

Confidential



Bio-based Fischer-Tropsch diesel production technologies

R.W.R. Zwart^{*}

R. van Ree^{}**

^{*} Energy research Centre of the Netherlands, Petten, the Netherlands

^{**} Wageningen University and Research Centre, Wageningen, the Netherlands

ECN-B--08-012

AUGUST 2008

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46

6

Bio-based Fischer-Tropsch Diesel Production Technologies

Robin Zwart

*Energy Research Centre of the Netherlands Biomass, Coal and Environmental
Research Petten, The Netherlands*

René van Ree

Wageningen University and Research Centre, Wageningen, The Netherlands

6.1 Introduction

Bio-based transportation fuels are expected to contribute significantly to the future transportation fuel portfolio both on national, EC and global levels. Bio-based transportation fuels that are currently produced and used are so called *first generation biofuels*. Examples are: pure vegetable plant oils, biodiesel produced from the seeds of oil-rich crops and from waste vegetable oils and animal fats, conventional bioethanol/ETBE produced from sugar and starch crops, and upgraded biogas produced from the digestion of organic residues. An advantage of these first generation biofuels is that production technologies are commercially available and that these fuels are already being produced for, and applied mainly as blending agents in, the current transportation fuel market. Disadvantages are (1) that the overall CO₂-reduction potential of these fuels compared to their fossil alternatives, taking into account the whole biomass–fuel application chain, is generally reported to be less than 50 %, and (2) that the production processes are relatively raw material specific, decreasing the overall market application potential.

Currently, technologies are being developed for the production of so called *one-and-a-half generation biofuels*, which have better properties. Examples are: the upgrading

1 (hydrogenation) of biodiesel to a higher-quality bio-based diesel, the production of higher
2 alcohols (i.e. biobutanol) from sugar and starch crops, and the production of bioethanol or
3 biobutanol from a wider range more difficult to convert raw materials.

4 Considering the European Policy goals on the implementation of biofuels, i.e. 2 %
5 and 5.75 % fossil fuel substitution on energy basis in 2005 and 2010, these have to be
6 met fully by the implementation of additional first and one-and-a-half generation biofuel
7 production capacity. To meet to the longer-term market demands, for example the 25 %
8 fossil fuel substitution directive for 2030, as mentioned in the Vision document of the
9 European Technology Platform on Biofuels, and to gradually shift to biofuels with a better
10 overall CO₂-reduction potential, the introduction of so called *second generation biofuels*
11 is a necessity. Examples are: bioethanol or biobutanol produced from lignocellulosic-rich
12 raw materials (cellulosic ethanol or butanol) and Biomass-to-Liquids (BtL) products, like
13 Fischer-Tropsch (FT) diesel, dimethylether (DME) and biomethanol.

14 This chapter will fully concentrate on the current technological status and market per-
15 spective for the production of FT-diesel from lignocellulosic-rich raw materials (wood,
16 straw, etc.). Aspects that will be described in more detail are: the theoretical background of
17 catalytic FT-diesel synthesis and the techno-economic aspects of biomass-based integrated
18 gasification-based FT-diesel production concepts considered in some major demonstration
19 projects.

20

21

22 **6.2 Theoretical Background Catalytic FT-Diesel Synthesis Process**

23

24 The Fischer-Tropsch (FT) synthesis was discovered in 1923 by the German scientists
25 F. Fischer and H. Tropsch at the Kaiser Wilhelm Institute for Coal Research in Mülheim,
26 Germany. In the synthesis hydrocarbons are produced from syngas, *viz.* a mixture of the
27 gases CO and H₂. Historically, FT-processes have been operated on a large industrial scale
28 to produce synthetic fuels as alternative for non-available fossil fuels (i.e. in Germany in
29 the 1930s and 1940s, and in South Africa during the oil boycott). To date, the FT-process
30 receives much attention because the hydrocarbon products are ‘ultra-clean’ due to the
31 nature of the synthesis process, i.e. they are essentially free of sulphur and aromatics. In
32 Thailand and Greece Shell Gas-to-Liquids (GtL) derived FT-diesel blended with fossil
33 diesel is available to reduce local soot and SO₂ emissions.

