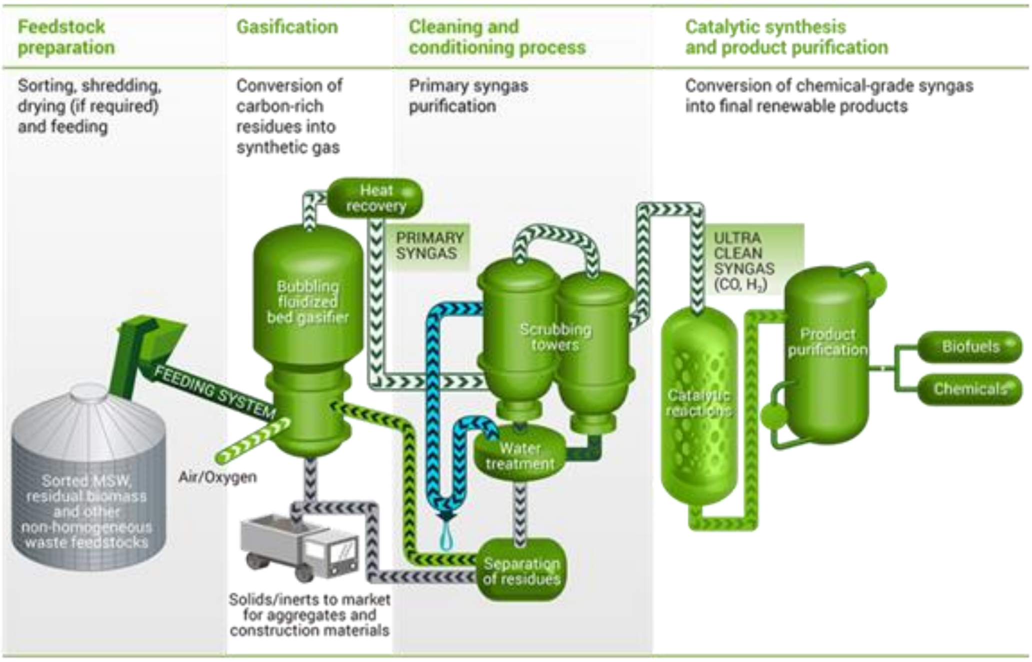
Enerkem develops renewable biofuels and chemicals from municipal solid waste. The company's process uses relatively low temperatures and pressures, which reduces energy requirements and costs. Its process and business model are designed to profitably produce cellulosic ethanol from a large municipal solid waste supply using proven, well-established and commercially available catalysts. Its exclusive process first requires the production of methanol as a chemical building block for the production of ethanol. *Enerkem* can also sell its methanol as an end-product, or use it as a key intermediate to produce other renewable chemicals. *Enerkem's* clean technology platform is a 4-step thermochemical process shown in Figure 29. In the medium to long term, *Enerkem's* platform is being expanded to the following products through its R&D team and partners: Acrylic acid, n-propanol, propionic acid, acetic anhydride, dimethyl carbonate [88].

Table 15 Worldwide existing and planned bio-MeOH, bio-EtOH, bio-DME production plants (2017) [81,87].

Company	Start-up year	Product	Capacity (kt/y)	Scale	Feedstock	Status
BioMCN, The Netherlands	2010	MeOH DME	200	TRL 8 Commercial	Glycerin	Stopped, currently from biogas
Enerkem, Sherbrooke	2003	Methanol, Ethanol	0.4 0.3	TRL 4-5 Pilot	Treated wood, MSW	Operational
Enerkem, Westbury	2009	Ethanol, Chemicals	4 1	TRL 6-7 Demo	Treated wood, MSW	Operational
Enerkem, Edmonton Waste-to-Biofuels Project	2014	Ethanol, Methanol, Chemicals	30	TRL 8 Commercial	MSW 100000 dry metric tons	Operational
Enerkem Vanerco	2017[a]	Ethanol	30	TRL 6-7 Demo	Treated wood, MSW	Planned
Karlsruhe Institute of Technology (KIT),'Bioliq project'	2014	DME, gasoline	0.6	TRL 4-5 Pilot	Straw	Operational
Carbon Recycling International, Iceland	2011	Renewable Methanol	4	TRL 6-7 Demo	Flue gas CO_2 (not biomass)	Operational
Varmlands Metanol, Sweden	2015	Methanol	100	TRL 8 Commercial	Forest residue	On Hold
Woodspirit, The Netherlands	2017	Methanol	400-900	TRL 8 Commercial	Wood	On Hold
DeBioM, Germany	-	Methanol	-		Wood	Planned
LanzaTech	2013	Ethanol[b]	0.3	TRL 6-7 Demo	Industrial off-gas (not biomass)	Operational

[a]Planned to start the constructions

[b]Produced from syngas fermentation



* Municipal solid waste

Figure 29:: Flowchart of Enerkem's 4-step thermochemical process [88]

3.7 Methanol applications

- Marine fuel

Methanol is a clean-burning marine fuel that can cost-effectively meet the shipping industry's increasingly stringent emissions regulations. New environmental regulations from the International Maritime Organization (IMO) and other governing bodies are requiring ships to decrease emissions of sulphur oxides (SOx) and nitrogen oxides (NOx). With its clean-burning qualities, methanol can reduce or eliminate these smog-contributing emissions, which can help improve air quality and related human health issues. Interest in methanol as a marine fuel is growing globally and methanol is being used in a number of projects and commercial activities around the world [89].

- Vehicle fuel

Across the world, methanol is emerging as a clean, sustainable transportation fuel of the future. It can be used on its own as a vehicle fuel or blended directly into gasoline to produce a high-octane, efficient fuel with lower emissions than conventional gasoline. Methanol can be blended with gasoline in low-quantities and used in existing road vehicles, or it can be used in high-proportion blends such as M85-M100 in flex-fuel or dedicated methanol-fueled vehicles. Technology is also being commercialized to use methanol as a diesel substitute. In China, methanol-gasoline blending has grown rapidly due to methanol's favorable economics, clean-burning benefits and energy security benefits. China's federal and provincial governments have implemented programs and fuel-blending standards in many provinces to promote methanol as a fuel. Some countries in Europe are also using gasoline blended with small quantities of methanol. Other countries, including Australia and Israel, have completed commercialization activities to support the commercialization of methanol fuels [89].

Table 16 Proposed mixing ratios for methanol with conventional petroleum products for use in transportation sector [82]

Name	Mixing	Required Modifications
M3	3% methanol, 2-3% solubilizers 94-95% motor fuel	Alteration to vehicles or fuel distribution systems not required
M15	15% methanol & solubilizers 85% motor fuel	Alteration to vehicles and fuel distribution systems
M85	85% methanol 15% C_4-C_5 hydrocarbons to improve cold-start properties	Alteration to vehicles and fuel distribution systems
M100	100% methanol	Substantial alteration to vehicles

Table 16 presents four mixing ratios most often proposed for direct use of methanol in the transportation sector: methanol fractions of up to 3% (M3) does not require any modifications to the vehicle, while admixing 3-15% methanol (M15) requires adaptation of fuel system materials (plastics) that come directly into contact with methanol. However, these modifications are relatively cheap and easy to install to any modern motor vehicle [82].

- Methanol-to-Gasoline

Another modern technology for gasoline production is the catalytic upgrading of methanol in the methanol to gasoline (MTG) process. Methanol has been successfully converted into a range of olefinic and aromatic hydrocarbons using different solid acid catalysts like zeolites and phosphate based catalysts. The technology is therefore being modified towards limiting the reaction selectivity to these compounds with enhanced selectivity to gasoline range alkanes [90]. Several MTG commercialization units are considered in different parts of the world. Mobil Oil Corporation commercialized a plant in New Zealand in 1987. TOPSOE technology (TIGAS process) was also one of those early commercial MTG processes. Recently, the Exxon Mobil and Uhde Corporation escalated the New Zealand technology to planned new plants in the United States [90]. The MTG process occurs in two steps. First, crude methanol (with around 17% water) is super-heated at 300°C and partially dehydrated over an alumina catalyst at 27 bar to yield an equilibrium mixture of methanol, dimethyl ether, and water (75% of the methanol is converted). This effluent is then mixed with heated recycled syngas and introduced into a reactor containing ZSM-5 zeolite catalyst at 350-366°C and 19-23 bar to produce hydrocarbons (44%) and water (56%). The overall MTG process usually contains multiple gasoline conversion reactors in parallel because the zeolites have to be regenerated frequently to burn off the coke formed during the reaction [12].

The MTG reactions may be summarized as follows:

$2\ CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$

$CH_3OCH_3 \rightarrow C_2$-$C_5$ olefins

C_2 - C_5 olefins → paraffins, cycloparaffins, aromatics

- Methanol-to-Olefins

Olefins such as ethylene, propylene, butene, etc., serve as the raw material for modern chemical manufacturers. They are also employed to produce diverse chemicals (benzene, isopropyl benzene, styrene, etc.), all of which are of high commercial importance. Along with the MTG process, Mobil developed several other processes for converting methanol to hydrocarbons based on zeolite catalysts. Since light olefins are intermediates in the MTG process, it is possible to optimize the methanol to olefins (MTO) synthesis. Higher reaction temperatures (~500°C), lower pressures, and lower catalyst acidity favor light olefin production. The rate of olefin production could be modified so that 80% of the product consists of C_2 to C_5 olefins rich in propylene (32%) and butenes (20%) with an aromatic rich C_{5+} gasoline fraction (36%). The process can also be modified for high ethylene and propylene yield (>60%) [12].

- Methanol-to-MTBE

MTBE $(CH_3)_3COCH_3$ is a volatile, flammable and colourless liquid, mildly soluble in water, which increases the octane number of gasoline and is used as a gasoline additive. Typically, more than 95% of MTBE production ends up as a gasoline additive. It also finds applications in the petrochemical industries for isobutene synthesis and in hydrocarbon industries as a solvent. At a commercial level MTBE production units consist of reaction and refining sections. It is synthesized when isobutene reacts with MeOH over an acidic catalyst, at a temperature range of 30 to 100°C and pressure range of 7 to 14 bar. The reaction takes place in liquid phase and is exothermic.

$$i\text{-}C_4H_8 + CH_3OH \rightarrow (CH_3)_3COCH_3,\ \Delta H = -37\ \text{kJ/mol}$$

The most commonly used catalysts are zeolites (H-ZSM-5), solid acids and macroporous sulphonic acid ion exchange resins (Amberlyst-15). A molar excess of methanol is used to increase isobutene conversion and inhibit the dimerization and oligomerization of isobutene. At optimum reaction conditions, MTBE yields approaching 90% can be achieved [12].

