

Process comparison of biomass-to-liquid (BtL) routes Fischer–Tropsch synthesis and methanol to gasoline

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Abstract Lignocellulosic biomass is currently seen as a renewable alternative to fossil fuels in the transport sector. There are two possible routes to produce liquid hydrocarbon fuels from biomass via synthesis gas: Fischer–Tropsch (FT) synthesis and methanol to gasoline (MtG). This paper evaluates, based on chemistry and chemical engineering aspects, the process design, the economic feasibility and the process potential for both synthesis routes. FT and MtG reactions can be described under the same overall chemical equation. However, the differences between the two syntheses were found in chemical mechanism, catalyst and product distribution. The material and energy balances do not establish a clear preference for any synthesis route, the market application of the product being a key parameter. The calculated overall chemical energy efficiencies to synthetic liquid hydrocarbons (C_5 – C_{20}) from biomass are 25.8–46.5% for FT and 23.4–44.4% for MtG. The calculated carbon efficiency to synthetic liquid hydrocarbons (C_5 – C_{20}) ranges between 18.6% and 33.5% for FT and 17.3–32.8% for MtG. The production costs for synthetic liquid hydrocarbon fuels

are calculated based on the efficiencies given above. They range between 21€ and 34€ per gigajoule. These values could drop to 18–28€ per gigajoule in the medium term based on optimistic predictions (increase of efficiencies and reduction of capital investment). If the prize difference between crude oil and biomass becomes as high as 20€ per gigajoule, the production of liquid hydrocarbons from biomass will probably become competitive with petroleum-based products.

Keywords Fischer–Tropsch · Methanol to gasoline · Biomass · Material and energy balance

Abbreviations

ASF	Anderson–Schulz–Flory
BtL	Biomass to liquids
CtL	Coal to liquids
DME	Dimethylether
FT	Fischer–Tropsch
GtL	Gas to liquids
HHV	High heating value (MJ/kg)
LTFT	Low-temperature Fischer–Tropsch
MtG	Methanol to gasoline
NC	Carbon number
NZ	New Zealand
r_p	Chain propagation rate
r_t	Change termination rate
$y_{C,frac}$	Molar fraction of a lump of hydrocarbons in mole C
y_i	Molar fraction of component i
X_i	Conversion of component i
α	Chain growth propagation
η	Efficiency

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1 Motivation and background

Today's liquid fuel supply is based to a large extent on hydrocarbons from petroleum. The IEA [1] projects that in the next 25 years, the world demand of liquid fuels will increase more rapidly in the transportation sector than in any other end-use sector. This rapidly growing transport energy demand will cause high and fluctuating oil prizes, an increase in the dependence on the Middle East and higher CO₂ emissions that will aggravate climate change. Therefore, significant changes regarding the raw material basis and processing are necessary, and new fuels produced preferably from renewable raw materials will be needed to replace the present petroleum-based fuels. Biomass is the only renewable alternative to fossil energy sources in the transport sector as long as electric drive systems do not contribute significantly. The production of liquid fuels from biomass via synthesis gas (biomass to liquid, BtL) is considered as a promising process in the short to medium terms, either by Fischer–Tropsch (FT) or methanol-to-gasoline (MtG) synthesis. The raw material basis includes all kinds of lignocellulosic biomass (e.g. wood, agricultural and forest residues), thus reducing competition with food production. An additional advantage of liquid hydrocarbon synfuels (diesel and gasoline) lies in its high potential to reduce CO₂ emissions and in its high quality, which allows their utilization in today's distribution infrastructures and engine technologies.

2 Objective

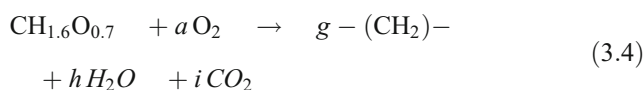
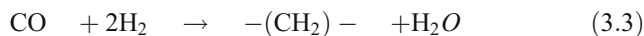
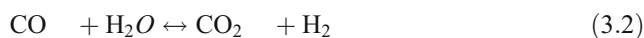
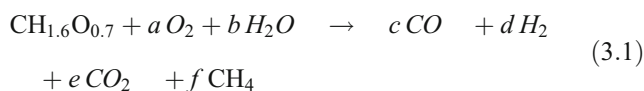
The BtL route describes the gasification of biomass and subsequent gas treatment to produce clean syngas and then hydrocarbons (or maybe alcohols or ethers). Nowadays, there are two major routes in the production of high-quality synthetic transportation fuels from syngas, as shown in Fig. 1. A first alternative is the Fischer–Tropsch synthesis and further product upgrading of the Fischer–Tropsch product. This route is mainly used to produce high-quality diesel. A second alternative is the production of methanol from syngas and its further conversion to gasoline (methanol to gasoline). This route is mainly used to produce a high-quality synthetic gasoline.

The aim of the present study was to evaluate technical and economic feasibility of the two different process routes based on chemistry and chemical engineering aspects. Chemistry and product quality, together with mass and energy balance, are presented and the selectivity and efficiency of both routes are compared. Based on the efficiency values, a simple economic evaluation is performed. Finally, the process potential of both routes is commented and conclusions are drawn.

3 Process description

3.1 Biomass to liquid

The BtL route is a complex process with numerous process configurations. A scheme of the overall process is shown in Fig. 1. The process can be divided into two steps: (1) production of syngas via biomass gasification and (2) synthesis of liquid hydrocarbon fuel from syngas. The conversion of biomass to syngas is done via gasification. A pretreatment of the biomass is needed, and drying is usually the most important process [2]. Nowadays, there are different gasification options including moving bed, fluidized bed and entrained-flow systems [3]. Gasification can take place at atmospheric or elevated pressure, either directly or indirectly heated. An important criterion among the gasification technologies is the source of oxygen to produce CO, which can be air, oxygen or steam. The syngas produced according to Eq. 3.1 consists mainly of H₂, CO, CO₂, CH₄ and some kinds of contaminants (particulates, condensable tars, alkali compounds, H₂S, HCl, NH₃ and HCN) that need to be removed before the synthesis step. A main indicator of the quality of the produced syngas is the H₂/CO ratio, which may range between 0.6 and 0.8 for entrained-flow systems [4, 5] and between 0.6 and 2 for fluidized bed reactors [6, 7]. Under certain considerations, it is desired to increase the H₂/CO ratio of the syngas before it is fed to the synthesis process. This step is referred to as CO shift reaction (Eq. 3.2). If the amount of CH₄ represents a significant part of the heating value of the syngas, methane reforming can be used to convert methane (with steam) to H₂ and CO. The removal of part of the CO₂ produced after the gasification could be needed before the synthesis process. The synthesis of liquid hydrocarbons from syngas can be achieved via the FT reaction or the methanol-to-gasoline process. In both cases, the global equation of synthesis is the same, Eq. (3.3). These two synthesis routes for the production of diesel and gasoline are briefly described in Sections 3.2 and 3.3.



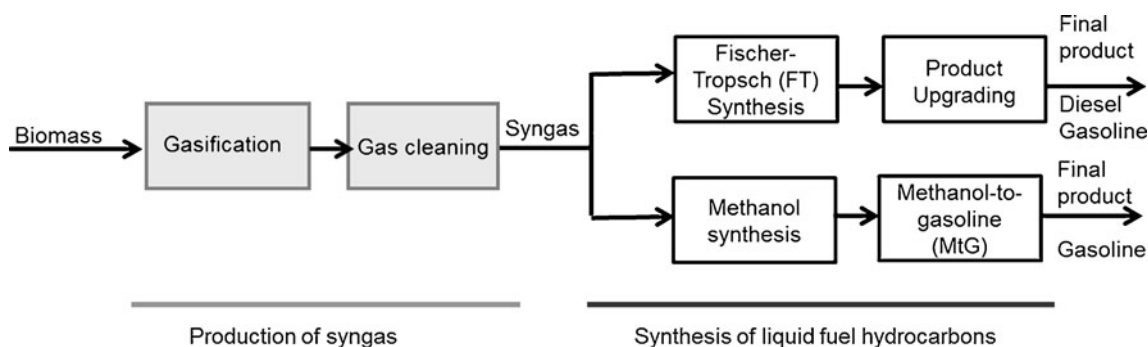


Fig. 1 Routes to synthetic transportation fuels from biomass

Overall, today's technological developments make the first pilot or large-scale plants for BtL production possible [8]. A technical feasible BtL concept is in commissioning in Freiberg, Germany, with a production of 350 bpd (barrels per day) based on FT synthesis [9].