34

35

36 **6.2.1 Chemistry**

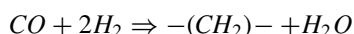
37

38

39 **6.2.1.1 Synthesis**

40

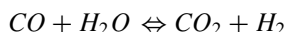
41 In the catalytic FT-synthesis one mole of CO reacts with two moles of H₂ to form mainly
42 paraffin straight-chain hydrocarbons (C_xH_{2x}), with minor amounts of branched and un-
43 saturated hydrocarbons (*i.e.* 2-methyl paraffins and α-olefins), and primary alcohols. Typ-
44 ical operation conditions for FT-synthesis are temperatures of 200–250 °C and pressures
45 between 25 and 60 bar.¹ In the exothermic FT-reaction about 20 % of the chemical energy
46 is released as heat:



6.2.1.2 Catalysts

Several types of catalysts can be used for the FT-synthesis; the most important are based on iron (Fe) or cobalt (Co). Cobalt catalysts have the advantage of a higher conversion rate and a longer life (over five years). The Co catalysts are in general more reactive for hydrogenation and produce therefore less unsaturated hydrocarbons (olefins) and alcohols compared to Fe catalysts. Iron catalysts have a higher tolerance for sulphur, are cheaper, and produce more olefin products and alcohols. The lifetime of the Fe catalysts is short and in commercial installations generally limited to eight weeks.

The FT-reaction consumes hydrogen and carbon monoxide in a molar ratio of $H_2/CO = 2$. When the ratio in the feed gas is lower, it can be adjusted with the water-gas shift (WGS) reaction:



Iron-based FT-catalysts show considerable WGS activity and the H_2/CO ratio is adjusted in the synthesis reactor. In the case of cobalt-based catalysts the ratio needs to be adjusted prior to FT-synthesis.

6.2.1.3 Product Distribution

The polymerization-like FT chain-growth reaction results in a range of products, comprising light hydrocarbons (C_1 - C_2), LPG (C_3 - C_4), naphtha (C_5 - C_{11}), diesel (C_{12} - C_{20}), and wax ($>C_{20}$) fractions. The theoretical chain length distribution can be described by means of the Anderson-Schulz-Flory (ASF) equation, which is represented as:

$$\log \frac{W_n}{n} = n \cdot \log \alpha + \log \frac{(1 - \alpha)^2}{\alpha}$$

where W_n is the weight fraction of a product consisting of n carbon atoms, and α the chain growth probability factor. Higher α values give more high-molecular weight products as can be seen in Figure 6.1. The value of α is characteristic of the particular catalyst employed in the FT-process and, depending on the needs of a particular production process, catalysts and process operation conditions can be tailored towards the production of predominantly low or higher molecular weight hydrocarbons.

In practice, there is often a deviation from the ideal ASF distribution especially with regards to the lower hydrocarbon yields. C_1 yields are usually higher than predicted, whereas C_2 (as well as C_3 and C_4) yields are lower. To incorporate the deviation from the ideal ASF distribution with regard to the yields of the C_1 - C_4 hydrocarbon, as 'rule-of-thumb' these values can be recalculated according to:

$$W_1 = \frac{1}{2} \cdot \left(1 - \sum_{i=5}^{\infty} W_i \right) \quad W_{2,3,4} = \frac{1}{6} \cdot \left(1 - \sum_{i=5}^{\infty} W_i \right)$$