- Methanol-to-Acetic acid

Acetic acid, CH_3COOH, is one of the most important chemicals produced from MeOH. Bio-methanol carbonylation is responsible for around 50% of acetic acid synthesis around the globe.

$$CH_3OH + CO \rightarrow CH_3COOH$$

It is precursor to synthesize terephthalic acid, vinyl acetate and acetic anhydride, which are further employed to manufacture latex emulsion resins, adhesives, paper coatings, cellulosic plastics, cellulose acetate fibers, etc. Acetic acid is synthesized by carbonylation of MeOH by CO in the presence of catalysts (Rh, Co, Ni), promoted by iodine. This is one of the most vital applications of homogeneous catalysis in industrial scale. *BASF's* and *Monsanto's* processes are two commonly employed liquid phase routes to synthesize acetic acid. The *BASF* process uses a Co/iodine catalyst at process conditions of 250°C and 500-700 bar with 90% selectivity to acetic acid (from methanol). The Monsanto process uses a Rh/iodine catalyst at process conditions of 180°C and 30-40 bar with over 99% selectivity. However, the chemical environment in this process is extremely corrosive and necessitates the use of expensive steels as construction materials. The high cost of Rh catalyst is another issue with this technology [12].

- Methanol-to-Formaldehyde

Formaldehyde, CH_2O, or methanol, is one of the most important products from MeOH. It is precursor to numerous chemical products and finds its largest application in the production of industrial resins. It is commercially produced by the catalytic partial oxidation of methanol with air.

Most of the commercial processes use MeOH mixed with air (1:1) passed through a thin fixed bed over Ag catalysts at slightly above atmospheric pressure and temperature of 600°C. Other commercial processes employ iron molybdate [$Fe_2(MoO_4)_3$] as catalyst, requiring a lean blend of MeOH and air. It is more exothermic and hence constant heat removal is mandatory to avoid volatilization of molybdenum oxide which decreases process selectivity [12].

$CH_3OH \rightarrow CH_2O + H_2$, $\Delta H = -84$ kJ/mol

$CH_3OH + \frac{1}{2} O_2 \rightarrow CH_2O + H_2O$, $\Delta H = -159$ kJ/mol

- Methanol-to-Ethanol

Selective conversion of MeOH and CO to an acetate-ester was achieved at the bench scale since 2008. This process was optimized for yield and selectivity and has since been scaled up at the demonstration facility in Westbury Quebec utilizing methanol produced from waste products at this same facility. The Enerkem *carbonylation process* is the first of two steps in Enerkem's proprietary methanol-to-ethanol conversion process. This process has been piloted at Enerkem's fully integrated Westbury demonstration facility. *Hydrogenolysis* utilizes hydrogen produced in the gasification process to split the ester into two moles of alcohol. This process has also been scaled up and fully integrated with the carbonylation process at the Westbury demonstration facility. *Enerkem's* exclusive waste-to-ethanol process has a key advantage over competing ethanol production technologies in that the final ethanol product does not need to be separated from water. Ethanol produced at the Westbury demonstration methanol-to-ethanol facility has been certified to meet ASTM-D4806 for fuel grade ethanol. Another key aspect of the methanol-to-ethanol demonstration completed is that all process steps required for the full scale methanol-to-ethanol process including intermediate separation and recycle streams have been operated together at this facility to produce the certified ethanol product. The yield of ethanol has also increased about 6% from initial projections to 380 liters of ethanol per dry tonne of waste entering the gasifier [12].

- Methanol-to-Propylene (via DME)

Over the last few decades, advances in chemical science have vastly expanded the use of propylene across a vast array of chemicals. Polymer-grade propylene is a feedstock for polyolefins, acrylates, methacrylates and acrylonitrile. Chemical-grade propylene is used for large commodities like oxo alcohols, propylene oxide and phenol. The *Lurgi MTP™* process combines an efficient reactor system and a very selective and stable zeolite-based catalyst. To produce propylene, methanol is first fed to an adiabatic DME pre-reactor, where it is converted to DME and water. The methanol-water-DME stream is then routed to the MTP reactor along with steam and recycled olefins, producing a propylene-rich mixture containing various hydrocarbons [12].

- Methanol-to-DME

Dimethyl-ether (DME) is one of the most useful derivatives of MeOH and it is currently produced mainly from methanol dehydration in the presence of an acid catalyst. The methanol-to-DME process is described in the following section.

4. DME synthesis

Dimethyl-ether (DME) is one of the most useful derivatives of MeOH with diverse applications such as paints, agricultural chemicals, cosmetics, etc. It can also be employed as a diesel substitute on account of its high cetane number.

DME can be produced by two different approaches, namely 2-stage synthesis (via MeOH) and direct synthesis employing syngas [81]. Today, it is primarily produced from methanol by dehydration in the presence of, for instance, a silica-alumina catalyst. It can also be produced directly from syngas using a dual catalyst system that permits both methanol synthesis and dehydration in the same process unit, without methanol isolation and purification, a procedure that promises efficiency advantages and cost benefits. Approximately 50,000 t/a of DME were manufactured in Western Europe, but DME is now being marketed as a 'multiuse, multisource low-carbon fuel' and major production facilities are being planned around the world. Although usually derived from hydrocarbons, DME can also be made using organic waste or biomass [14]. Moreover, there is a growing interest on direct DME production from CO_2-rich mixture.

The two-steps (indirect) and one-step (direct) DME production processes are relatively well established, with a number of companies proposing the one-step (*Topsoe, JFE Ho., Korea Gas Co., Air products, NKK*) or two-steps (*Toyo, MGC, Lurgi, Udhe*) architecture [91].

4.1 Indirect DME Synthesis

In 2-stage production of DME, first MeOH is produced using a typical methanol synthesis catalyst (e.g. $Cu/ZnO/Al_2O_3$) followed by its dehydration in the presence of an acid catalyst (e.g., γ-alumina or HZSM-5) in MeOH production conditions [81], according to the reactions:

$$2\,CO + 4\,H_2 \rightleftharpoons 2CH_3OH,\ \Delta H = -182\ kJ/mol$$

$$2\,CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O,\ \Delta H = -23\ kJ/mol$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2,\ \Delta H = -41\ kJ/mol$$

The methanol formation from syngas and the DME production from methanol are supported in two separated reactors as shown in the block diagram of Figure 30.

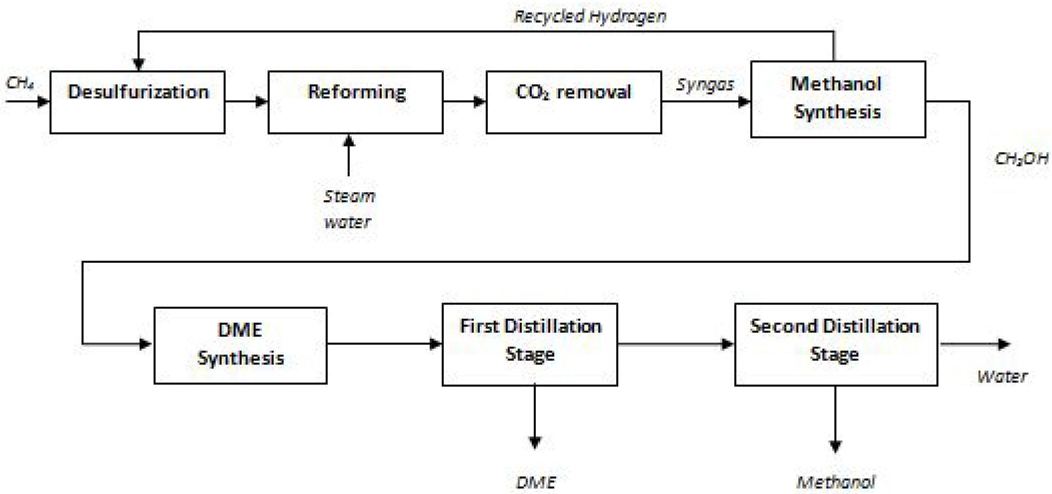


Figure 30: Block diagram of the 2-steps DME synthesis from syngas (via MeOH).

The syngas conversion to methanol is limited by the thermodynamics, especially at high temperatures. Approximately 90% of the methanol is converted to DME which result in a mixture of 10% methanol, 45% DME and 45% water on molar bases. In industrial applications the substances is separated by distillation. The two-stage process is currently considered as the most mature route for DME synthesis. Methanol, however, is an expensive chemical feedstock, making the produced DME very costly. The direct DME synthesis from syngas is an attractive alternative to the two-stage process.

4.2 Direct DME Synthesis

The direct DME synthesis, which proceeds on a single catalyst and in a single reactor, overcomes the thermodynamic constraints of methanol synthesis, leading to higher per-pass CO conversions and higher DME productivities. In addition, the number of process units is reduced and the price of feedstock is disconnected from the methanol market, and this has hence been pursued by several researchers and developers [92].

The direct synthesis of DME is overall somewhat more exothermic than methanol synthesis alone, so again the thermal control is essential.

$3\ H_2 + 3\ CO \rightleftharpoons CH_3OCH_3 + CO_2$, $\Delta H = -246$ kJ/mol

For the DME synthesis, one product in each reaction is consumed by another reaction. Because of the synergy between these reactions, syngas conversion to DME gives higher conversions than syngas conversion to methanol. The typical per-pass and total conversion for the synthesis of methanol, methanol/DME and DME is shown in Table 17, according to Spath et al. [12]. The optimum H_2/CO ratio for DME synthesis is lower than that for methanol synthesis and, ideally, should be around one [12].

Table 17: Conversions for Methanol, Methanol/DME, and DME [12]

Conversion	MeOH	MeOH/DME	DME
Per-pass (%)	14	18	50
Total (%)	77	85	95

Direct DME synthesis requires highly efficient bifunctional catalytic systems which would combine a carbon monoxide hydrogenation function for methanol synthesis and an acidic function for methanol dehydration. The crucial issue in catalyst design could be therefore, optimization of the catalyst composition and interaction between these catalyst components. Both well dispersed copper particles with a high reducibility and large amounts of weak acidic sites are required for preparation of the bifunctional catalysts with satisfactory catalytic performance. The hybrid catalysts for direct DME can be prepared using mechanical mixing of methanol synthesis catalyst and solid-acid catalyst, co-precipitation (sol–gel), impregnation or even more complex methods (e.g. capsule, core–shell catalysts) [93].