3.2 Fischer–Tropsch synthesis

The synthesis of liquid hydrocarbons from syngas via FT is a well-known process already under use throughout the world in coal and natural gas-based (CtL, GtL) plants. In 2000, the installed CtL capacity was about 140,000 bpd (operated by Sasol). The installed GtL capacity comprised the Shell SMDS plant (14,700 bpd) in Malaysia and the PetroSA plant (former Moss gas, 25,000 bpd) in South Africa. The new generation of GtL plants is located in Qatar. Oryx GtL was started in 2007 (34,000 bpd), and Pearl GtL is currently starting up its production (140,000 bpd).

The FT synthesis is an exothermic, heterogeneously catalyzed polymerization reaction. The key reaction is the hydrogenation of CO under typical FT conditions towards a wide range of mostly linear hydrocarbons and water, Eq. 3.3, with $\Delta_R H^\circ_{250^\circ\text{C}} = -158 \text{ kJ mol}^{-1} \text{ mol}^{-1} \text{ CO}$ [10].

The most active metals for FT synthesis are Co, Fe, Ru and Ni. What these metals have in common is that they are active for hydrogenation reactions and susceptible to metal carbonyl formation [11]. Only Fe and Co are applied in large-scale industrial applications.

Currently, two different reactor technologies have prevailed in commercial low-temperature synthesis (LTFT) where wax is the main product: three-phase slurry bubble column reactors and multitubular fixed bed reactors. In slurry reactors (Oryx GtL), the catalyst is suspended in the liquid product phase and the synthesis gas flows upwards. This system is characterised by high mass and heat transfer rates due to extensive mixing in the heterogeneous hydrodynamic regime. Reactor scale-up and the separation of the catalyst and product are known key problems. In a multitubular fixed bed reactor (Shell, SMDS and Pearl), the catalyst is loaded into

several thousand tubes which are cooled by boiling water in the shell side. The main issue is the heat removal and higher specific cost compared with the slurry reactor.

Several FT reaction mechanisms have been developed based on different assumptions for the CO activation, the formation of monomer species and the addition of monomers to growing chains [12]. The carbide mechanism seems to be the most accepted one to explain the hydrocarbon formation on Co, Fe and Ru catalysts (Fig. 2), though it cannot explain the formation of oxygenates. The monomer of the carbide mechanism is CH_2 (10). CO and H_2 are assumed to adsorb dissociatively (1, 5).

Chain growth reaction (3) occurs by the insertion of the monomer in a growing alkyl species. Termination reaction (4) can take place by the abstraction of hydrogen to an alkene or the addition of a CH_3 species or hydrogen to form an alkane. Under typical FT operation conditions, the chain growth mechanism is kinetically controlled; therefore, the products obtained depend largely on the selectivity of the catalyst. However, the thermodynamics can explain the formation of methane, being the preferred product at all FT synthesis conditions from a thermodynamic perspective [13].

The FT synthesis always produces a wide range of products due to the catalytic C–C and C–H bond formation and C–O bond rupture. The hydrocarbon chain length distribution can be explained by a polymerization reaction. The general product distribution is determined by the ratio of the chain propagation rate (r_p) and the chain termination rate (r_t , Eq. 3.5). A high chain propagation rate will lead to a high-molecular-weight product distribution, whilst a high chain termination rate will yield to predominantly light products. The product distribution can be predicted by an Anderson–Schulz–Flory (ASF) model with the chain growth propagation probability α as single parameter:

$$\alpha = \frac{r_p}{r_p + r_t} \quad (3.5)$$

The value of α is dependent on the reaction conditions and the catalyst type. The distribution of alkanes after the

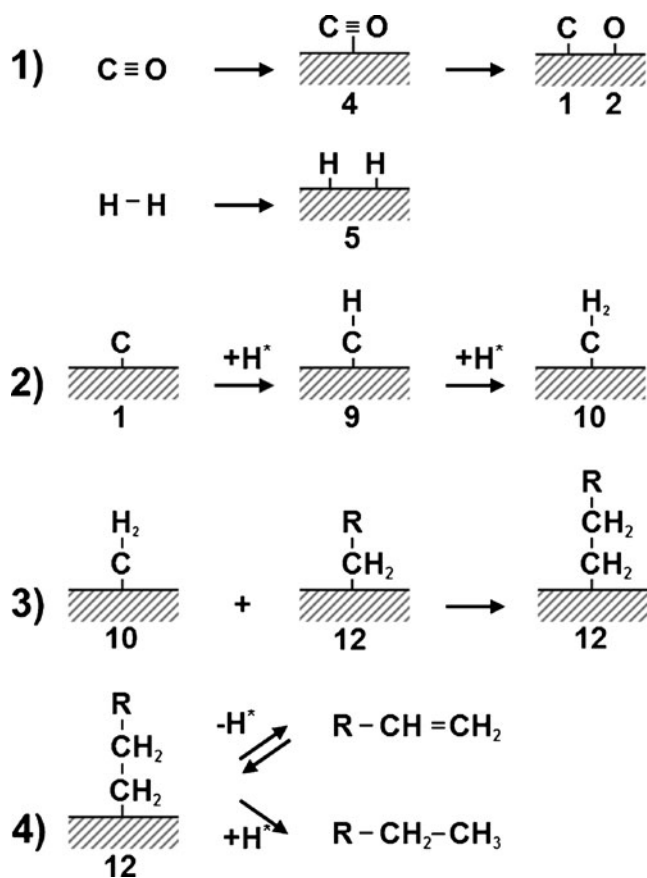


Fig. 2 Carbide mechanism for the FT synthesis [12]

FT synthesis follows an ASF distribution, Eq. 3.6 in molar fractions and Eq. 3.7 in weight fractions.

$$y_{NC} = (1 - \alpha) \cdot \alpha^{(NC-1)} \quad (NC : \text{carbon number}) \quad (3.6)$$

$$y_{C,NC} = NC \cdot \alpha^{(NC-1)} \cdot (1 - \alpha)^2 \quad (3.7)$$

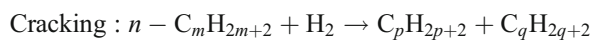
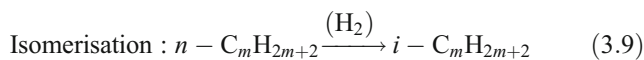
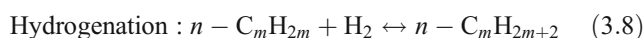
The FT product presents very positive characteristics for the production of high cetane diesel fuel. It is mainly formed by unbranched alkanes and low amounts of aromatics (Table 1). However, the FT synthesis, irrespective of the operating conditions, cannot uniquely produce hydrocarbons in the diesel carbon number range (Fig. 3) [10]. The strategy selected by the new generation FT plants to maximise the diesel yield is to maximise the production of C_{21+} fraction (wax) via FT synthesis using cobalt-based catalysts ($\alpha > 0.9$), minimising the formation of undesired light products. Subsequently, the wax molecules are converted into the desired diesel fraction through a hydroprocessing treatment.

The hydroprocessing step performs four functions [15, 16]: (1) hydrogenation of the alkenes present in the FT product (Eq. 3.8); (2) removal of the small amount of

Table 1 FT product selectivity (%C) with a cobalt-based catalyst at 220°C [14]

	Product selectivity (%C)		
	C_5-C_{12}	$C_{13}-C_{18}$	$C_{24}-C_{35}$
Alkanes	60	95	100
Alkenes	39	5	Low
Aromatics	0	0	0
Oxygenated	1	Low	0

oxygen-containing compounds, mainly primary alcohols; (3) hydroisomerisation (Eq. 3.9); and (4) hydrocracking of the n -alkanes to the desired chain length and/or boiling point (Eq. 3.10).



$$p + q = m ; p \geq 3q \leq m - 3$$

(3.10)

The hydroprocessing of the FT wax requires bifunctional catalysts with both metal and acid sites. Amorphous silica-alumina or zeolites provide the cracking activity and metals provide the (de-)hydrogenation function and are also responsible for heteroatom removal. Nobel or base transition metals from group VIA (molybdenum and tungsten) or group VIIIA (cobalt, nickel) are used in commercial catalysts [17].