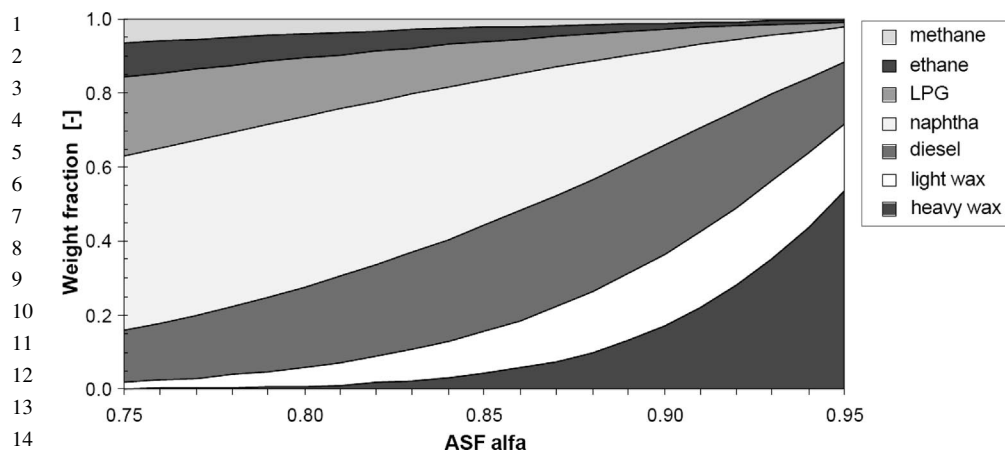


Figure 6.1 Theoretical ASF product distribution for FT-synthesis, with LPG (C_3 - C_4), naphtha (C_5 - C_{11}), diesel (C_{12} - C_{20}), light wax (C_{21} - C_{30}), and heavy wax ($>C_{30}$).

6.2.2 Feed Gas Specifications

The catalysts used in FT-synthesis are intrinsically very sensitive to small amounts of impurities. In commercial operation, catalysts are replaced or regenerated after a certain operational period. The definition of the gas cleaning is therefore based on economic considerations: investment in gas cleaning versus accepting decreasing production due to poisoning of the catalyst. Therefore, there are no 'hard' data on maximum levels for impurities in FT feed gas. For each plant the acceptable levels may be different. Rule-of-thumb specifications are presented in Table 6.1 for known impurities, and for impurities that might be present in biomass-derived gases.^{2,3}

A maximum value of less than 1 ppmV is defined for both the sum of the N_2 -containing and S-containing compounds. For the halides and alkaline metals a lower level of less than 10 ppbV is assumed. With respect to the organic constituents that are present in biomass product gases (i.e. tars and BTX), tars in general, there are no limits regarding poisoning

Table 6.1 FT feed gas specifications

Impurity	Removal level
$H_2S + COS + CS_2$	< 1 ppmV
$NH_3 + HCN$	< 1 ppmV
$HCl + HBr + HF$	< 10 ppbV
alkaline metals	< 10 ppbV
Solids (soot, dust, ash)	essentially completely
Organic compounds ^α (tars)	below dew point
- class 2 ^β (hetero atoms)	< 1 ppmV

^α organic compounds include also benzene, toluene and xylene (BTX).

^β class 2 tars comprise phenol, pyridine, and thiophene.

1 of the catalyst. However, as the gas needs to be compressed to 25–60 bar for FT-synthesis,
2 the concentration of the organic compounds must be below the dew point at FT pressure
3 to prevent condensation and fouling in the system. Specifically, class 2 tars with S or N
4 hetero atoms (e.g. thiophene and pyridine) need to be removed below ppmV level, as they
5 are intrinsically poisonous for the catalyst. Solids must be removed essentially completely,
6 as they foul the system and may obstruct fixed-bed reactors.

7 With respect to the other possible constituents (depending on the gasification concept) of
8 the FT feed, i.e. CO₂, N₂, CH₄, and larger hydrocarbons, there are no hard specifications.
9 However, similar to the gas cleaning, specifications are set by economic considerations.
10 For the concentration of these gases, which are inert in the FT-synthesis, a soft maximum
11 of 15 vol % is defined (but the lower, the better). The presence of inert components requires
12 larger reactors and higher total gas pressures. CO₂ can readily be removed with standard
13 techniques, but N₂ and the light-end hydrocarbons cannot be removed at reasonable costs.
14 Therefore, in the production of the FT feed gas the presence of significant concentrations
15 of the latter compounds should be avoided.

16

17

18 **6.2.3 Commercial Processes**

19

20 **6.2.3.1 Fischer-Tropsch Synthesis**

21

22 Today, FT-synthesis is an established technology^{4–6} and two companies have already
23 commercialized their FT-technology, i.e. Shell (1st plant in Malaysia) and Sasol (several
24 plants in South Africa), using natural gas and coal as feedstock to produce the syngas,
25 respectively. Sasol uses iron catalysts and operates several types of reactors, of which the
26 slurry bubble column reactor is the most versatile (i.e. applied in the Sasol Slurry Phase
27 Distillate (SSPD)). Shell operates the Shell Middle Distillate Synthesis (SMDS) process
28 in Bintulu, Malaysia, which produces heavy waxes with a cobalt-based catalyst in multi-
29 tubular fixed bed reactors. In 2003 Shell has started the engineering for a 75,000 bbpd
30 SMDS plant in Qatar, while Sasol has a 30,000 bbpd cobalt-based SSPD plant under
31 construction, also in Qatar.