It appears that strong interaction between hydrogenation and acidic functions in the catalysts prepared by impregnation and co-precipitation could lead to lower activity and poor stability. The Cu–Zn–Al catalyst for methanol synthesis has been successfully developed several decades ago. The advantages of the Cu/Zn systems include low cost and high selectivity to methanol. The catalyst composition has been carefully optimized in numerous reports. Copper nanoparticles associated with a promoter, i.e. Zn, are usually considered as active phase for methanol synthesis. It is believed that in these nanoparticles copper can be either completely metallic or partially oxidized under the reaction conditions. Other reports suggest, however, that the specific interaction at the Cu/ZnO interface and stabilization of particular Cu morphologies may influence the catalytic performance [93].

Both carbon monoxide hydrogenation to methanol, methanol dehydration to DME and transport phenomena could be kinetically-relevant steps in direct DME synthesis. At the temperature characteristic of direct DME synthesis, carbon monoxide hydrogenation to methanol over copper based catalysts is a reversible catalytic reaction. Recently, major efforts have been dedicated to the design of methanol dehydration active phase in the bifunctional DME synthesis catalysts. The methanol dehydration occurs on an acid catalyst. Alumina has been first used as an acid catalyst for methanol dehydration. The alumina-based catalysts, however, either pure or doped, are relatively sensitive toward deactivation by competitive adsorption of water and also by coke formation. The zeolite based catalysts have several advantages for methanol dehydration to DME with respect to more conventional alumina such as tunable acidity and better stability in the presence of steam. The ZSM-5 zeolite has mostly been used as the acid component in bifunctional DME synthesis catalysts. Other zeolites and microporous materials such as ferrierite, MCM- 22, ITQ-2, IM-5, and TNU-9, polymeric Naflon resins, several microporous silicoaluminophosphates (SAPO-5, SAPO-11, SAPO- 18 and SAPO-34) and phosphorus modified γ-Al_2O_3 have also been investigated. The catalytic performance of the zeolites for methanol dehydration was correlated with the concentration of Brönsted acid sites. In addition to zeolite acidity, other zeolite characteristics such as morphology and porous structure could be also important for the design of efficient catalysts [93].

The activity of the bifunctional catalysts decreases with time on stream due to the deactivation. The catalysts for direct DME synthesis have been susceptible to deactivation by copper oxidation, sintering, coke deposition and contamination with impurities in syngas (see paragraph 1.3) which could also affect the acid sites for methanol dehydration [93]. A typical process flow diagram for the direct synthesis of DME, that is used by *JFE Corporation*, Japan, is shown in Figure 31.

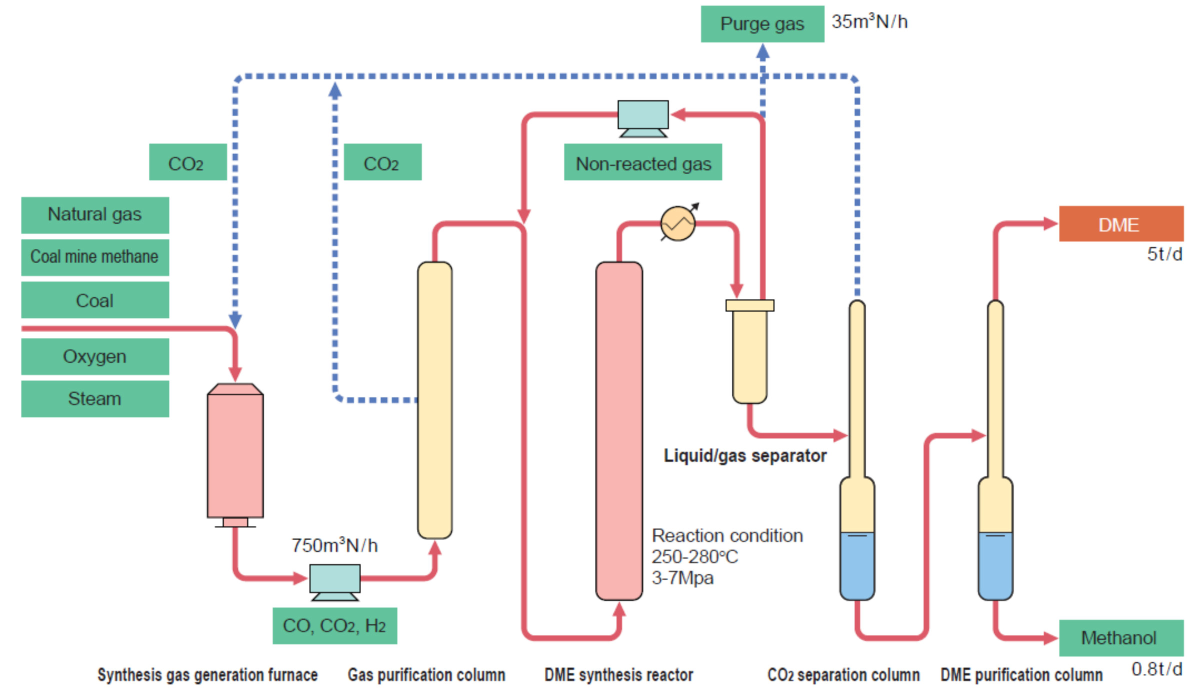


Figure 31: Process flow diagram of DME direct synthesis from coal or natural gas, used by JFE Corporation, Japan [14]

4.3 Commercial DME Production

Among the many applications for DME industrial production, the most interesting are mentioned below: *TOYO company* has developed an indirect DME production catalyst and technology, fabricating a DME synthesis plant able to be installed in methanol production plant. The high performance *MRF-Z® reactor* [94], which has the features of multi-stage indirect cooling and a radial flow to the methanol synthesis unit, has a capacity up to 6,000 ton/day in a single train [94]. The *Lurgi MegaDME process* is a combination of *Lurgi MegaMethanol* (capacity > 5000 tons/d) and a Dehydration Plant.

China is the world leader of DME production and use. Currently, there are various DME to Olefins and DME to Propylene facilities in China, while many other projects are advancing toward completion. Fourteen to fifteen facilities are currently operational. Most of them are based on the double-function ($CuO/ZnO/Al_2O_3$ and HZSM-5) catalyst, developed by the Dalian Institute of Chemical Physics (DICP) for the one-step process [94]. Methanol-to-Gasoline (MTG) is also an emerging demand segment. Today, six plants use the *ExxonMobil's* MTG two-steps technology, with DME as intermediate. *Fuel DME Production Co*, a company of *Mitsubishi Gas Chemical*, has fabricated a DME production plant in Niigata Factory (Japan), with a capacity of 240 tons/d and which is fed by a methanol stream transported by pipelines [93].

4.3.1 Existing bio-DME Plants

The *Bioliq®* pilot plant (see Figure 32) covers the complete process chain required for producing customized fuels from residual biomass [95]. For energy densification of the biomass, fast pyrolysis is applied. The liquid pyrolysis oil and solid char obtained can be processed into intermediate fuels of high energy density. Fuel and chemicals production from syngas requires high pressures. Therefore, syngas production is already performed at pressures up to 80 bar by entrained flow gasification. Gas cleaning and conditioning are conducted at the same pressure at high temperatures allowing for optimal heat recovery and thus improved energy efficiency. In the *Bioliq®* pilot plant the purified syngas is firstly converted into dimethyl ether and then further to gasoline. Innovative approaches, for example single-stage DME synthesis prior to fuel synthesis, are implemented at the *Bioliq®* pilot plant to reduce the length of processes and achieve a continuous increase in economic efficiency. The catalyst, developed by *Karlsruhe Institute of Technology (KIT)* for DME production, is a $Cu/ZnO/Al_2O_3$ @ZSM-5 core@shell catalyst and the typical reaction conditions used for DME synthesis are H_2:CO:CO_2 ratio of 16:8:1, 50 bar, 250 °C. The flow chart of the overall *Bioliq®* process and the fuel synthesis part are shown in Figure 32 (a) and (b), respectively.

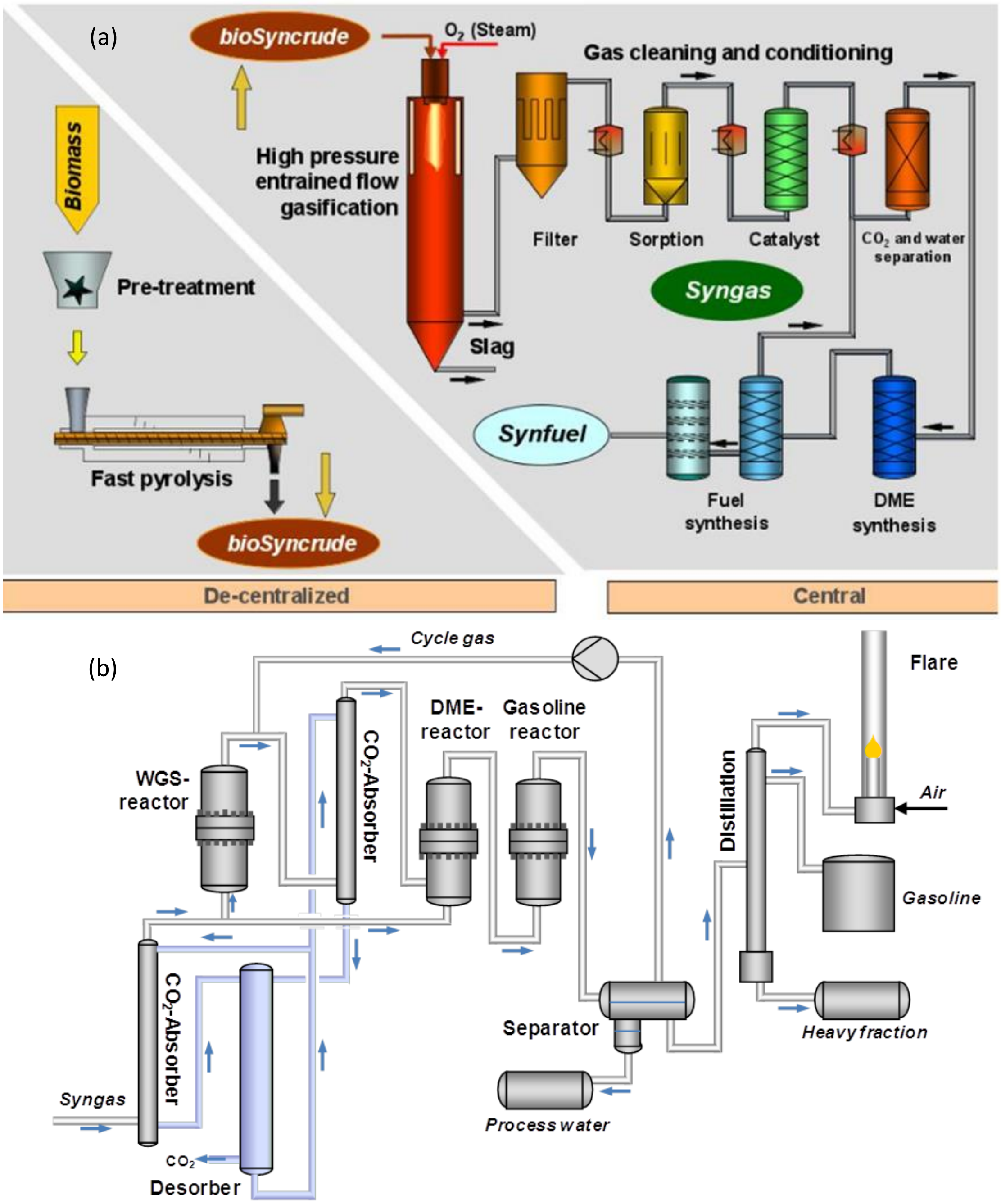


Figure 32: Process flow chart of Bioliq® overall process (a) and Bioliq® fuel synthesis process (b) [95].