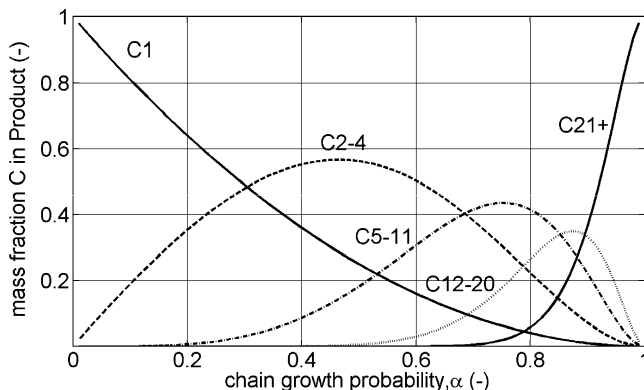


Fig. 3 Molar carbon fractions in different product lumps as function of the chain growth probability, α , calculated with the ASF model

The hydroprocessing operation conditions [15] are typically 30- to 50-bar total pressure and a temperature of about 300–350°C. The H₂ demand for the hydroprocessing step is very modest compared with the synthesis gas requirement for the total process [18]. An advantage of the hydroprocessing operation is its flexibility with regard to the product distribution. However, the coproduction of hydrocarbons in the C_{1–4} fraction implies a reduction in the liquid yield C₅₊ (Table 2). The selectivity values for individual hydroprocessing catalysts are variable, and literature data regarding this point are very limited. Typical selectivity values (wt.%) could be around 4% C_{1–4}, 23% C_{5–9} and 73% C_{10–20} [19]. Considering the chain growth in FT synthesis and the selectivity of the hydroprocessing catalyst, the calculated product distributions of the two-stage concept are shown in Table 2.

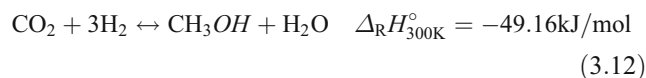
The products obtained after hydroprocessing are pure alkanes, free from impurities such as nitrogen or sulphur and from aromatic species. The products are fractionated in a conventional distillation section (Fig. 4) The fraction boiling above the gas oil range is recycled to hydroprocessing. The naphta fraction (C₅–C₉) is equivalent in quality to ‘straight run’ naphta obtained via crude oil distillation (octane number≈40) and is suitable for blending into gasoline after its octane number has been increased by catalytic reforming. In view of its paraffinic nature, it is also an ideal chemical feedstock [15]. The diesel fraction has excellent combustion properties (smoke point, cetane number) and show low particle emissions. It can be either used in areas with very tight constraints on diesel quality or as blending stock to upgrade lower quality diesel fuel [20]. The characteristics and properties of the FT diesel are compared with the properties of conventional diesel presently sold in the EU (Table 3).

3.3 Methanol to gasoline

The methanol-to-gasoline process belongs to the more general group, methanol-to-hydrocarbons (MtH), which also comprises the methanol-to-olefin (MtO) and methanol-to-propene processes [22]. The criterion for discrimination is the choice of catalyst and reaction

conditions. The MtG technology is based on the conversion of methanol over ZSM-5 zeolite producing a high-quality gasoline. A commercial plant to produce gasoline from natural gas based on the MtG process was constructed in New Zealand (NZ) in 1985, with a capacity of 14,500 bpd. Today, there is only the methanol production part still in operation [23]. Currently, there is renewed interest in the MtG technology. For example, a coal-to-gasoline process via MtG is under construction in China by Jincheng Anthracite Mining Co. (initial capacity of 100,000 tpy (≈2,000 bpd) expected to expand to 1 million tons per year (≈20,000 bpd)). Exxon Mobil recently announced the first US CtL project based on MtG technology. The envisaged plant in Medicine Bow, Wyoming, has a planned capacity of 15,000 bpd. Both plants incorporate significant improvements beyond the earlier NZ plant [24].

The first step in the production of gasoline from syngas is the production of methanol, which is a proven industrial process. However, the mechanism has been the subject of much controversy. The formation of methanol can be described by the following equilibrium reactions, whereby the CO shift reaction must also to be taken in account (Eq. 3.2):



Both reactions are exothermic and accompanied by a decrease in volume. The catalyst used is (metallic) copper on zinc oxide, thermally stabilized with alumina (Cu/ZnO/Al₂O₃). This catalyst is highly selective and gives a methanol purity >99.5% [10]. The desired operation conditions with this catalyst are relatively low pressure (5–10 MPa) and temperature (200–250°C), achieving a 25% syngas conversion per pass [13]. The total conversion of CO varies from 73% (250°C, 5 MPa) to 99% (200°C, 10 MPa) [10]. For the methanol synthesis, a stoichiometric ratio defined as (H₂–CO₂)/(CO+CO₂) of about 2 is preferred. For kinetic and selectivity reasons, a value

Table 2 Product selectivity after the FT reaction process and after the FT+hydroprocessing as a function of α (hydroprocessing selectivity: C_{1–4}, 4%; C_{5–9}, 23%; C_{10–20}, 73%) [19]

Product	ASF distribution of FT product, $\alpha=0.90$	Calculated distribution in the two-stage process	ASF distribution of FT product, $\alpha=0.95$	Calculated distribution in the two-stage process
C _{1–4} (wt.%)	8.5	12.2	2.4	6.3
C _{5–9} (wt.%)	18.4	21.0	6.4	22.4
C _{10–20} (wt.%)	37.0	66.8	19.7	71.3
C _{>20} (wt.%)	36.1	–	71.5	–

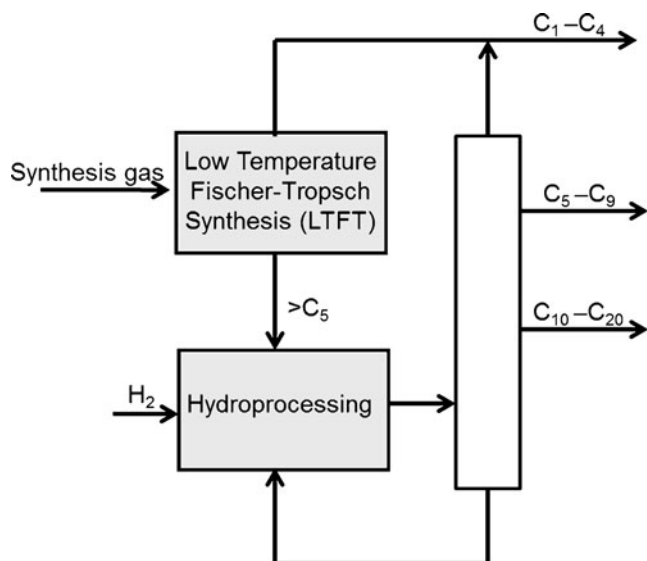


Fig. 4 Schematic layout of the SMDS process: reactors (grey), separation units (white) [34]

slightly above 2 is normally preferred. The syngas mixture is typically adjusted to contain 4–8% CO₂ for maximum activity and selectivity [25]. The presence of CO₂ accelerates the reaction by a factor of about 100; however, higher concentrations decrease the catalyst activity by inhibiting methanol synthesis.

A highly simplified reaction scheme of the MtG process is shown in Fig. 5. The first step, the dehydration of methanol to dimethyl ether, can occur over both zeolites and mildly acidic oxides like γ -alumina. The subsequent formation of hydrocarbons requires zeolitic catalysts. The precise mechanism of the corresponding reactions has been a matter of debate for many years. Today, it is widely accepted that the primary C–C bond formation as well as the buildup of higher hydrocarbons proceeds via a pool of adsorbed hydrocarbons (hydrocarbon pool mechanism). More specifically, it is assumed that adsorbed methylbenzenes function as autocatalysts which promote alkylation with methanol and DME [26] (Fig. 6).

ZSM-5 (crystal structure MFI) with atomic Si/Al ratios of the framework of 15:30 is the preferred catalyst for MtG.

This is a so-called medium-pore zeolite (average pore diameter=0.55 nm) that primarily yields aromatics and lower alkanes (a combination required by the overall H/C mass balance) and some non-aromatic C₅₊ products depending on the conversion level [27]. The geometry of the zeolite pores controls the selectivity, i.e. the size and shape of molecules diffusing into (reactants selectivity) and out of the zeolite pore network (product selectivity). Over ZSM-5, the largest aromatic molecules produced are tetramethylbenzenes [27], among which durene (1,2,4,5-tetramethylbenzene) causes problems because of its high melting point. Despite the shape selectivity of the ZSM-5 catalyst, carbonaceous deposits are formed upon MtG operation which block the zeolite pores and give rise to a marked deactivation. Catalyst deactivation and removal of the reaction heat are two factors of particular importance in the design of the reaction system. In fixed bed operation, the dehydration of methanol to dimethyl ether, which produces about 20% of the total heat of reaction, is carried out in a separate adiabatic reactor with γ -alumina as a catalyst. The formation of hydrocarbons proceeds in the second stage, which consists of five to six fixed bed reactors in parallel that are operated in swing mode: by turns, one of these reactors is off-line such that coke can be removed from the catalyst through burn-off with air. The exothermic character and the necessity of cyclic catalyst regeneration suggest fluid bed operation as an alternative. Here, it is possible to continuously remove the deactivated catalyst from the reactor and replace it by fresh or regenerated material. Gasoline yield and octane quality are reported to be higher than in fixed bed operation [28]. The commercial feasibility of the fluid bed operation was studied in a 100-bpd demonstration unit in Wesseling (Germany), from 1982 to 1985. Although the fluid bed technology appears to be ready for commercialization, no commercial plants have been built [25].