32

33

34 **6.2.3.2 Syngas Production and Clean-up**

35

36 Most syngas is produced by partial oxidation of natural gas (84 %); the remaining part
37 is produced by gasification of coal, while some additional small amounts are generated in
38 refinery processes. The cleaning of the raw syngas from partial oxidation is a well-known
39 and commercially available process.⁷ The general approach is to quench the raw hot gas
40 with water to cool the gas and removed solid particles (viz. dust, soot, and ash) and the
41 volatile alkaline metals. Upon syngas production, H₂S, NH₃, COS and CS₂, and HCN are
42 formed from sulphur and nitrogen in the fuel. The NH₃ is removed downstream together
43 with the halides (viz. HCl, HBr, and HF) with a water scrubber and H₂S is removed either
44 by absorption or after conversion to elementary sulphur (i.e. the Claus process). The
45 adsorption removal is preferred when relatively small amounts of H₂S are present. Similar
46 is valid for the presence of COS and HCN. These impurities are hardly removed in the gas

1 economy of scale, which is necessary to reduce costs. For illustration, the Shell GTL plant
 2 in Malaysia of 12,500 bbpd (*i.e.* ~ 1000 MW) is considered as a demonstration plant, while
 3 the new plant in Qatar will have a six times higher capacity (75,000 bbpd or ~ 6000 MW).
 4 Another possibility is that there are several smaller plants in the size of ~ 500 MW, which
 5 produce only intermediate products, e.g. raw liquid products, where the final work-up is
 6 done in a central facility.

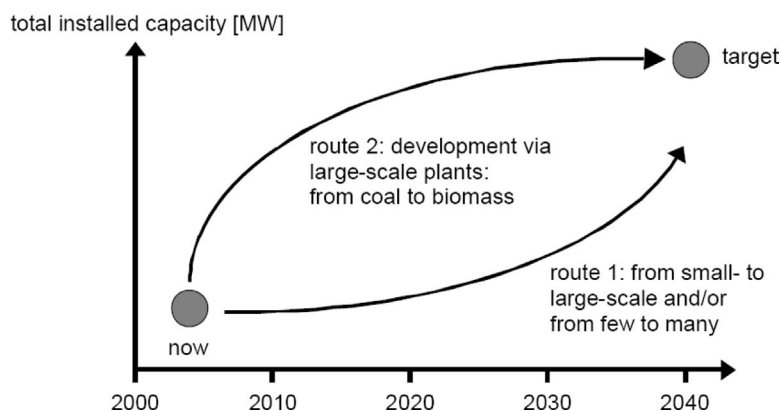
7 The typical syngas demands for chemical processes correspond to 50–200 MW_{th}. Even
 8 though the scale of an individual biosyngas plant may be relatively small, in most cases the
 9 plant will be part of a larger centralized chemical infrastructure with several other processes
 10 and plants to optimize energy and product integration (*i.e.* the syngas consumer). There
 11 is only a limited market for stand-alone small-scale biosyngas production for distributed
 12 chemical plants; although there will always be exceptions.

13 To ensure cost-effective biomass supply (*i.e.* avoid land transport) biosyngas production
 14 plants will be constructed close to ports or larger waterways. For the selection of the location
 15 the same considerations apply as for current coal-fired power plants and their coal logistics.
 16 Also the main large concentrations of chemical industry are located on locations easy acces-
 17 sible from water, e.g. the Dutch Maasvlakte near Rotterdam, and the German Ruhrgebiet.
 18

20 6.3.1.2 Implementation

21
 22 As a large total installed biosyngas production capacity with large individual plants is
 23 required to meet the ambitious renewable energy targets,¹¹ a robust, fuel-flexible, and
 24 high-efficient technology for optimum biomass utilization is required to guarantee avail-
 25 ability. In developing BtL technology, two possible routes can be followed, see Figure 6.3.