4.4 DME Applications

DME generated via biomass gasification derived syngas can be considered a ‘green’ fuel. Its calorific content is almost 1.4 times higher than MeOH [81] and it is mildly toxic (like liquid petroleum gas), but less so than MeOH. However, it does not have any corrosive influence on metals and is not an ozone depleting chemical either. It has a very high potential to be used as cooking gas but can also be employed as a diesel substitute and/or additive on account of its high cetane number, as its combustion prevents soot formation [81].

Currently, the largest use of DME is as substitute for propane as a fuel, especially in China. Other important applications are as a replacement for chlorofluorocarbons as a propellant in aerosol canisters in the cosmetics and paint industry, as blowing agent for foams and insulation boards and as a precursor to dimethyl sulfate by reaction with sulphur trioxide. It can also be used as a feedstock for acetic acid synthesis and as a refrigerant [14]. Also the DME conversion to hydrocarbons is a relevant emerging market. The processes usually known the general terms ‘Methanol-to-Hydrocarbons’ (MTH), ‘Methanol-to-Olefins’ (MTO), ‘Methanol-to-Propylene’ (MTP), ‘Methanol-to-Gasoline’ (MTG) and ‘Methanol-to-Aromatics’ (MTA) are more effective if the starting reagent is DME instead of methanol.

For all these reasons, a projected value of DME market equal to 9.7 billion USD by 2020 is foreseen, with a yearly growth of 19.65% between 2015 and 2020 [96].

5. Higher alcohol synthesis

5.1 Background

The key product of this catalytic process is a mixture of alcohols, including mainly ethanol, propanol and butanol (in case methanol is included in the product pool, the process is called mixed alcohols synthesis). Some developers produce a mix of alcohols for blending whereas others focus exclusively on optimising for ethanol production, selling co-produced alcohols and excess power [78]. Higher alcohol synthesis (HAS) from syngas has a long history of more than 100 years. It has been investigated early in the 20th century after alcohols were obtained as by-product from the Fischer-Tropsch process. However, shortcomings such as poor catalyst selectivity and low product yields have been limiting the commercial capability of such process. In 1913, BASF obtained a patent to produce a blend of mixed alcohols and other organic compounds such as ketones and aldehydes, from syngas. They carried out the process at elevated temperatures (300-400°C) and pressures (100-200 bar) in the presence of alkalized cobalt oxide catalyst. In 1923, Franz Fischer and Hans Tropsch, also developed a process known as 'Synthol' for mixed alcohols synthesis from syngas, over an alkalized iron oxide catalyst at around 450°C and 100 bar. In the 1940s, Du Pont developed an alkalized Mn-Cr catalyst to synthesize methanol and higher alcohols from syngas for commercial purposes. In the late 1940s, Farbenindustrie et al. introduced the Synol process for the manufacture of alcohols from syngas. This process uses pressures of around 200 bar with higher productivity of alcohols by modifying the Fischer–Tropsch alkalized iron catalyst. Natta et al. reviewed the synthesis of higher alcohols from CO and H_2, in 1957 and reported that the synthesis of higher alcohols was always related to the presence of strongly basic substances. The demand for mixed alcohol production from syngas decreased after 1945 with the increasing availability of petroleum and the desire for neat alcohols for manufacturing chemicals [97].

The oil embargo of the 1970s provided incentive for renewed interest in the synthesis and utilization of higher alcohols as a stand-alone transportation fuel or a fuel to be blended with gasoline. Mixed alcohols are a more attractive gasoline blending stock for octane enhancement compared to methanol and ethanol. The higher the octane number is, the less likely is that a spurious ignition will occur. The undesirable properties of using neat methanol as a gasoline additive include high volatility, phase separation tendency when water is present, and incompatibility with certain engine fuel system components. Using mixed alcohols, containing methanol and higher alcohols, avoids these problems. Mixed alcohols have lower vapor pressure, better solubility with hydrocarbon components, improved water tolerance, and higher overall heating value compared to methanol [12, 81]. More importantly, higher alcohols have been identified as suitable blending component for aviation [98], a transport sector with limited alternative fuel options due to the extremely stringent fuel specifications. Mixing 10% of C2-C6 alcohols in jet fuel was shown to meet current jet fuel specifications. The use of the fuel blend in aircraft engines led to reduced emissions, with no compromise in the engine performance [98].

Higher alcohol synthesis has only been developed and tested at pilot scale (TRL 5 to 6). Several companies, including Snamprogetti - Haldor Topsoe - Enichem (SEHT), Lurgi, Dow, IFP, have been involved in HAS research for processes to be used for coal or natural gas as a feedstock without excluding biomass. However, most only demonstrated their technologies at pilot scale. In the 1980's Snamprogetti and Haldor-Topsoe jointly developed an HAS process known as MAS [12]. They started a 12000 tons/y pilot plant, and they sold the alcohol mixture as a 5 vol% blend in a gasoline called SUPER E, which is no longer available. Dow also patented a process known as Sygmal in the 1990's but its continuation is already abandoned. The latest development in IFP's (Institut Francais de Petrole) commercial mixed alcohols process occurred also in the late 1980's when they built their 20 BPD pilot plant in Chiba, Japan and since then no further work has been done towards commercializing their process [99]. In addition, another reason that hindered the commercial prospect of all the aforementioned processes is the economic feasibility of such venture. In some cases, the production of alternative additives was economically preferable such as in the case of Lurgi. More specifically, in the 1990's Lurgi developed the so-called Octamix process in collaboration with Sudchemie which was producing a mixture of alcohols rich in methanol. This additive was eventually certified and a waiver was granted by the Environmental Protection agency (EPA). However, its production was also abandoned due to economic reasons [12]. More recently, Power Energy Fuels Incorporation (PEFI), attempted to commercialize a modified version of Dow's technology, the process was named Ecalene™, although there is no status update since 2006. There are currently no known developers working on mixed alcohols liquids routes; they have either failed or shifted their focus to other synthesis options. Fulcrum Bioenergy, for example, is now concentrating on Fischer-Tropsch synthesis.

It can be concluded that, although the conversion of syngas to methanol over $Cu/ZnO/Al_2O_3$ catalysts is an established, large-scale industrial process, CO hydrogenation to higher alcohols still remains challenging. Despite the substantial amount of research work, the commercialization of the higher alcohols synthesis (HAS) process is still hindered by low yields and poor catalyst selectivity. Single-pass yields amount to around 39% for carbon monoxide conversion to alcohols, and methanol is usually the dominant product [100]. Research needs to increase the single-pass carbon monoxide conversion and the selectivity to alcohols. It also needs to reduce the operating pressure to significantly lower production costs, and reactor designs need to improve for more precise temperature controls. In this chapter, a brief overview of the chemistry, main catalysts, and reaction conditions that have been studied for the HAS will be presented and more detailed information for the synthesis of the most important higher alcohols (ethanol and isobutanol) will be addressed.

5.2 Higher Alcohol Synthesis Chemistry

The most important reactions occurring over the alcohol synthesis catalysts are the alcohols synthesis (C_1-C_6OH), the methanol dehydration to DME and the water-gas-shift reaction:

$n\,CO + 2n\,H_2 \rightleftharpoons C_nH_{2n+1}OH + (n-1)\,H_2O,$ ΔH_1 = -91 KJ/mol to ΔH_6 = -925 KJ/mol

$2\,CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O,$ ΔH = - 23 kJ/mol

$CO + H_2O \rightleftharpoons CO_2 + H_2,$ ΔH = - 41 kJ/mol

The dominant by-product in the higher alcohol synthesis is typically short-chained hydrocarbons:

$$n\ CO + (2n+1)\ H_2 \rightleftharpoons C_nH_{2n+2} + n\ H_2O \qquad \Delta H/n = -154\ KJ/mol$$

The catalysts and process for the higher alcohol synthesis can be divided into 4 main groups [101]:

- Alkali doped MeOH synthesis catalysts high temperature and pressure (Alkali/ZnO/Cr_2O_3) or low temperature and pressure (Alkali/Cu/ZnO).
- Modified Fischer-Tropsch catalysts: Alkali/Cu/Co/M_2O_3 (M = Cr/Al).
- Alkali promoted molybdenum catalysts in sulfide or carbide form.
- Promoted rhodium based catalysts.