Low temperatures and high pressures are beneficial for MtG. In contrast, temperatures above 400°C and pressures below 0.5 MPa favour the formation of small olefins (MtO mode) through cracking of higher hydrocarbons. Exemplarily, two different product compositions obtained at

Table 3 Characteristic property ranges for conventional petroleum diesel fuel (European standard) and Fischer–Tropsch product

	FT Diesel [18]	Petroleum Diesel [21]
Density (kg/l)	<0.8 (20°C)	0.82–0.845 (15°C)
Boiling range (°C, ASTM D86)	Variable	250°C (<65% volatile) 350°C (>85% volatile)
Cetane index	75	>51
Content		
Total aromatics (wt.%)	<1	n.a
Sulphur (ppm w)	<5	<10
Polycyclic aromatics (wt.%)	n.a.	<11

na data not available

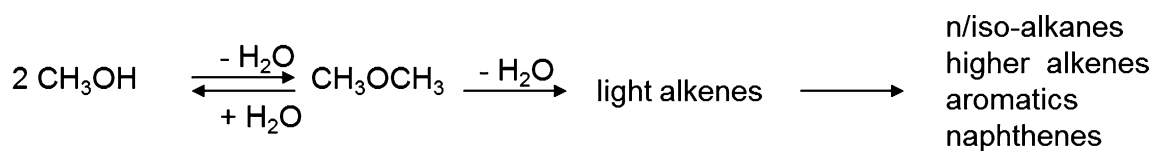


Fig. 5 Simplified reaction scheme of the formation of hydrocarbons from methanol

typical MtG conditions are presented in Table 4. The data by Schreiner [30] or Wender [13] correspond to a reactor inlet temperature of 330°C and an outlet temperature of 400°C. The reactor pressure is 2.06 MPa. For Exxon Mobil distribution, the inlet temperature is 350°C and the inlet pressure 2 MPa [29].

The detailed composition of each fraction was presented by Schreiner [30]. The data correspond to the product yields projected for the fixed bed operation in the NZ plant. The fraction C_{1–4} is mainly paraffinic, with butane as the predominant component (63 wt.%). The according composition of the fraction C_{5–9} is shown in Table 5. A most up-to-date distribution of alkane, alkene and aromatics is shown in Table 6, however with less detail.

The MtG reactor effluent is cooled to 25–35°C and passed to the product separator, where gas, liquid hydrocarbons and water are separated. The liquid hydrocarbon product (raw gasoline) contains mainly gasoline boiling range material. The C_{1–4} fraction is removed by distillation. The stabilized gasoline is then passed to a gasoline splitter where it is separated into light and heavy gasoline fractions. The MtG gasoline produced in fixed bed operation usually contains levels of 1,2,4,5-tetramethylbenzene (durene) higher than allowed. After the splitter, durene is concentrated in the heavy gasoline fraction and is subjected to a mild hydrofinishing process. Here, durene undergoes isomerisation, disproportionation and demethylation in the presence of hydrogen. The product is recovered in nearly quantitative yield with virtually unaltered octane number, but with greatly reduced durene content [24] (Fig. 7). Durene is an undesired product as its formation consumes large amounts of hydrogen and it has a high freezing point (79°C). The MtG gasoline properties are shown in Table 6 compared with today's gasoline specifications [32].

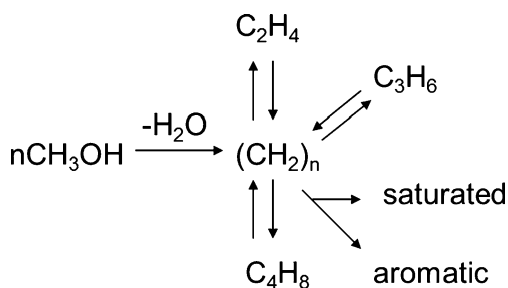


Fig. 6 Hydrocarbon pool mechanism [26]

4 Approach and criteria for comparison

4.1 Process design calculations

To compare the yields and selectivity of both routes, material and energy balance are estimated. In a first approach, the balance is calculated from syngas and afterwards is extrapolated to biomass. The comparison is based on commercial synthesis data found in the open literature. However, the shortage of information and low levels of detail made estimations necessary. A low-performance case and a high-performance case were defined for both processes, making possible the definition of a range of results for each route. No complex flow-sheeting calculations were carried out.

4.2 Economic evaluation

The production cost of liquid hydrocarbons from biomass via FT and MtG are calculated with a simple static shortcut method based on investment estimates for full-sized plants from the open literature. In addition, chemical energy efficiencies resulting from our own process calculations are used as input. The basic assumption is that the total operating cost can be approximated as a fixed percentage of capital investment (20%) per year, including capital-related cost, maintenance, labour and utilities, but excluding feedstock cost. The latter is treated as a variable, allowing a comparison with the reference feedstock petroleum (with refining as upgrading technology).

4.3 Process potential

Potential process improvements in terms of catalyst selectivity and capital-related cost are commented. Both parameters will directly influence the economic viability of hydrocarbon synfuel production from biomass

Table 4 Product selectivity after the MtG reaction (for conditions, see text)

Product	[13, 30]	[29]
C _{1–4} (wt.%)	19	13
C _{5–9} (wt.%)	81	87
C _{10–20} (wt.%)	–	–

Table 5 Product selectivity of the fraction C_{5–9} [30, 31]

Alkane	wt.%	Alkene	wt.%	Aromatics	wt.%
Pentane	17.3	Pentene	2.5	Toluene	2.5
Hexane	17.3	Hexene	2.5	Xylene	11.1
Heptane	7.4	Heptene	4.9	Trimethylbenzene	12.4
Octane	2.5	Octene	6.2	Tetramethylbenzene	9.9
Nonane	1.2	Nonene	2.5		
Total (wt.%)	45.5		18.6		35.9
(vol.%) ^a	40.5		17.2		42.3

^aVolume fractions are calculated assuming the density of pure compounds [33]

5 Results

5.1 Process design and calculations

5.1.1 Syngas as feedstock

Material balance Values for the distribution of mole C in the different hydrocarbon fractions and CO conversion are used to solve the material balance of each route. The same feedstock is considered for both routes, synthesis gas with a 2:1 ratio (basis: 500 mol CO and 1,000 mol H₂). The hydrocarbon distribution is dependent on α in the case of FT and on the MtG catalyst selectivity in the case of methanol to gasoline. A high and a low value of CO conversion and selectivity are assumed (Tables 7 and 8).

Fischer–Tropsch route The FT route balance is solved from syngas, considering a fixed bed LTFT operation. The conversion of CO is assumed as indicated for the Shell GTL plant in Malaysia [34]. The higher conversions can be achieved optimising a gas recycle after the FT synthesis. The α value for the LTFT synthesis using a cobalt-based catalyst is assumed based on information from [34, 15], where α values of 0.95 are reported as being achievable. The selectivity of the hydroprocessing catalyst is considered constant for both cases [19], being conscious that this

is a key factor in the total selectivity of the process (Table 7). In the case of the FT route, no extra H₂ is fed in the hydroprocessing step and also no extra conversion of H₂ is considered. The balance is calculated using the data in Tables 2 and 7.

Methanol-to-gasoline route The balance of the MtG route is calculated using the global synthesis equation (Eq. 3.3) with methanol considered as intermediate obtained with 100% selectivity [10, 25]. The conversion of CO considered is 80% and 99%. The lowest conversion value for low-temperature and low-pressure conditions (see Section 3.3) is 73%. For comparison reasons, 80% is assumed as the lowest value. The values of selectivity of the MtG cover the range of the two references [29, 30] (Table 4). To solve the material balance, no CO₂ was considered as the source of C because its only function is to maximise the activity and selectivity of the methanol synthesis (see Section 3.3).

It is important to remark that the quality of the fraction C_{5–9} is not the same in the case of the FT route and the MtG route. In the case of FT, this fraction contains mainly linear alkanes, with a representative H/C ratio of 2.3; therefore, it is not ready to be used and requires upgrading reactions (see Section 3.2). In the case of MtG, the H/C ratio is 2.0, and the fraction contains alkane, alkene and aromatics (Table 5).