26 The first route comprises up-scaling of the small and medium scale biomass-based
 27 gasification technologies that are currently mostly used for distributed heat and power
 28 (CHP) production. In this route it will take a long time before a significant biosyngas
 29 production capacity is installed. Either, a large number of plants will have to be put in
 30 operation or the technology has to be up-scaled, which will take an additional development
 31



46 **Figure 6.3** Roadmap to reach for large-scale implementation of biosyngas and BtL products.

1 period of a decade. Therefore, it is questionable if the ambitious renewable energy targets
2 can be met by following this route.

3 The second and perhaps to be preferred route comprises adapting today's large-scale
4 coal-based (entrained flow (EF)) gasification technology, initially by co-firing biomass and
5 later on construct biomass-based gasifiers. In this way the installed biosyngas capacity can
6 be increased rapidly, as basic technology is already proven on large scale.

7

8

9 **6.3.2 Biomass Feedstock**

10

11 Approximately 50 % of the biomass globally available for energy purposes (i.e. the technical
12 potential) is wood or wood residues. A further 20 % is strawlike, which share will increase
13 to 40 % when strawlike crops are selected as energy crops.¹² Hence, for utilization of the
14 large amounts of biomass for biosyngas production, it is important to develop technical
15 routes that are able to utilize both wood and straw materials. Biomass materials like manure
16 and waste streams will play only a minor role in the biosyngas production, as the absolute
17 amounts of these streams available for biosyngas production are very low compared to
18 the required total amounts of biomass. Therefore, they are not of significance for large-
19 scale biosyngas production.

20 Due to the distributed and global generation of the biomass, large transport distances are
21 unavoidable. Transport by truck is the major cost driver in biomass transport; therefore,
22 the transport over land should be minimized.² Strawlike materials have a much lower bulk
23 energy density, which would result in higher transport and transshipment costs. Therefore,
24 energy densification of straw is desired to reduce transport costs and allow easier handling,
25 *viz.* grasses and straw are converted into a bioslurry via flash pyrolysis,¹³ as will be discussed
26 in Section 0.0. Wood, although already relatively high-energy dense, will preferable
27 also be densified (e.g. by torrefaction discussed in Section 0.0 or again pyrolysis, resulting
28 also in simplification of the biomass feeding system of gasification) before being transported
29 by ship to large centralized conversion facilities.

Au: Pls. update
Section nos.

30 The transition to green alternatives requires biomass, which should be available in large
31 quantities. Since wood and grasslike material make up 70–90 % of the total technically
32 available amount of biomass world-wide, it is reasonable to focus on these biomass fuels
33 as main renewable energy sources for chemicals and fuels.¹⁴

34

35

36 **6.3.3 Syngas Production Technology**

37

38 In order to produce biosyngas cost-effectively, high biomass-to-syngas yields are required.
39 This implies that upon gasification of biomass the maximum share of energy contained in
40 the biomass should be converted into the syngas components H₂ and CO.

41 There are two thermo-chemical ways to produce synthesis gas (H₂ and CO) from
42 biomass: either by applying high temperatures or by using a catalyst at a much lower
43 temperature Figure 6.4.¹⁵ The first route includes a fluidized bed gasifier and a down-
44 stream catalytic reformer, both operating at approximately 900 °C. In product gas from low
45 temperature gasification the syngas components H₂ and CO typically contain only ~50 %
46 of the energy in the gas, while the remainder is contained in CH₄ and higher (aromatic)

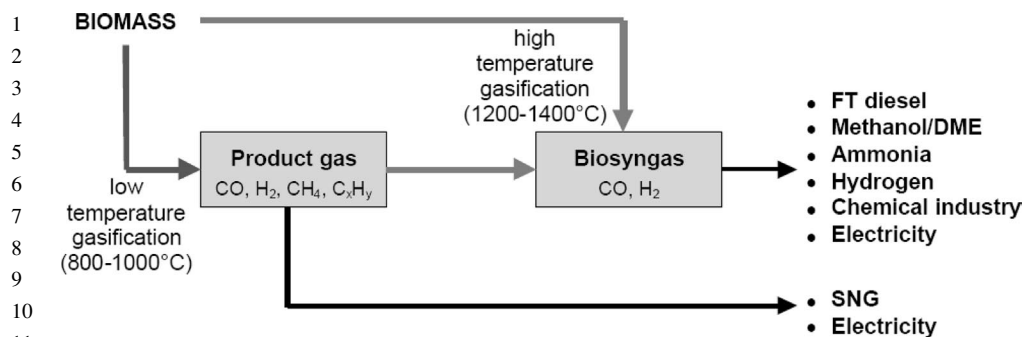


Figure 6.4 Two biomass-derived gases via gasification at different temperature levels.