Methanol formation is favored at low temperatures and high pressures. At high pressures, the rate of higher alcohol synthesis improves as the temperature is increased at the expense of methanol and hydrocarbons formation. To maximize higher alcohols, the H_2/CO ratio should be close to the usage ratio, which is about 1-2. Higher alcohols are favored by CO-rich feed mixtures because the rate of C-C chain growth increases with increasing partial pressure of CO. High H_2 partial pressures have the effect of inhibiting the rate of C1–C2 chain growth step by enhancing the conversion of C1 intermediates to methanol [101]. In general, the reaction conditions for HAS are more severe than those for methanol production. To increase the yield of higher alcohols, methanol can be recycled for subsequent homologation provided the catalyst shows good hydrocarbonylation activity. Unavoidably, the main reactions stated above produce H_2O and CO_2 as byproducts. WGS plays a major role and, depending on the catalyst's shift activity, some chemical dehydration of alcohols can be undertaken in-situ to produce higher alcohols, esters, and ethers. Thermodynamic constraints limit the theoretical yield of HAS, and as in other syngas-to liquids processes, one of the most important limitations to HAS is removing the considerable heat of reaction to maintain control of process temperatures. Compared to methanol, less alcohol product is made per mole of CO, more byproduct is made per mole of alcohol product, and the heat release is greater. Promotion of Cu-based methanol synthesis catalysts with alkalis, such as Li, Na, K and Cs, shifts the synthesis to higher molecular weight products, however almost always at the expense of CO conversion. The addition of transition metals has also been reported to act beneficially towards higher alcohols formation. Among others, the IFP-developed Cu-Co catalysts, Fe-Cu and Ni-Cu catalysts have been shown to be active in the higher alcohols synthesis reaction. The addition of Mn, Cr, Th, Ce together with alkali compounds to Cu-based ZnO or Cr_2O_3 catalysts improved selectivity to higher alcohols, especially to isobutanol [102].

The mechanism of higher alcohols formation and the nature of the active site(s) still remain unclear. Several different mechanistic routes and reactive intermediates have been proposed in literature and these have been nicely summarized in several older and more recent reviews. It is generally accepted that the reaction mechanism depends on the type of catalyst employed. Over noble metals, modified Fischer-Tropsch and Mo-containing catalysts, the reaction yields mostly linear alcohols, produced via the insertion of non-dissociated CO in $(CH_x)_{ad}$ species formed from the hydrogenation of dissociative CO. This reaction mechanism is often described as 'dual-site' mechanism, where one active site catalyzes CO dissociation and chain propagation, while another site has functionalities for CO non-dissociative activation and insertion [102]. The mechanism is much more complex on Cu-based catalysts and comprises several reaction steps, depending on the metals and promoters used: CO adsorption (associative/dissociative), hydrogenation of the adsorbed CO to formyl species, carbon chain growth via aldol-type condensation of formyl species to acetyl and higher species or CO insertion to form a C–C bond followed by hydrogenation of the intermediate species to produce a complex product mixture consisting of linear and branched alcohols, other oxygenates and hydrocarbons. In this context, the C-C growth over alkali-promoted Cu catalysts has been ascribed to the aldol condensation reactions over basic sites provided by the alkalis. Most studies point out to a common intermediate for the synthesis of methanol and higher alcohols, with syngas or methanol forming a C_1 surface species that further reacts leading to carbon chain growth. There is consensus that the synthesis of methanol and higher alcohols occurs via the same C_1 intermediate, but it is still not clear if the two syntheses share the same catalytic site and the exact nature of this site [102].

5.2.1 Catalyst Selection

Currently there is no commercial catalyst available for the Higher Alcohol Synthesis. A set of criteria to evaluate each catalyst should be developed. The key criteria that should be used in each analysis are per-pass conversion, alcohol yield, product selectivity, operating conditions required, sensitivity to impurities, and cost.

No catalyst is clearly superior when it comes to per-pass conversion. Conversions are dependent on a number of factors, including catalyst formulation, doping agents, syngas impurities, and process conditions. Regardless of the catalyst chosen, recycle of anywhere from ~40 to 90% of the process stream will be necessary to maximize production of mixed alcohols. Both modified methanol and molybdenum catalysts have shown higher alcohol yields than modified Fischer-Tropsch catalysts. The most recent research into process conditions, catalyst formulations, and metal promoters have shown that molybdenum catalysts can outperform modified methanol catalysts in this criterion under certain conditions. Molybdenum catalysts have shown superior performance for higher alcohols synthesis over either modified methanol or Fischer-Tropsch catalysts. The relative benefit of this must be evaluated on an economic basis. The tolerance of molybdenum catalysts to both sulphur and carbon dioxide give it another advantage over the other types of catalysts. These benefits must be weighed against process condition requirements, catalyst costs, and final product specifications to determine the catalyst appropriate for each design. Table 18 illustrates the typical operating conditions, catalytic materials and performance for the higher alcohol synthesis that have been reported by several commercial manufacturers in the past. Taking into consideration the data tabulated in Table 19.

Table 18: Information and typical operating conditions for various higher alcohol synthesis processes reported in the literature [80, 101]

	Modified HP MeOH	Modified LP MeOH	Modified FT	Mo-sulfide	Rh-based
Company	Enichem-Shamprogetti-Haldor Topsoe	Lurgi - Sud Chemie	IPF, Idemitsu Kosan,	Dow Chemicals, Power Energy Fuels, Union carbide	Sagami Research Center, Union carbide
Catalyst	Alkali/ ZnO/ Cr_2O_3	Alkali/Cu/ ZnO/ Al_2O_3	Alkali/CoO/ CuO/ Al_2O_3	Alkali/MoS_2/Co	Rh/SiO_2
P (bar)	70-300	50-100	60-200	30-175	50-175
T (°C)	240-445	275-310	260-340	260-350	200-350
H_2/CO	0.5-3	0.5-1.2	1-2	1-2	1-3
GHSV (h^{-1})	3000-15000	3000-6000	3000-8000	5000-7000	30000-45000
CO_2 sensitivity (%)	6	0-1	0.5-3	7 (plus resistant to S)	0
CO conversion per-pass (%)	5-20	20-60	5-40	10-40	2-40
Products	MeOH, Branched primary Alcohols	MeOH, Primary Alcohols	HC, Linear primary OH	Linear Alcohols (C_1-C_4)	EtOH, MeOH, Methane, oxygenates
Total Alcohol STY (g/kg_{cat}/h)	100-200	100-900	100-850 (g/L_{cat}/h)	115-370	120-240 (g/L_{cat}/h)
C_{2+OH} Selectivity (%)	n.a.	5-40	30-50	20-50	n.a.
Product Alcohol purity (%)	98+	87-95	97.5-99	<97.4	n.a.

Table 19: Benefits and drawbacks of the various catalytic systems used for higher alcohols synthesis

	Modified HP MeOH	Modified LP MeOH	Modified FT	Mo-sulfide	Rh-based
Benefits	• Highest isobutanol production rates than any catalyst group	• Lower pressure requirements	• Greater selectivity for higher linear alcohols than modified MeOH catalysts	• High selectivity towards EtOH • Sulphur resistant (50-100 ppm H_2S in syngas) thus reducing clean-up costs • Less sensitive to CO_2 in syngas	• Mild operating conditions
Drawbacks	• High Pressure & Temperature requirements • Decreased C_{2+}OH yields with CO_2 rich syngas (6%) • High MeOH selectivity	• Higher MeOH selectivity • Decreased C_{2+}OH yields than the HP MeOH synthesis catalyst	• Decreasing H_2/CO ratio increases higher alkane yield • Long term stability and selectivity issues	• High selectivity towards HC and CO_2 • Possible sulphur impurities in the final product	• Not active and selective enough for industrial scale • Easily poisoned by CO_2 • Rh price

5.2.2 Reactor technology

Similar to other syngas conversion processes, one of the most important aspects of HAS is removing the large excess heat of reaction to maintain control of process temperatures, maximize yields, and minimize catalyst deactivation by sintering. HAS is performed in reactors that are similar to methanol and FT synthesis processes. Research and development is being conducted to investigate the use of slurry phase reactors for HAS. *ChemSystems* has conducted a pilot-scale study of isobutanol synthesis in a slurry reactor using a Cs-promoted $Cu/Zn/Al_2O_3$ catalyst in hydrocarbon oil (40 wt% slurry) at 125 bar and 350°C. Other HAS processes based on a 'double bed' configuration have been explored. The idea is to optimize methanol production from syngas in the first reactor using a Cu-based catalyst at a lower temperature. The second reactor usually operates at a slightly higher temperature with a non-Cu Zn-chromite based catalyst to increase the yield of higher alcohols, particularly isobutanol by maximizing the C-C forming steps [12].

5.3 Ethanol synthesis

Ethanol is a key oxygenated compound, which is used as fuel additive, hydrogen carrier for fuel cells, solvent, feedstock, and for a variety of other applications. Currently, ethanol is commercially produced by ethane hydration (catalysed by phosphoric acid) or by fermentation of biomass-derived sugarcane (in Brazil) or corn (in the United States). The catalytic conversion of syngas to ethanol has been widely studied, but only recently it has been practiced at commercial scales. The heterogeneous catalytic processes for converting syngas into ethanol suffer from low C-C bond formation and fast chain growth of the C_2 intermediate. Modification of the catalysts and conditions for the Fischer-Tropsch and methanol synthesis can lead to higher oxygenates [12]. The reaction typically occurs at high temperature (250-350°C) and pressures as high as 200 bar. One of the major difficulties in catalytic synthesis of ethanol from syngas is that the mechanism requires both associative and dissociative adsorptions of CO at close proximity in order to form the C-C bond and increase the oxygenated product selectivity. A bimetallic catalyst, such as Co–Cu, where CO can dissociate at one metal and can be associatively adsorbed on another, can be used. Rh is a unique metal in that respect because it can adsorb CO both associatively and dissociatively. For the same reason, Rh-based catalysts have been shown to have the best selectivity for syngas to ethanol formation. The formation of methane, the most thermodynamically favorable product, poses a significant challenge for this reaction, and researchers are trying to understand the mechanism of methane formation and ways to minimize methanation. Direct production of ethanol and higher oxygenated compounds from syngas is ongoing.

The Institut Francais du Petrole/Idemitsu process based on a copper–cobalt alloy catalyst made ethanol in a 950 t/a pilot plant near Tokyo. The process used steam reforming of natural gas followed by multiple synthesis reactors to give mixed linear C_1–C_7 alcohols suitable for blending. The purity of the alcohol phase was very good [12]. Snamprogetti, Enichem, and Haldor Topsoe (SEHT) used a modified methanol synthesis catalyst (in a 400 t/day plant that operated between 1982 and 1987) in a series of fixed bed adiabatic reactors operated in the temperature range of 260–420°C and pressures as high as 180–260 bar to give mixed alcohols. The crude mixture containing 20% water was purified using three distillation columns; the first column removed methanol and ethanol, the second removed water, while the third recovered C_{3+} alcohols by an azeotropic distillation using cyclohexane. The final water content of the mixed alcohol product was below 0.1%; it was blended at 5 vol% in gasoline and marketed successfully as a premium fuel. In contrast, the Lurgi–Octamix process used a low-pressure, low-temperature modified methanol synthesis catalyst, reported to contain 25–40 wt% CuO, 10–18 wt% Al_2O_3, 30–45 wt% ZnO, and 3–18 wt% promoter oxides. Typical operating conditions used were 350°C and 100 bar. The process gave a 21–28% CO conversion, a 66–79% selectivity to alcohol products, and 17–25% selectivity to CO_2. The selectivity to methanol was 41–58%, but that to ethanol was only 1–9% [12].