Table 6 Product selectivity of the gasoline fraction (comparison of properties and composition versus specifications) [32]

		MtG gasoline [29]	Specifications [32]
Research octane number, RON	92	>95	
Motor octane number, MON	82	>85	
Density (kg/m ³)	730	720–775	
Composition			
Sulphur (ppm)	0	<10	
Alkanes (vol.%)	53	n.a.	
Alkenes (vol.%)	12	18	
Napthene (vol.%)	9	n.a.	
Aromatic (vol.%)	26	35	
Benzene (vol.%)	0.3	n.a.	

na data not available

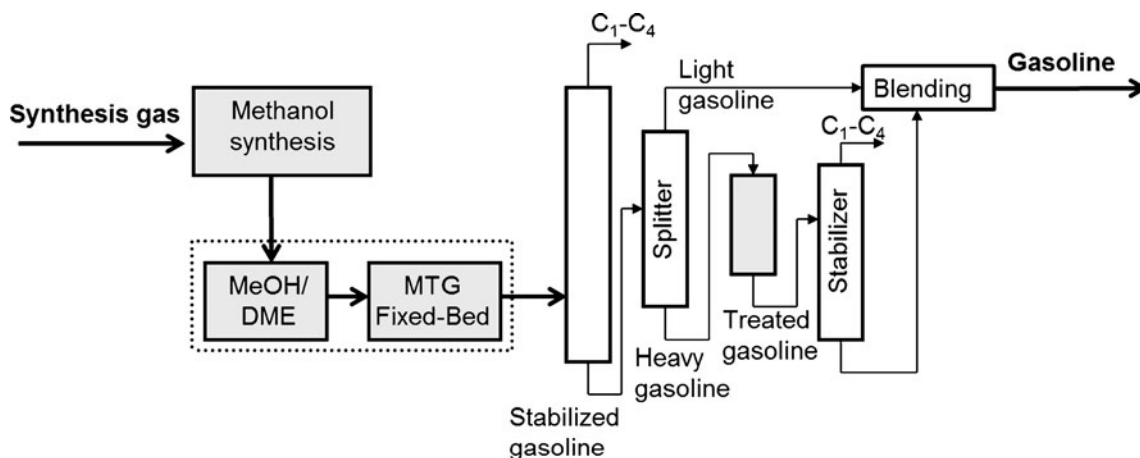


Fig. 7 MtG process flow diagram (grey, reactor unit; white, separation units) based on [24]

Energy balance The overall chemical energy efficiency is defined as the ratio between the higher heating values (HHV) in the outputs and the feedstocks.

$$\eta = \frac{HHV_{out}}{HHV_{in}} \quad (5.13)$$

$$HHV = \frac{-\Delta_R H_{298}^\circ}{M_{mass}} \text{ (MJ/kg)} \quad (5.14)$$

The HHV values for organic compounds are approximated on the basis of the elemental composition carbon/hydrogen/oxygen (CH_xO_y) according to the reaction enthalpy released during combustion (Eq. 5.15) [35, 36]. The carbon/hydrogen composition of each fraction is calculated considering the proportion of alkanes, alkenes and aromatics in the fraction. In the case of FT, the product is considered to be formed only by alkanes. The MtG product distribution is found in Table 5. The representative unit, CH_x, is also used to calculate the molecular mass (M_{mass}, Table 12).

$$\Delta_R H_{298}^\circ = -422.5 - 117.2 \cdot x + 177.5 \cdot y \text{ (kJ/kmol)} \quad (5.15)$$

The HHV value obtained with Eq. 5.14 is multiplied by the number of kilograms obtained in each fraction depending on the case (Tables 9 and 10). The HHV of CO and H₂

(10.1 and 142.9 MJ/kg, respectively) are multiplied by the number of kilograms fed. The chemical energy efficiencies of each fraction are calculated with Eq. 5.13. The results are shown in Table 13. The fraction C₅–C₂₀ groups the liquid hydrocarbons and is considered to be the desired fraction.

It can be seen that (1) a higher overall CO conversion has a beneficial effect on efficiency and that (2) the chemical energy efficiencies are similar for both routes. The chemical energy efficiency for the total production of hydrocarbons (C₁-C₂₀) is slightly higher in the case of MtG; however, when only the liquid hydrocarbons are compared, the FT route gives a result slightly higher than MtG (Table 11).

The HHV (MJ/kg) of the fraction C₁₋₄ is the highest (Table 12) due to the highest proportion of hydrogen. The MtG route produces more kilograms of this fraction (see Tables 9 and 10), which explains the higher chemical energy efficiency when all product hydrocarbons are considered.

5.1.2 Biomass as feedstock

In a second approach, the biomass is considered as feedstock for the production of hydrocarbons using syngas as intermediate. The objective here is to calculate the mole of C from biomass that go to each hydrocarbon fraction (the stoichiometric coefficient of Eq. 3.4) and the chemical energy efficiency of each route from biomass. There is

Table 7 Assumptions for the FT route

	FT synthesis		Hydroprocessing			
	X _{CO}	α-FT	X _{C21+}	Selectivity (wt.%)		
				C ₁₋₄	C ₅₋₉	C ₁₀₋₂₀
Low case	0.80	0.90	1	4	23	73
High case	0.95	0.95	1	4	23	73

Table 8 Assumptions for the MtG route

	Methanol synthesis		Methanol-to-gasoline			
	X _{CO}	Selectivity (wt.%)	X _{CH3OH}	Selectivity (wt.%)		
				C ₁₋₄	C ₅₋₉	C ₁₀₋₂₀
Low case	0.80	100	1	19	81	–
High case	0.99	100	1	13	87	–

Table 9 Material balance FT route

Component	In		Out					
	Mole	Kilogram	Low case			High case		
			Mole	Mole C	Kilogram	Mole	Mole C	Kilogram
CO	500	14	100	100	2.8	25	25	0.7
H ₂	1,000	2	200	–	0.4	50	–	0.1
H ₂ O	–	–	400	–	7.2	475	–	8.5
–(CH ₂)–	–	–	400	400	5.6	475	475	6.7
C ₁ –C ₄				48.6	0.7		30	0.4
C ₅ –C ₉				84.3	1.2		106.4	1.5
C ₁₀ –C ₂₀				267.1	3.7		338.6	4.8

currently no practical experience with large-scale plants for the conversion of biomass to synthetic liquid hydrocarbons. Therefore, the overall material balance and achievable product yields have been calculated based on estimations.

The syngas requirements in both synthesis routes are the same (ratio H₂/CO ≥ 2 and limited amounts of sulphur, halides and metals); therefore, the same process for the production of syngas from biomass is assumed. Tijmensen et al. [3] analysed the production of Fischer–Tropsch liquids and power via biomass gasification. They considered five different types of gasifiers and subsequent gas cleaning operations previous to the FT synthesis. They obtained overall energy efficiency¹ values for the production of FT liquid from biomass are between 30% and 50%. Avoiding the evaluation of different gasification and gas cleaning systems in the present study, the data of Tijmensen et al. [3] are considered as a reference. A range of efficiency values for the production of syngas from biomass ($\eta_{\text{syngas/biomass}}$) is calculated using Eq. 5.16. The chemical energy efficiency of the production of hydrocarbons from syngas ($\eta_{\text{C}_{1-20}/\text{syngas}}$) is used as calculated in Section 5.1.1 (Table 13).

$$\eta_{\text{HHV}(C_{1-20}/\text{biomass})} = \eta_{\text{HHV}(\text{syngas}/\text{biomass})} \cdot \eta_{\text{HHV}(C_{1-20}/\text{syngas})} \quad (5.16)$$

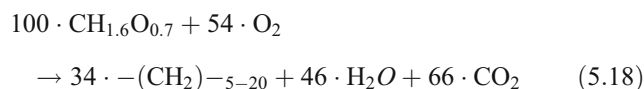
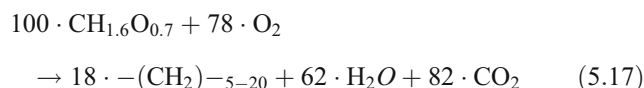
Energy balance The overall efficiency of the process is calculated multiplying the values in Table 13 by the calculated chemical energy efficiency values of producing syngas from biomass (47–67%) [3], in accordance with Eq. 5.16.

Material balance The molar stoichiometry of the overall process can be calculated based on the overall chemical energy efficiencies of Table 14 and with the definition of η (Eq. 5.13).