hydrocarbons that have to be catalytically reformed. The second route generally requires temperatures as high as 1300 °C and generally involves an entrained flow gasifier. Upon high temperature gasification (>1300 °C) all the biomass is completely converted into biosyngas. Biosyngas is chemically similar to syngas derived from fossil sources and can replace its fossil equivalent in all applications. The two options concern two different evolution trajectories. The following paragraphs cover the two options.

6.3.3.1 Fluidized Bed Gasification with Catalytic Reformer

Fluidized bed gasification of biomass presently is a common way of converting biomass. Many different technologies are available. The air-blown circulating fluidized bed (CFB) is the most common one. Most fluidized bed applications involve close-coupled combustion with little or no intermediate gas cleaning. Power and/or heat are the usual end products. The gas produced by a fluidized bed gasifier (typically operated at 900 °C) contains H₂, CO, CO₂, H₂O, and considerable amounts of hydrocarbons like CH₄, C₂H₄, benzene and tars. Although this so-called product gas is suitable for combustion processes, it does not meet the requirements of synthesis gas, which is needed to produce biofuels or chemicals. The product gas needs further treatment in a catalytic reformer where hydrocarbons are converted into H₂ and CO (and CO₂ and H₂O). Since most syngas to liquid fuels conversion processes require a raw gas with very little or no inert gases, gasification and reforming should apply pure oxygen instead of air. Steam is usually added as a moderator. Another option to avoid N₂ dilution is to use an allothermal or indirect gasifier. In these reactors, gas production and heat generation do not take place in the same reactor. This enables the use of air (in the heat generating reactor), without having the N₂-dilution of the gas coming from the gas generation reactor. Examples of indirect gasifiers are: the SilvaGas-process developed by Battelle in the US,¹⁶ the MTCI-process,¹⁷ the MILENA developed by the Energy research Centre of the Netherlands (ECN),^{18,19} and the FICFB-concept developed by the Vienna University²⁰ and in operation at the Biomass-CHP in Güssing. The FICFB based biomass-CHP plant in Güssing is one of the facilities (as well as the Choren and Chemrec plants discussed in Sections 0.0 and 0.0) used in the EU-funded project RENEW. Within this project production routes for BTL fuels will be demonstrated and the full supply chain will be assessed in terms of biomass potential, life-cycle, costs and technological

1 options. Fuels will be produced and will be tested in order to demonstrate benefits of
2 optimized fuels for advanced power trains.

3 In the EU-funded project Chrisgas, the existing 18 MW_{th} pressurized CFB-gasifier in
4 Värnamo will be refurbished to produce syngas.²¹ This includes operation on oxygen/steam
5 instead of air, the installation of a high temperature filter, a catalytic reformer, and a shift
6 reactor. In five years time, the plant should produce 3500 m_n³/h H₂ and CO at 10 bar. The
7 project is carried out by the VVBGC consortium (Växjö Värnamo Biomass Gasification
8 Centre). In the next phase, fuel synthesis will be added to the plant.

9 Another initiative in this category is by VTT that advocates fluidized bed gasification as
10 the process to generate clean fuel gas as well as syngas from biomass. Fuel flexibility is
11 considered the major advantage. VTT recently started the UCG-programme (Ultra Clean
12 Fuel Gas) and a 500 kW_{th} PDU is under construction.²² It consists of a pressurized fluidized
13 bed, catalytic reforming, and further cleaning and conditioning. The catalytic reformer is
14 meant to reduce hydrocarbons (benzene and larger) completely and methane by over 95 %.
15 The test unit will support RD&D focusing on methanol and FT-diesel production via syngas
16 as well as the production of SNG, H₂, and electricity by fuel cells. The present estimate of a
17 300 MW_{th} plant based on above described VTT process show that FT-diesel and methanol
18 can be produced for approximately 12 €/GJ (feedstock price 2.8 €/GJ). A plant this size
19 can be largely constructed as a single train.