An alternative route to upgrade CO rich syngas to ethanol (and 2,3 butanediol), is gas fermentation. CO, H_2 and CO_2 are converted to ethanol by acetogenic autotrophic microbes. These microbes are also able to consume H_2 free streams due to the operation of a highly efficient biological water gas shift reaction occurring within the microbe [103].This reaction allows the bacteria to compensate for any deficiency in H_2 in the input gas stream by catalysing the release of hydrogen from water using the energy in CO. The low temperature, low pressure gas fermentation route benefits from tolerance to a wide variety of impurities and pollutants, eliminating the need for extensive gas clean-up or conditioning. The microbes used in the gas fermentation process convert carbon to ethanol at very high selectivities compared to the conventional chemical synthesis routes. The result is higher overall fuel and thermal efficiency, as well as reduced CO_2 emissions.

5.3.1 Commercial Bioethanol Production

Currently there are not many commercial plants producing bio-ethanol thermochemically. As mentioned previously, Enerkem developed an exclusive process that first requires the production of methanol as a chemical building block for the production of ethanol from municipal solid waste, using relatively low temperatures and pressures.

LanzaTech has developed novel fermentation processes, using a naturally-occurring organism in the family of acetogens, or gas-fermenting organisms (clostridium autoethanogenum), to convert carbon monoxide and hydrogen-containing gases into mainly ethanol. The company has successfully demonstrated its gas fermentation technology at a 300 tons/y demonstration plant with Baosteel in Shanghai, China, and is currently operating a second demonstration plant with Shougang Steel at Caofeidian, China. In Ghent, Belgium, a consortium of ArcelorMittal, LanzaTech, Primetals Technologies and E4tech agreed to start the construction of Europe’s first-ever commercial demonstration facility, in 2017, at ArcelorMittal’s integrated steel plant to create bioethanol from waste gases produced during the steelmaking process. Bioethanol production is expected to start mid-2017. Construction will be in two phases, with phase one providing an initial ethanol capacity of 16000 tons/y by mid-2017 and phase two, which will be completed in 2018, bringing the total ethanol capacity to 47000 tons/y [104].

5.4 Isobutanol

Similar to ethanol, isobutanol also can serve as a clean fuel additive and a neat alternative fuel. Compared to ethanol, higher alcohols are better gasoline substitutes due to their higher energy density, lower hygroscopicity and lower volatility. Although linear alcohols are of interest as chemical intermediates, branched-chain alcohols (such as isobutanol) have higher octane numbers than their straight-chain counterparts. Isobutanol is also known to be a preferred kinetic end product due to its steric hindrance and the lack of two α-hydrogens that are required for chain growth processes via aldol condensation pathways. In addition to its potential application as a transportation fuel, isobutanol has also been considered as a feedstock for the synthesis of a variety of chemicals and fuel additives, such as isobutene, MTBE, and isooctane [12].
Another advantage is that biobutanol has a higher energy content than ethanol, almost 20% more by density. Due to its similarities to conventional gasoline, it is able to blend much better than ethanol with gasoline. It has even shown promise when using 100% biobutanol in a conventional gasoline engine. Besides these, biobutanol experiences a lower chance of separation and corrosion than ethanol. Biobutanol also resists water absorption, allowing it to be transported in pipes and carriers used by gasoline. A very exciting advantage of biobutanol is that vehicles require no modifications to use it. This means that with effective pumping systems, it can be implemented immediately. Currently, funds are quickly rising for biobutanol production and the only requirement is a cheap and fast modification to the ethanol plants which already exist. As yield

efficiencies rise, the cost of biobutanol will continue to drop from its already reasonable price. However, the technology is far from being commercialized due to poor product selectivity (11-14%) [12, 105].

6. Effect of CO_2 in syngas

The typical bio-synthesis gas, that is produced from gasification of wood using gasification, results in relatively large amounts of CO_2 (see Table 1). The effect of CO_2 on catalyst activity for the main oxygenated products (methanol, DME and mixed alcohols) synthesis is discussed first and some novel ideas to overcome this problem are mentioned in this section. As mentioned in Section 2.1.2, the influence of the CO_2 partial pressure on the Fischer-Tropsch catalyst activity is negligible. However, large CO_2 concentration in the syngas should be avoided as it leads to bigger plant size and thus increased cost.

6.1 Effect of CO_2 and Novel Ideas in Methanol Synthesis

As discussed previously in this report, a certain amount of CO_2 is required for methanol synthesis, ideally 3-5%. However, under-stoichiometric gas composition, $(H_2\text{-}CO_2)/(CO+CO_2)$ below 2, should be avoided since it leads to high formation of byproducts and to loss of synthesis gas as increased purge. Relatively low ratio between carbon dioxide and carbon monoxide and a high concentration of carbon dioxide will lead to unfavorable equilibrium, high water concentration in the raw product, low reaction rate and increased rate of catalyst deactivation [80].

A novel idea to by-pass the thermodynamic limitations of the methanol synthesis process, in order to shift the equilibrium towards products formation, is the sorption-enhanced reaction. According to a recent theoretical study, a water adsorbent, such as zeolite 4A can be used for in-situ removal of water. Zeolite 4A is a solid particle with high water adsorption affinity which makes it favorable for water removal or separation. In situ water removal in a gas-flowing solids-fixed bed methanol synthesis reactor contributes to the displacement of water gas-shift equilibrium which increases CO_2 conversion into methanol through a sorption-enhanced reaction process [106].

6.2 Effect of CO_2 and Novel Ideas in DME Synthesis

Indirect DME production comprises the production of intermediate methanol and methanol dehydration in separate reactions. Both reactions are thermodynamically limited which leads to limited DME yield and extensive separations and recycles. The direct DME synthesis proceeds in a single reactor via intermediate methanol, offering a reduction in process steps and an increase in DME yield. The direct DME synthesis is a more efficient process but the need for separation and recycling remains. In the direct DME synthesis, the O-surplus in the feed ends up in CO_2, which means that about equal molar amounts of DME and CO_2 are produced. Since the reaction is equilibrium limited, downstream separation produces recycle streams of syngas CO, H_2, CO_2 and methanol. Syngas and methanol are recycled back to the DME synthesis reactor, while CO_2 needs to be removed.

An interesting and novel process route, based on the use of a solid adsorbent (i.e. CaO, zeolites) for the in situ removal of water, is called sorption enhanced DME synthesis. According *to Le Chatelier's principle*, the removal of one of the products will shift the equilibrium-limited conversion to the product side. The process has been analyzed theoretically, indicating that in situ water adsorption leads to an increased yield and selectivity to DME.

6.3 Effect of CO_2 in Higher Alcohol Synthesis

The effect of CO_2 in higher alcohols synthesis strongly depends on the catalyst type. Unfortunately there are not many references focusing on the hydrogenation of a mixture of CO and CO_2. The effect of the mixture composition on the hydrogenation reaction is important, however, because biomass-derived syngas (as well as syngas from other sources) will contain significant levels of both. In addition, the high levels of steam in syngas as well as CH_4 will also affect the reaction, but there is no available literature in which the effects of varying levels of CO, CO_2, H_2, CH_4 and H_2O on the synthesis of ethanol and higher alcohols are studied [83].

A review by Spivey and Egbebi [101] describes the effect of replacing a portion of CO in the feed with increasing concentrations of CO_2 (up to 25%) on a 1% Rh–Mo/ZrO_2 catalyst. The yields of methanol and ethanol increase at low levels of CO_2, reaching a maximum at about 5–10% CO_2, then declining steadily. This effect was attributed this to the reverse-WGS reaction, which presumably produces additional CO that is converted to the alcohols. Methane yield increases continuously over the range of CO_2 concentrations studied, however. The decline in alcohol yield at higher levels of CO_2 is attributed to strong adsorption on sites that lead to the alcohols, with the reaction then being shifted toward methanation. An alternative explanation is that CO_2 reacts more readily to form methane than CO over the entire range of CO_2 concentrations, causing the monotonic increase in methane yield with CO_2 content. Up to about 20% CO_2, the combined yields of methanol and ethanol follow the conversion quantitatively, meaning that the alcohol selectivity over this range is more constant than the yield alone would suggest. At CO_2 concentrations above 20%, the r-WGS reaction may indeed produce sufficient strongly adsorbing CO to inhibit the reactions leading to the alcohols.

A few recent experimental works that study the effect of CO_2-containing syngas or the direct CO_2 hydrogenation are also summarized in a review by Luk Et al. [83]. According to this review, CO_2 has been found to have beneficial effects when fed in an adequate amount (5–6%), using a set of carbon nanotubes (CNT) promoted Co_3Cu_1 catalysts. Specifically it is reported that an increase in CO conversion (38 versus 27%) and selectivity to oxygenates (71 versus 42%), especially butanol (45 versus 7%), was observed along with the suppression of C_1–C_4 HC (28 versus 50%) and CO_2 (1 versus 7%). Based on characterization by different techniques, CO_2 was reported to play an important role in stabilizing a CoO(OH)/Co_3O_4 composition and increasing the probability of chain termination to form oxygenated products. It also effectively inhibited the WGS reaction. A similar conclusion was also proposed for a K–CoMo catalyst promoted by Co-decorated CNT. In this case, small part of CO_2 enhanced the surface concentration of active Mo (Mo^{4+}) and Co (CoO(OH)/Co_3O_4) species. H_2-TPR also indicated that it prevented the deep reduction of the metals.

In contrast, for a K-Ni-MoS_2 catalyst, it was observed that adding 20 vol% of CO_2 to syngas greatly decreased the CO conversion (from 15 to 5%) and increased the contribution of C1 species, i.e., methanol and methane. Still, a minimal impact was found on the total alcohols and HC selectivity. The optimal H_2/CO ratio was also reported to change upon CO_2 introduction. A value of 0.66 favored HAS by suppressing methanol and HC formation, while the trend reversed at 1.52. Even if the significance of these results is dubious, since 95% of Ni volatilized from the catalyst in form of

Ni-carbonyl species, a clear picture of the effect of CO_2 is not available yet. Mostly, the application of very different CO_2 feed contents and distinct types of HAS catalysts makes a comparison difficult [101].