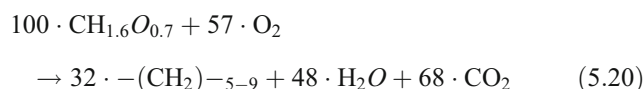
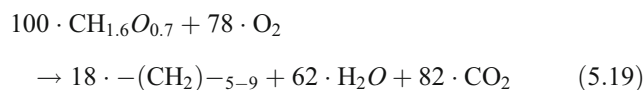
¹ Here defined as the sum of all outputs/total biomass input (as HHV).

The stoichiometric equations are approximated using entire numbers, showing the C efficiency for the production of liquid fuels from biomass (Table 15).

Fischer–Tropsch route



Methanol-to-hydrocarbons route



In CO₂ are included all carbon species that are not in the desired C_{5–20} fraction (C_{1–4}, CO₂, CO).

5.2 Economic evaluation

Production cost estimates, depending on feedstock cost per heating value, are shown in Fig. 8 for both biomass conversion routes (FT and MtG) as well as for petroleum-based hydrocarbon fuels. The parameter values used as input are given in Table 16. The intercept value on the vertical axis represents the total operating cost per chemical energy unit of product, excluding feedstock cost (approximated as 20% of the total capital investment per year). Slope values correspond to reciprocal chemical energy efficiencies of each upgrading route (100/ η energy, in per cent).

Table 10 Material balance of the MtG route

Component	In		Out					
	Mole	Kilogram	Low case			High case		
			Mole	Mole C	Kilogram	Mole	Mole C	Kilogram
CO	500	14	100	100	2.8	5	5	0.14
H ₂	1,000	2	200	–	0.4	10	–	0.02
H ₂ O	–	–	400	–	7.2	495	–	8.91
–(CH ₂)–	–	–	400	400	5.6	495	495	6.93
C ₁ –C ₄				75.7	1.1		64.3	0.90
C ₅ –C ₉				324.3	4.5		430.7	6.03
C ₁₀ –C ₂₀				–	–		–	–

Capital investment figures exhibit a high degree of uncertainty as no full-sized BtL plant has been built so far. The difference between the FT and MtG routes can be expected as relatively low because the largest contribution is due to feedstock pretreatment, gasification and gas treatment (about 70%), process steps applied in both cases [3].

The range of capital investment assumed results in areas between the dotted and dashed lines (FT and MtG, respectively). The slope is slightly lower in the case of the FT route due to the higher overall efficiency; nevertheless, in both cases, the efficiency is almost half as from petroleum refining. The intercept is higher in the FT case than in the MtG due to the higher capital investment. Both biomass-derived routes are very similar due to the low influence of the synthesis step in the total capital investment (30%) and the similar efficiencies.

The current prize of providing biomass varies greatly depending on the biomass in question and ranges from 1.2 to 9.7€ per gigajoule [8]. Assuming a biomass feedstock cost of 5€ per gigajoule, the production cost of liquid hydrocarbons from FT would range between 22€ and 34€ per gigajoule (MtG, between 21 and 29€ per gigajoule; Fig. 8). For comparison, gasoline and diesel based on petroleum refining reach production costs of 27€ per gigajoule when the crude oil feedstock is around 21€ per gigajoule ($\approx 129\text{€}$ per barrel). However, large-scale demand

for biomass for fuel production will affect its prize, given the competition with other kinds of utilization (for food, material application).

In the case of MtG, the prize of methanol is also relevant as it is a high-value intermediate (one of the top 10 organic chemicals manufactured in the world). Methanol today is used as a precursor to a large and varied number of high-value chemicals and polymers. It can be used as a fuel itself, as an octane extender, and in the manufacture of other fuels and higher alcohols. The production of gasoline from methanol becomes more interesting at lower methanol and higher gasoline prizes. In 2005, the difference between both average prize products in Europe was 7.3€ per gigajoule (methanol, 4.9€ per gigajoule; gasoline EU-95, 12.2€ per gigajoule). This difference increased until 10€ per gigajoule in 2010 due to the increase in gasoline prices (average 2010: methanol, 5.4€ per gigajoule; gasoline EU-95, 15.4€ per gigajoule) [38, 39].

5.3 Process potential

The most influential parameters in economic feasibility of both BtL synfuel production routes are chemical energy efficiency, capital-related cost and feedstock availability.

Table 11 Overall carbon efficiency of the FT and MtG routes from syngas (mole $C_{\text{fraction}}/100$ mol CO in syngas)

	FT		MtG	
	Low case	High case	Low case	High case
C ₁ –C ₄	9.7	6.0	15.1	12.9
C ₅ –C ₉	16.8	21.3	64.9	86.1
C ₁₀ –C ₂₀	53.5	67.7	–	–
CO not reacted	20.0	5.0	20.0	1.0

Table 12 Representative units and HHV for each final product fraction in the form CH_x

	FT ^a		MtG	
		HHV (MJ/kg)		HHV (MJ/kg)
C ₁ –C ₄	CH _{3,2}	52.5	CH _{3,2} ^b	52.5
C ₅ –C ₉	CH _{2,3}	48.4	CH _{2,0} ^c	46.9
C ₁₀ –C ₂₀	CH _{2,1}	47.4	–	–

^a Pure paraffinic C_nH_{2n+2}

^b Mainly paraffinic [30]

^c See Table 5

Table 13 Overall chemical energy efficiency for the FT and MtG routes from syngas ($\text{HHV}_{\text{CH}_4}/\text{HHV}_{\text{syngas}}$)

	FT		MtG	
	Low case	High case	Low case	High case
C ₁ –C ₄	8.4	5.2	13.0	11.1
C ₅ –C ₉	13.4	16.9	49.9	66.2
C ₁₀ –C ₂₀	41.5	52.5	–	–
C ₅ –C ₂₀	54.9	69.4	49.9	66.2

5.3.1 Syngas production and gas cleaning

Gasification of biomass and gas cleaning must be considered a bottleneck in the development of BtL process technology. Efficiencies are low (47–67%) and increases of this value will benefit both routes [3, 8]. Large-scale experience with syngas production from biomass is only presently getting available.

5.3.2 Fischer–Tropsch synthesis route

In the case of FT, CO conversion has been an optimization criterion (to be affected by catalyst activity, residence time, by-product water removal, etc.). However, a conversion of 100% is not possible in a once-through operation. Low partial pressures of H₂ and CO near the outlet of the reactor due to the formation of water and hydrocarbons are critical with respect to catalyst stability and reaction rates. Improvement potential can be seen, however, in catalyst selectivity of the hydroprocessing step, where an increase in selectivity of the fraction C_{5–20} would be desirable.

5.3.3 Methanol-to-gasoline synthesis route

In the case of MtG, optimization can be seen mainly in an improvement of the catalyst with focus on the coke stability and the quality of the products. A reduction in the polymethylbenzene content in the gasoline fraction in favour of toluene and xylenes will reduce the rate of the coke formation without modifying the octane number of the

Table 14 Overall chemical energy efficiency (HHV) for the FT and MtG routes from biomass ($\text{HHV}_{\text{CH}_4}/\text{HHV}_{\text{biomass}}$)

	FT		MtG	
	Low case	High case	Low case	High case
C ₁ –C ₄	3.9	3.5	6.1	7.4
C ₅ –C ₉	6.3	11.3	23.4	44.4
C ₁₀ –C ₂₀	19.5	35.2	–	–
C ₅ –C ₂₀	25.8	46.5	23.4	44.4

Table 15 Overall carbon efficiency from biomass (mole C_{fraction}/100 mol C_{biomass})

	FT		MtG	
	Low case	High case	Low case	High case
C ₁ –C ₄	2.4	2.1	3.7	4.5
C ₅ –C ₉	4.4	7.9	17.3	32.8
C ₁₀ –C ₂₀	14.2	25.6	–	–
C ₅ –C ₂₀	18.6	33.5	17.3	32.8

gasoline. The deposition of coke requires catalyst regeneration in cycles after about 1 month on stream [30]. Coke is burned off with a hot air–nitrogen mixture. An improved catalyst would allow for longer times on stream between regenerations and would contribute to a decrease in capital cost as a lower number of parallel reactors would be necessary.

The integration of the methanol synthesis with the MtG step to produce gasoline in a single loop (without isolation of methanol as intermediate) is a process already demonstrated but not commercially operated. The desired H₂–CO₂/CO+CO₂ value for the so-called TIGAS process is 1, which makes it very suitable for combination with biomass gasification, reducing the module adjustment. The capital and energy cost of the process can be reduced due to the moderate synthesis pressure and the low recycle rate [40].