20 The German institute CUTEC has recently constructed an oxygen-blown 0.4 MW_{th} CFB
21 gasifier connected to a catalytic reformer. Part of the gas is compressed and directed to a
22 FT-synthesis reactor.²³ Apart from these above-mentioned initiatives to develop technology
23 to produce syngas by fluidized bed gasification and catalytic reforming, many others apply
24 catalytic reforming reactors for gas conditioning. This, however, generally focuses on
25 the catalytic reduction of large hydrocarbon molecules (*viz.* tars). Reforming of methane
26 usually is not one of the goals in these concepts.

27

28

29 **6.3.3.2 Entrained Flow Gasification**

30

31 The non-catalytic production of syngas (H₂ and CO) from biomass generally requires
32 high temperatures, typically 1300 °C. The most common reactor for this is the entrained
33 flow gasifier.²⁴ Since biomass contains mineral matter (ash), a slagging entrained flow
34 gasifier seems to be the most appropriate technology.²⁵ Entrained flow reactors need very
35 small fuel particles to have sufficient conversion. This requires extensive milling of solid
36 fuels, which is energy intensive and generally produces particles that cannot be fed by
37 conventional pneumatic systems.²⁵ R&D therefore focuses on ways to technically enable
38 the fuel feeding, as discussed in Section 0.0, as well as on the improvement of the
39 economics of the whole chain. The most promising pre-treatment options are torrefaction
40 and pyrolysis. These options enable efficient and cheap production of syngas from biomass,
41 mainly because it is characterized by relatively cheap (long-distance) transport.

Au: Pls. update
Section nos.

42 Different slagging entrained flow gasifiers are operated worldwide, but only few have
43 experience with biomass. Former Future Energy, now Siemens, in Freiberg Germany
44 commercializes entrained flow gasifier technology for biomass, waste, and other fuels.²⁶
45 It owns a 3 MW_{th} pilot plant that has been operated with many different biomass fuels.

46

1 Furthermore, Future Energy supplied the 120 MW_{th} entrained flow gasifier, which is
2 commercially operated on waste material in the Schwarze Pumpe complex in Germany.²⁷
3 Another example is the Buggenum IGCC-plant in the Netherlands where biomass is co-
4 gasified with coal in a slagging entrained flow gasifier. Tests have been conducted using up
5 to 34 wt % biomass in the feeding mixture.²⁸ This biomass was mainly sewage sludge and
6 chicken manure, not generating pulverizing problems and feeding problems when mixed
7 with coal. Also a mix of coal and wood dust has been tested successfully.

8

9

10 **6.3.3.3 Polygeneration**

11

12 The fluidized bed gasification with catalytic reforming and entrained flow gasification pro-
13 cesses, described above, focus on the production of syngas with high yields of H₂ and CO.
14 This is desirable in order to get the maximum production efficiency of biofuels/chemicals
15 like methanol and FT-diesel. The alternative approach is called polygeneration. In this case,
16 the H₂ and CO from a gas are used for the (once-through) synthesis of a biofuel/chemical,
17 and the remaining components in the gas are used in a different way, e.g. the production
18 of power. The waste gasification plant of the Schwarze Pumpe complex in Germany is
19 an example where waste is converted into a product gas containing considerable amounts
20 of hydrocarbons. The gas is cleaned and used as feedstock to produce methanol. The re-
21 maining gas (mainly methane) is used as fuel for a 75 MW_e combined-cycle to produce
22 power.^{27,29}

23

24

25 **6.3.3.4 Biorefinery**

26

27 Another integrated biofuel concept is sometimes referred to as biorefinery, a concept that
28 is of great interest in the US where conventional (biological) fermentation is combined
29 with thermo-chemical conversion with syngas as intermediate product. This concept effi-
30 ciently produces ethanol and other alcohols from different kinds of biomass. This so-called
31 advanced ethanol refinery plant is expected to produce alcohols for less than 1 \$/gallon
32 (approximately 10 €/GJ).³⁰

33

34

35 **6.3.3.5 The Optimum Syngas Production Technology**

36

37 The pressurized oxygen-blown entrained flow (EF) gasifier is considered to be the heart
38 of the optimum large-scale syngas/FT biodiesel production process, as presented in
39 Figure 6.5. This technology was identified as optimum technology for biosyngas produc-
40 tion as it has the advantages of (i) high efficiency to biosyngas, (ii) fuel flexibility for all
41 types of biomass, e.g. wood, straw, and grassy materials, (iii) suitability for scales of several
42 hundreds to a few thousand megawatt, and (iv) possibility to operate on coal as back-up fuel.