The effect of CO_2 in syngas over modified methanol catalysts seems to be beneficial for methanol synthesis, but it inhibits higher alcohol formation. For example, no higher alcohols were formed on Cu/ZnO when a feed mix containing only CO_2 and H_2 (with no CO) was used. The inhibition effects of CO_2 on higher alcohols synthesis over Cu-based catalysts was attributed to an increase in the oxygen coverage on Cu surfaces and titration of the basic sites necessary for condensation reactions [101]. Therefore, the removal of CO_2 prior to the alcohol synthesis is crucial.

7. Production costs of FT liquids and oxygenates

In this chapter, the overall efficiency and economics, as reported in literature, of the advanced liquid biofuels technologies that are discussed in this report and have already reached Technology Readiness Level (TRL) of 7-9 from fossil resources, are reviewed. Specifically, the production process of Methanol and FT liquids, as well as DME and Gasoline (via Methanol) are mentioned. This overview provides a clear estimation of the latest production costs of biofuels via biomass gasification. The overall conversion efficiency evaluation is based on the individual conversion efficiencies of four main process steps; biomass pre-treatment, biomass gasification, syngas conditioning and purification and finally desired product synthesis and upgrading. The production cost estimation comprises of the Capital Expenditure (CAPEX), the Operating Expenses (OPEX) and the feedstock contribution.

The reported evaluations are based on overall processes that are optimized in terms of optimal production costs. This includes variations in plant size, gasifiers type and operating conditions, feedstocks, gas cleaning and CO_2 removal, syngas recycling. For detailed process designs and exact specifications of the unit components configurations we refer to the source literature. The fuel calculations (feedstock, biofuel) energy are based on lower heating value, unless stated otherwise. Because different alternative fuels are investigated in this report, costs per unit energy is a good measure for comparison. The production costs mentioned in this section need to be taken with a degree of scepticism, especially when comparing costs from different authors with different models. However, these studies provide some indication about the relative potential of the different fuels.

7.1 FT Liquid Production Costs

Various detailed techno-economic evaluations on the thermochemical conversion of biomass to liquid fuels have been published in the last 15 years. A small selection of the overall economics of FT liquid (C_5 - C_{20}) production, usually in combination with electricity production, is summarized in Table 20. All entries represent individual techno economic evaluations except for the entries 4 and 5. These contain cost estimates (via peer-reviewing by industrial parties) from the Sub-group on advanced biofuels (SGAB) and the international renewable energy agency (IRENA), respectively.

Table 20: Overall production costs of FT liquid via biomass gasification, in €$_{2017}$.

Entry	Products	Scale (MW)	Biomass price	Overall process efficiency (%)	Production costs [a]	Reference
			€/GJ	%	€/GJ	
1 [b]	FT liquid	367	2.10	42-50 [c]	15-32	Tijmensen et al., 2002 [10]
2	FT liquid	400 HHV	3.00 HHV	40-50 HHV	16-30 HHV	Hamelinck et al., 2004 [107]
3	FT liquid	300	4.70	51-57 (~80% with CHP)	18-21	VTT report, 2013 [108]
4	FT liquid	~440	5.60 [d]	40-55	25-39	SGAB report, 2017 [109]
5	FT liquid	75-750	3.50	43	26-44	IRENA report [78]

[a] Cost variations are based on specific process designs (with corresponding efficiencies) at fixed feedstock prices.

[b] Excluding FT crude hydro treatment (0.72 US$/GJ).

[c] Pressurized gasification. For atmospheric gasification: 33-40% LHV

[d] High end of the feedstock cost prices (2.8-5.6 €/GJ) was chosen, probably closest to 2016 price.

Conversions: 1 MWh = 3.6 GJ and dollar to euro exchange rate for each year adopted from [110]

A process size in the range of 300-450 MW (based on biomass input) was used in the evaluated models. The variations in production prices are based on different process configurations that lead to different production prices. FT liquid (C_5 - C_{20}) is considered the main product, which is obtained via hydro-treatment of the C_{5+} fraction of the syncrude. In entry 1, the hydro treatment of FT crude was not included, however an estimated additional 0.75 €/GJ was calculated to be added to the total production price. Some overall conclusions can be summarized as follows:

- Pressurized O_2-blown direct gasifiers (CFB, for instance IGT) were found most suited for FT liquid production due to the formation of little hydrocarbons and costly bio-syngas compression can be avoided.
- Tar scrubbing leaves much hydrocarbons in the product gas giving low FT yield when compared to tar cracking. A reformer (steam or ATR) should then be added to the process. This is also true for low T, atmospheric gasification that produces gas with much energy in the form of hydrocarbons.
- Removal of CO_2 from the bio-syngas is not necessarily beneficial for the overall economics as it provides a higher selectivity and efficiency in FTS, but its investment costs are considerably higher.
- Once through FTS with high (80-90%) per pass conversions are desired. Otherwise, a long recycle of gaseous by-products to the gasifier could be used or recycling via a reformer are required.
- Utilizing waste heat for district heating can improve the efficiency up to 80% (Entry 3).

7.2 Methanol, DME and Gasoline (MTG) production costs

Similar to the FT liquid production costs, a small selection of the overall economics from various detailed techno economic analyses on the thermochemical conversion of biomass to methanol, as well as DME and Gasoline via methanol (MTG) is summarized in Table 21. It should be noted that the costs indicated here come from different studies by different investigators with different assumptions. Most entries represent individual techno economic evaluations that include conceptual design issues, process descriptions, mass and energy balances and production cost estimates. Entries 4 and 9 represent the current economic status of biofuel production, based on available literature data and peer-reviewing by industrial parties.

Table 21: Overall production costs of methanol (DME and MTG included) via biomass gasification, in 2017 €.

Entry	Products	Scale (MW)	Biomass price	Overall process efficiency (%)	Production costs [a]	Reference
		MW	**€/GJ**	**%**	**€/GJ**	
1	Methanol	400 HHV	2.20 HHV	55-57 HHV	10-13 HHV	Hamelinck et al., 2001 [111]
2	Methanol	300	4.70	57-67	16-18	VTT report, 2013 [108]
3	Methanol	230 HHV	5.60	63 HHV	18 HHV 20 LHV	Huisman et al., 2011 [112]
4	Methanol/DME	~330	5.60 [b]	60 LHV [c]	20-25	SGAB report, 2017 [109]
5	DME	300	4.70	56-66	16-18	VTT report, 2013 [108]
6	DME	230 HHV	5.60	60 HHV	19 HHV 21 LHV	Huisman et al., 2011 [112]
7	Gasoline (MTG)	300	4.70	50-57	19-22	VTT report, 2013 [108]
8	Gasoline (MTG)	100	5.00	51-52	30-31	Hannula, 2016 [113]
9	Gasoline (MTG)	75-750	3.50	55	22-33	IRENA report [78]

[a] Cost variations are based on specific process designs (with corresponding efficiencies) at fixed feedstock prices.

[b] High end of the feedstock cost prices (2.8-5.6 €/GJ) was chosen, probably closest to 2016 price.

[c] In case of black liquor gasification the process efficiency and production cost is 70% and 19.2 €/GJ, respectively.

Conversions: 1 MWh = 3.6 GJ and dollar to euro exchange rate for each year adopted from [110]

A process size in the range of 100-400 MW (based on biomass input) was used in the evaluated models. The variations in production prices are based on different process configurations that lead to different production prices. Some of the reports use pressurized direct steam/O_2-blown gasification [108, 112] for the calculations, while others use both direct steam/O_2 gasification and indirect steam gasification [111, 113] for comparison. According to Hamelinck [111], the atmospheric indirect gasifier leads to lower production cost for methanol synthesis, while Hannula

[113] concluded that the type of gasifier does not influence the final Gasoline production cost. Some overall conclusions can be summarized as follows:

- The four large cost determining factors are the biomass price, capital cost, plant size and revenues from sales of district heat.
- Reforming (usually steam) is always considered for methane and remaining tars conversion to syngas. Autothermal reforming is attractive only for facilities that already require oxygen for biomass gasification.
- The cost of DME production is in the same range as Methanol.
- The production of synthetic Gasoline via Methanol (MTG) and DME routes leads to an increase of the investment as well as a decrease in yield and consequently to higher production cost.

7.3 Comparison of Production Costs

The overall conversion efficiency, for all the aforementioned processes, starting from biomass as received, up to ready for delivery product, is in the range of 40-65%. Utilization of the by-products like steam/heat can increase the overall energy efficiency of the plant up to 30% when integrated to district heating or combined heat and power production. Another general observation is that long chain hydrocarbons are more energy consuming products. FT products have the lowest yield from feedstock to product, and for this reason the highest production costs. Production of Methanol (and also DME), on the other hand, have high overall conversion efficiency with relatively low investment costs [109].

In general, two cost elements dominate the cost of production, the capital and the feedstock costs. These two contribute to 75 to 90 % of the total cost of production (typically with a 50/50 split). The cost contribution of CAPEX, OPEX and feedstock to the total Methanol and FT liquids production cost, is shown in Figure 33 (DME production process is considered similar to Methanol). According to the SGAB report [109], for an overall efficiency of Methanol and FT liquids between 55-65 % and 40-55 %, respectively - depending on biomass source and process - the biomass cost contributes largely to the overall production cost. The overall cost of production for Methanol ranges between 20 – 25 €/GJ, while for FT liquids it is 25 – 39 €/GJ.

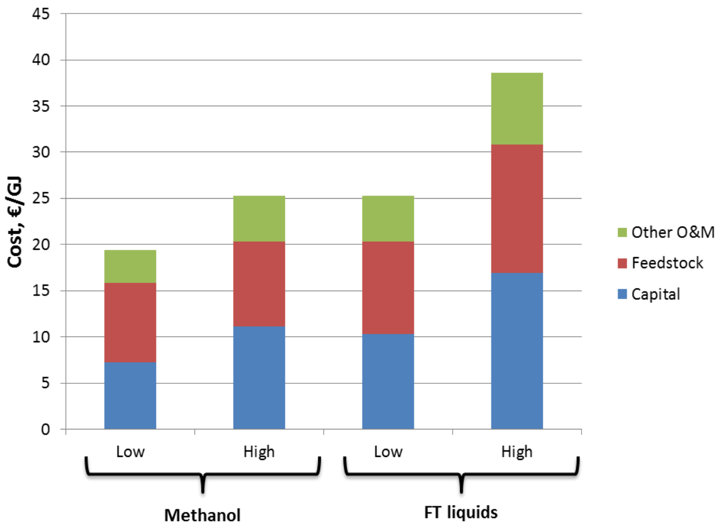


Figure 33: Contribution of capital, feedstock and operational costs to the overall production price (in 2017 €), based on 200MW product output and a feedstock price of 5.60 €/GJ, according to SGAB [109].