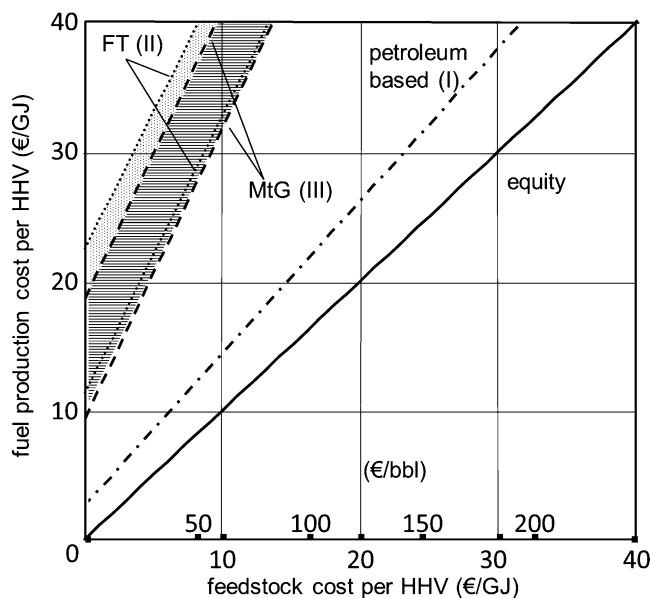


Fig. 8 Production cost estimates of liquid hydrocarbon liquid fuels: petroleum refining (I), biomass upgrading via FT synthesis (II) and MtG (III). Characteristic parameter values of intercept/slope: equity, 0/1; petroleum refining (I), 2.5/1.18; BtL–FT (II), 11.6/2.15–23.2/2.15 (dotted lines); BtL–MtG (III), 9.3/2.25–18.7/2.25 (dashed lines). For assumptions, see Table 16 and text

Table 16 Process parameters as basis for production cost estimate

	$\eta_{\text{energy,C5-C20}}$ (%) ^a	$\eta_{\text{C, C5-C20}}$ (%) ^b	Capital investment (Mio €)
Petroleum ^c	85	n.a	7,000–12,000
BtL (FT)	46.5	33.5	500–1,000 ^d
BtL (MtG)	44.4	32.8	405–810 ^e

na not available

^a Table 14

^b Table 15

^c Own estimate, European standard (15 million tons crude oil/year)

^d Range for 1 million t/year biomass based on [8]

^e 81% of investment for FT route based on [37], analogous study for coal to liquid

5.3.4 Overall process economics

Process optimization and reducing capital investment are two variables direct related with a decrease in the production cost of hydrocarbon liquids based on biomass. A reduction of the capital cost is also possible mainly due to scaling up [3]. An increase in the efficiency will reduce the effect of the biomass prize. Table 17 shows the future production cost of liquid hydrocarbons based on a potential increase in carbon and chemical energy efficiency and a reduction of capital investment. The production of hydrocarbon liquids from biomass will probably become competitive if the prize difference between crude oil and biomass becomes as high as about 20€ per gigajoule.

6 Conclusions

The present comparison of BtL routes based on FT synthesis and MtG leads to the following main results:

Operation and conditions

- Both synthesis reactions can be described under the same general synthesis equation (Eq. 3.3). However, the

Table 17 Future production cost scenario of liquid hydrocarbons from biomass based on optimistic predictions (reference: Table 16)

	FT	MtG
Overall energy efficiency (increase 9%) ^a (%)	50.7	48.4
Carbon efficiency (increase 9%) ^a (%)	36.5	35.7
Capital investment (reduction 15%) ^b (Mio €)	425–850	344–688
Production cost ^c (€/GJ)	18.7–27.5	17.6–24.9

^a Based on [8]

^b Extrapolation according to [3]

^c Calculated with Fig. 8, biomass cost=5€ per gigajoule

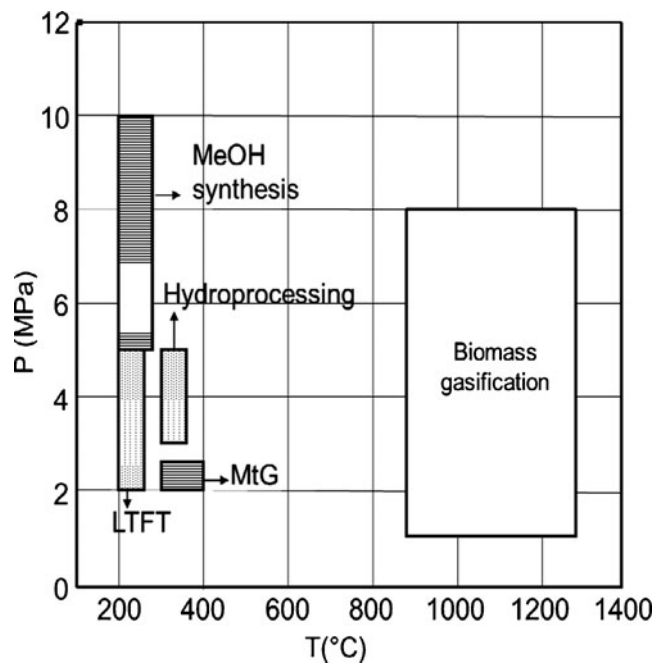


Fig. 9 Pressure and temperature ranges for gasification (with heat demand) and synthesis (with heat release)

chemistry of both routes is different (catalyst, mechanism), having an impact on the product distribution.

- The product distribution in the FT process is kinetically controlled and the hydrocarbons formed are mainly long unbranched alkanes (up to C₂₀₀) that require upgrading reactions. The MtG process is shape selective-controlled and produces aromatics and alkane/alkene hydrocarbons shorter than C₁₀.
- The flexibility of the LTFT is found in the upgrading reactions. In contrast, the products from MtG are limited to the gasoline range and the flexibility of the process lies in the possibility of methanol storage.
- The FT technology is already under use throughout the world in CtL and GtL plants, and it would be analogous in the case of BtL. The production of methanol from syngas has also been proven successfully in large-scale application, but the experience with the synthesis of gasoline from methanol in commercial scale is limited.

Table 18 Comparison of overall HHV efficiencies of biomass conversion to hydrocarbon

	FT		MtG	
	Low case	High case	Low case	High case
BtL study, Freiberg [41]	27.8	50.2	18.4	43.3
Present study (C ₁₋₂₀)	30	50	29.5	51.8

Material and energy balances

- The differences found do not establish a clear preference for any of the two technologies. The application of one or other route could depend on the market application of the product.
- The overall chemical energy efficiency is considered relatively low for both routes (<50%). Both cases have in common a high-temperature gasification step (requires heat at high temperature), followed by an exothermic synthesis step at a lower temperature. Therefore, the heat release in the exothermic reaction cannot be used in the endothermic one, requiring extra energy for the gasification step (Fig. 9).

The hydrocarbon liquid selectivity (fraction of the biomass that is converted to the hydrocarbon liquid product C_{5-20}) and the chemical energy efficiency (46.5% FT, 44.4%, MtG) are very similar for both routes. The carbon selectivity is slightly higher in the case of the FT route (33.5% FT versus 32.8% MtG) due to the lighter hydrocarbons formed (C_{1-4}).

The overall efficiencies obtained here can be compared with a recent study of the Technische Universität Bergakademie Freiberg [41]. Both results are similar in the case of the FT route and minor differences are found in the MtG route, although the approach for comparison in both studies was different. Simulations with ASPEN using seven different gasification systems were used in the study of Stahlschmidt (Table 18).

Economic evaluation

- High investment figures and low chemical energy efficiencies for both FT and MtG routes lead to higher production costs for BtL synfuels as compared with today's state-of-the-art petroleum refining with actual petroleum price levels. Chemical conversion of biomass molecules to syngas and subsequent hydrocarbon synthesis requires more complex and expensive process equipment than petroleum refining. In petroleum, only a minor fraction of the molecules must undergo chemical reactions, and these reactions are less complex and energy-intensive.
- The difference in estimated production cost between FT and MtG synfuels (FT, 22–34€ per gigajoule; MtG, 21–29€ per gigajoule) is not significant as compared with the present uncertainties in investment figures. These similarities in production costs are also due to the fact that gasification and syngas cleaning—which are the same in both routes—involve about 70% of the total capital investment.
- The price difference between methanol and gasoline has increased in the last 5 years, making the conversion of methanol to gasoline more attractive.

- Political and fiscal regulations based on environmental policy commitments should favour BtL synfuels significantly compared with the present situation. Motivation here is the non-food raw material lignocellulose and the high value of the synfuel product. There is, however, competition with other conversion routes for lignocellulosic biomass (e.g. fermentation to ethanol, conversion to chemicals).

Process potential

- The gasification process and gas cleaning can be considered the bottleneck of the process ($\eta=47-67\%$). Improvements in this step will benefit both routes.
- The potential of the FT route is to maximise the production of diesel with a more selective hydro-processing catalyst and to achieve an α value as high as possible to minimise the formation of hydrocarbons in the C_{1-4} fraction.
- The potential of the MtG route is to improve the stability of the catalyst and extend the cycles of regeneration. Minimization of methyl aromatics would improve the quality of the product.
- Increased overall efficiency corresponding to carbon selectivity and reduced capital investment would make liquid hydrocarbons synfuels more competitive. Political and fiscal regulations as logical consequence of political commitment to global environmental policies would accelerate market introduction of synfuels made from non-food lignocellulosic biomass.

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References

1. IEA (2009) Transport, Energy and CO₂. Moving towards sustainability. International Energy Agency. www.iea.org/press/pressdetail.asp?PRESS_REL_ID=293. Accessed 16 November 2010
2. Dabelstein W, Reglitzky A, Schütze A, Reders K (2008) Automotive fuels. In: Elvers B (ed) Handbook of fuels: energy sources for transportation, Chapter 3. Wiley-VCH, Weinheim, pp 97–197
3. Tijmensen MJA, Faaij APC, Hamelinck CN, van Hardeveld MRM (2002) Explorations of the possibilities for production of Fischer–Tropsch liquids and power via biomass gasification. Biomass and Bioenergy 23:129–152
4. Henrich E, Dinjus E (2003) Pyrolysis and gasification of biomass and waste. Proceedings of Expert Meeting, Strasbourg 2002. CPL Press, Newbury, p 511
5. Althapp A (2003) Synthetic transportation fuels from biomass via Fischer–Tropsch synthesis—principles and perspectives. Paper presented at the Conference “Regenerative Kraftstoffe”, November 13–14, Stuttgart, Germany, pp 218–227
6. Hofbauer H, Rauch R, Foscolo P, Matera D (2000) Hydrogen rich gas from biomass steam gasification. Paper presented at 1st World

- Conference on Biomass for Energy and Industry, Proceedings 1999–2001
7. Van der Meijden CM, van der Drift A, Vreugdenhil BJ (2007) Experimental results from the Allothermal Biomass Gasifier Milena. Paper presented at the 15th European Biomass Conference, May 7–11, Berlin, Germany
 8. Dena (2006) Biomass-to-liquid BtL. Realisierungsstudie (Summary). Final Report (Deutsche Energie-Agentur)
 9. Choren (2010). www.choren.com. Accessed 16 November 2010
 10. Makino E, Gray D (2001) Coal liquefaction. In: Ullmann's Encyclopedia of Industrial Chemistry, Chapter 2. http://onlinelibrary.wiley.com/doi/10.1002/14356007.a07_197/pdf. Accessed 16 November 2010
 11. Schulz H (2003) Major and minor reactions in Fischer–Tropsch synthesis on cobalt catalysts. *Top Catal* 1–4:73–85
 12. Van der Laan AB (1999) Kinetics and selectivity of the Fischer–Tropsch synthesis: a literature review. *Catalysis Rev* 41:255–318
 13. Wender I (1996) Reactions of synthesis gas. *Fuel Processing Technology* 48:189–297
 14. Steynberg A, Dry M (2004) Chemical concepts used for engineering purposes (edited by Steynberg A, Dry M). *Stud Surf Sci Catal* 152:196–257
 15. Eilers J, Posthuma SA, Sie ST (1990) The Shell Middle distillate synthesis process (SMDS). *Catal Lett* 7:253–270
 16. Weitkamp J, Jacobs PA, Martens JA (1983) Isomerization and hydrocracking of C9 through C16 *n*-alkanes on Pt/HZSM-5 zeolite. *Applied Catalysis* 8:123–141
 17. De Klerk A (2008) Fischer–Tropsch refining. Dissertation, University of Pretoria, South Africa
 18. Sie ST, Senden MMG, Van Wechem HMH (1991) Conversion of natural gas to transportation fuels via the Shell Middle distillate synthesis process. *Catalysis Today* 8:371–394
 19. Hoeck A (2006) The Shell GTL process. Towards a world scale project in Qatar: The Pearl Project. DGMK-Conference “Synthesis gas Chemistry”, October 4–6, Dresden
 20. Dry ME (2002) The Fischer Tropsch process: 1950–2000. *Catalysis Today* 71:227–241
 21. Deutsches Institut für Normung (2009) DIN EN 590. Beuth Verlag, Berlin
 22. Kvisle S, Fuglerud T, Kolboe S, Olsbye U, Lillerud K, Vora B (2008) Methanol to hydrocarbons. In: Ertl G, Knözinger H, Schüth F, Weitkamp J (eds) *Handbook of heterogeneous catalysis, electronic version*. Wiley-VCH, Weinheim, pp 2950–2965
 23. Stöcker M (1998) Methanol-to-hydrocarbons: catalytic materials and their behaviour. *Microporous and Mesoporous Materials* 29:3–48
 24. Zhao X, McGihon R, Tabak S (2008). ExxonMobil's methanol to gasoline (MTG) technology for the production of clean gasoline from coal. *Hydrocarbon engineering, Coal to clean gasoline*. www.exxonmobil.com/Apps/RefiningTechnologies/files/article_CoaltoLiquids_HydrocarbonEng.pdf. Accessed 2 November 2010
 25. Spath PL, Dayton DC (2003) Preliminary screening—technical and economic assessment of synthesis gas to fuels and chemicals with emphasis on the potential for biomass-derived syngas. National Renewable Energy Laboratory, Colorado NREL/TP-510-34929
 26. Olsbye U, Bjorgen M, Svelle S, Lillerud K, Kolboe S (2005) Mechanistic insight into the methanol-to-hydrocarbons reaction. *Catalysis Today* 106:108–111
 27. Maxwell IE, Stork WHJ (2001) Hydrocarbon processing with zeolites. In: van Bekkum H, Flanigen EM, Jacobs PA, Jansen JC (eds) *Introduction to zeolite science and practice*. Studies in Surface Science and Catalysis 137, Chap 17
 28. Gierlich H, Dolkemeyer W, Avidan A, Thiagarajan N (1986) Umwandlung von Methanol zu Benzin nach dem Wirbelbett-Verfahren. *Chem.-Ing.-Tech.* 58 Nr 3 238–239
 29. Exxon Mobil (2009) An alternative for liquid fuel production. Gasification Technology Conference
 30. Schreiner M (1978) Research guidance studies to assess gasoline from coal by methanol-to-gasoline and Sasol-type Fischer–Tropsch technologies. Report No. FE-2447-13, U.S. Department of Energy, Washington
 31. Probst H (1990) Synthetic fuels. Dover, New York
 32. Deutsches Institut für Normung (2008) DIN EN 228. Beuth Verlag, Berlin
 33. Perry (1984) Perry's chemical engineers' handbook, 6th edn. McGraw-Hill, New York
 34. Leckel D (2009) Diesel production from Fischer–Tropsch: the past, the present and new concepts. *Energy and Fuels* 23:2342–2358
 35. Boie W (1953) Beiträge zum feuerungstechnischen Rechnen—Teil 1: Ableitung neuer Heizwertformeln mit umfassendem Gültigkeitsbereich. *Energietechnik* 3:309–316
 36. Meunier J (1962) Vergasung fester Brennstoffe und oxidative Umwandlung von Kohlenwasserstoffen. Verlag Chemie, Weinheim
 37. America's Energy Future Panel on Alternative Liquid Transportation fuels, National Academy of Science, National Academy of Engineering, National Research Council (2009) Liquid Transportation fuels from coal and biomass. Technological status, costs and environmental impacts. www.nap.edu/openbook.php?record_id=12620. Accessed 13 December 2010
 38. Methanex (2010) www.methanex.com. Accessed 12 November 2010
 39. European Commission Energy (2010) ec.europa.eu/energy/observatory/oil/bulletin_en.htm. Accessed 24 January 2010
 40. Rostrup-Nielsen et al (2007) Polygeneration—integration of gasoline synthesis and IGCC power production using Topsoe's TIGAS process. In: Sonderberg PL, Larsen H (eds) Conference Proceedings, Energy Solutions for Sustainable Development, Roskilde, Denmark. RisØ-R-1608 (EN)
 41. Stahlschmidt R (2010) Evaluierung aktueller BtL-Prozesse. Technische Universität Bergakademie Freiberg, 4th BtL-Congress, 1–2 December, Berlin