8. Discussion and Conclusions

Multiple thermochemical production routes to liquid fuels exist either via one or several synthesis steps. Promising direct conversion routes of biomass derived syngas to liquid fuels, that are based on mature (industrial) technology, include Fischer-Tropsch, methanol and dimethyl-ether synthesis. Indirect gasoline synthesis via methanol or DME is also a promising route, as it is also at an early commercial status from fossil feedstock. In Table 22, the main characteristics and technology status of the advanced liquid biofuels via biomass gasification are reported. Also, efficiencies and cost prices are included for the overall production process.

Table 22: Technology status of the main advanced liquid biofuels via biomass gasification.

Process	Application	Status	General process remarks	Overall production costs and efficiency
Fischer-Tropsch Liquid	Diesel drop-in (60% of the FT liquid), fuel blend	TRL 5-6 (from biomass)	• Per pass conversion up to 80-90% • Low sensitivity to CO_2 and CH_4	25-39 €/GJ 40-55%
Methanol	Platform molecule, Fuel, Fuel additive	TRL 8 (from biomass)	• Up to 10% CO_2 concentration in bio-syngas • > 99.5% selectivity	20-25 €/GJ 55-65%
DME	Fuel, Fuel additive, Platform molecule	TRL 4-5 (from biomass)	• Direct DME synthesis results in high per-pass (>50%) and total (>95%) conversions • Low H_2/CO ratio required (~1)	20-25 €/GJ 55-65%
	Indirect Process (from biomass via intermediate product)			
Gasoline via Methanol (MTG)	Gasoline	TRL 3-4 (from biomass)	• Low aromatic content in Gasoline	22-33 €/GJ 50-55%

One advantage of the FTS is that its products are most equivalent to liquid transportation fuels. Only Co-LTFT (not Fe-HTFT) is considered, due to its high selectivity to liquids (C_{5+} > 80%), while only one hydro-treatment step of the C_{5+} fraction is required to obtain a FT liquid product (FT-L). This distillate blendstock could be considered an end product and be sold in a conventional oil refinery for further processing or it could be fractioned into diesel (drop-in) with naphtha and kerosene as co-products.

All the aforementioned products are referred to as liquid fuels, but MeOH and DME are not only promoted as alternative transportation fuels. MeOH is a high octane fuel that can be applied as a gasoline blend with today's vehicle technology at minimal incremental costs, but is especially attractive as a highly versatile platform molecule for the manufacture of hundreds of chemicals. So its value should not only based on its potential as fuel. DME can be used for domestic cooking and heating, without modifications to equipment or distribution networks and it has also been approved for use in gas turbines. DME's calorific content is almost 1.4 times higher than MeOH and it can be used as a fuel (diesel or propane substitute) but vehicles and gas tanks would have to be modified accordingly. Gasoline synthesis, via Methanol or DME process, is the only viable route to produce drop-in gasoline from biomass gasification. Since it is an indirect process, its benefit is that both MeOH and Gasoline can be marketed as an end product, depending on the demand.

The technology readiness of MeOH/DME/MTG/FTS processes is high (industrial production) when combined with coal or natural gas gasification, but not when integrated with biomass gasification. The bottleneck here is that liquid fuel production via gasification has not yet been shown economically feasible in economic evaluations partly due to the low price of crude oil. For this reason, no money is invested in 200 MW gasification plants. It is not economically feasible due to the high biomass price and high investment costs. Biomass price and capital investments account for 70 to 85% of total production costs and most of the capital investments are in gasification and gas cleaning (roughly 80%). The highest TRL of a biomass gasification to MeOH process is 8 based on the *Enerkem* process.

The FT liquid/MeOH /DME/MTG production processes via biomass gasification can be compared according to current market consensus/techno economic studies. Clearly, both MeOH and DME syntheses are about an order of a magnitude more efficient (overall energy efficiency from biomass to final product) than the production of FT-L, based on the current technological status, while MTG synthesis is in the same order as FTS. This results in an estimated production cost of 20-25 €/GJ for MeOH/DME, 22-33 €/GJ for MTG and 25-39 €/GJ for FT liquid based on studies with similar gasification-gas cleaning trains. Besides production costs, also market prices are important, although highly fluctuating. The MeOH price is about 19.9 €/GJ and the brent crude oil price is 7.3 €/GJ in the EU, market conditions clearly indicate that production of MeOH is more economically feasible.

Table 23: Market spot prices of gaseous and liquid chemical products. Prices are indicative and based on 2017 global prices unless stated otherwise.

	Price	Price range	LHV	Price	Price
	\$/ton	\$/ton	GJ/ton	\$/GJ[a]	€/GJ
Henry Hub	148 (US), 259 (EU)	100-600	47.1	3.10 (US), 5.50 (EU)	2.60(US), 4.60 (EU)
Crude oil brent, EU	381	300-800	43.6	8.70	7.30
Methanol, EU	480	200-600	20.1	23.90	19.90
Ethanol	313	300-600	27.0	11.60	9.70
DME	1.5x methanol		28.9	24.90	20.80
MTBE, global	650	400-700	35.1	18.50	15.40
Ethylene	1080	800-1500	47.2	22.90	19.10
BTX	~650	650-900	40.2[b]	16.20	13.50

	Price	Price range	LHV	Price	Price
	\$/ton	\$/ton	GJ/ton	\$/GJ[a]	€/GJ
Benzene	700		40.2	17.40	14.50
Toluene	800		40.6	19.70	16.40
Slack wax paraffin wax, unrefined, 2015	1300	(800-1500)	~44	29.50	24.60

[a]Calculated: Price (\$/GJ) = price (\$/ton) / LHV

[b]LHV of benzene

Conversion: 1.00 € = 1.20 \$

To sum up

- FTS, MeOH, DME and MTG are mature syngas conversion technologies to liquid fuels production, however not integrated with biomass gasification (probably due to expected production costs and lack of investments).
- Gasoline (MTG) and FT diesel could be directly used as a drop-in fuel. DME and MeOH can be used as fuel additives or replacements.
- Based on process efficiency and production price, MeOH and DME seem the most economically feasible processes. For instance, bio-MeOH has an expected production price of 20-25 €/GJ where the market price is currently 20 €/GJ.
- Other promising bio-syngas catalytic conversion routes to valuable products (not necessarily fuels) include low olefins production via FTO, OX-ZEO or MTO processes, as well as the production of higher alcohols. However, TRL are still low so that justified cost/efficiency comparisons cannot be made.

8.1 Recommendations

The effect on economics of integrating novel gasification and gas cleaning technologies (including MILENA/OLGA) into evaluated production processes should be investigated both for bio-MeOH/DME and FT production. Also, the effect of co-production and isolation of by-products, such as BTX and ethylene, on the production costs should be evaluated. Moreover, extra value in FT could be created, for instance, via co-production of high-value waxes.

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Appendix A Sasol synfuels refinery

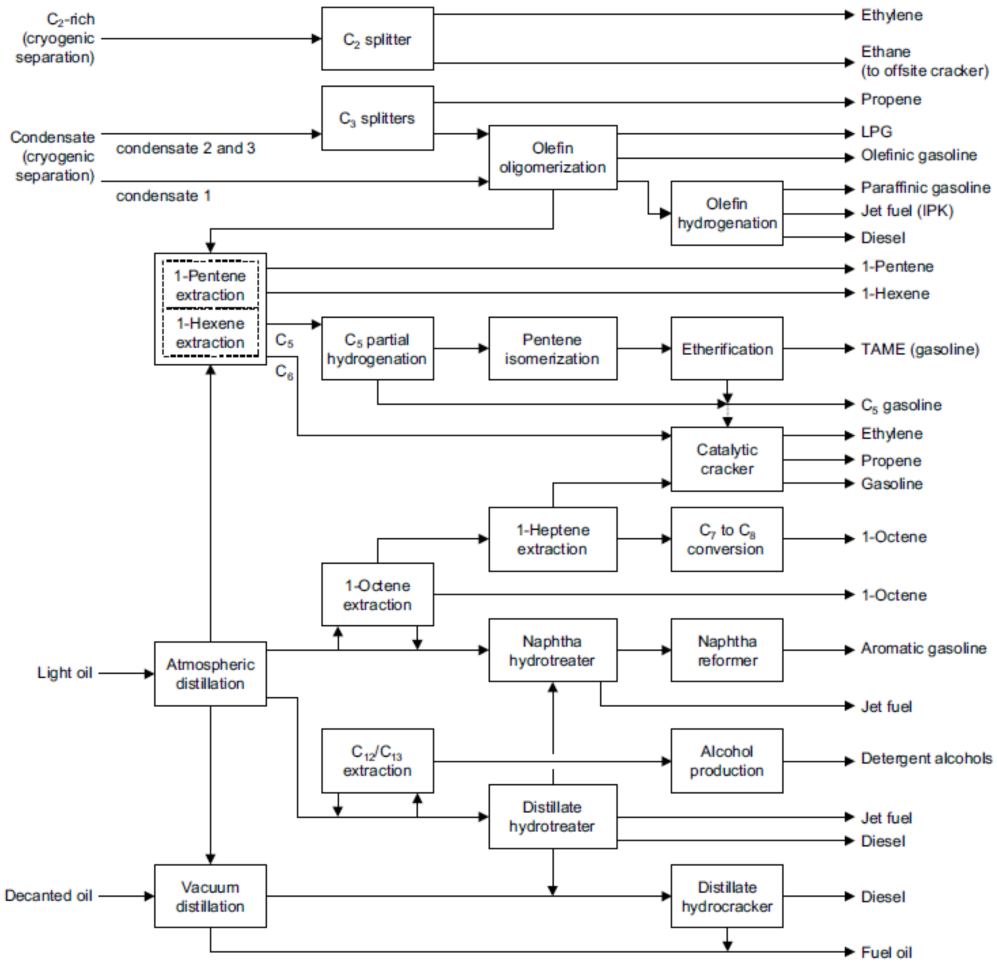

Figure 34: Chemicals and fuels production at Sasol Synfuels [60].

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