43 As the EF gasification for coal is a well-established and commercial available technology,
44 and has been demonstrated to be able to co-fire significant amounts of biomass,²⁸ it also
45 enables a short-term graduate transfer from coal-to-liquid (CTL) plants to biomass-to-liquid
46 (BTL) plants.

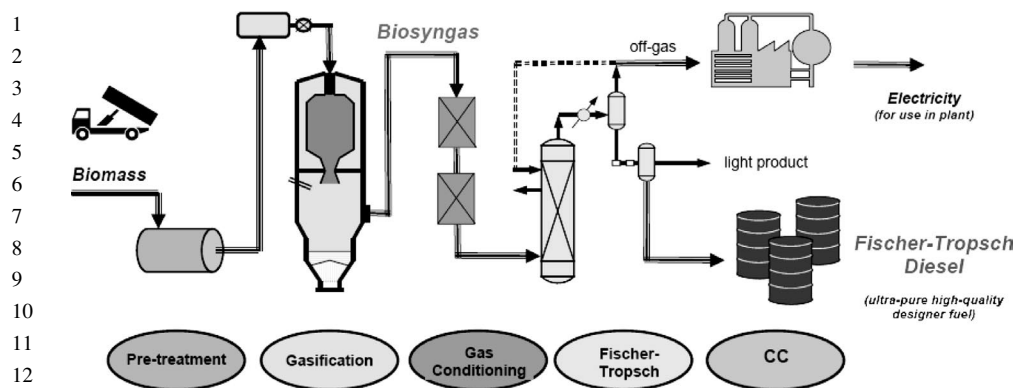


Figure 6.5 Schematic line-up of the optimum syngas/FT biodiesel production process.

6.3.4 Biomass Feeding and Pre-treatment

Biomass is different from coal in many respects; the most relevant relates to feeding. Biomass requires significant pre-treatment to allow stable feeding into the gasifier without excessive inert gas consumption. In addition to the requirement to pre-treat the biomass for feeding, it may also be desired for purpose of densification of the material. Due to the smaller volume transport costs are reduced and the stability of the gasifier operation is increased, due to the higher energy density of the feed.

The development of new approaches to biomass feeding and pre-treatment is necessary to reach high biomass-to-biosyngas and overall system efficiencies in biomass-fired entrained flow gasifier systems.

In Figure 6.6 four possible specific pre-treatment and feeding options are shown for different biomass streams. A fifth feeding option, not presented in this figure, is feeding a residual product, e.g. black liquor from pulp and paper industry, and hence integrate the

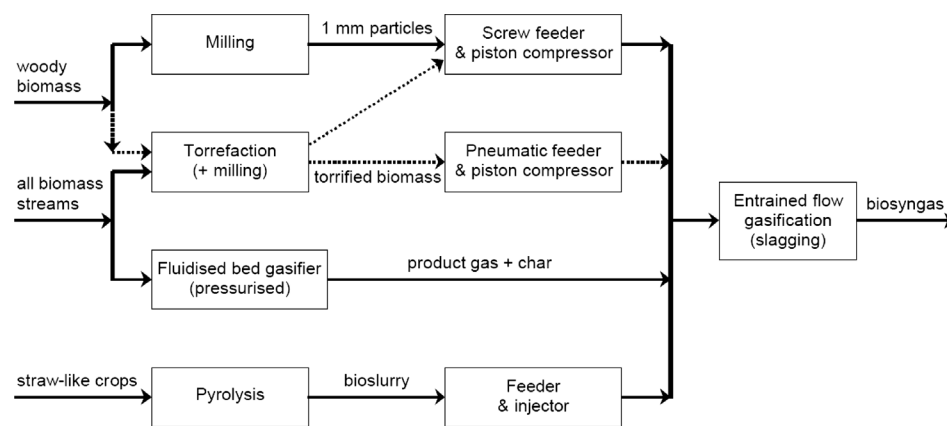


Figure 6.6 Different biomass pre-treatment and feeding option.

1 syngas production in existing industries. The pre-treatment and feeding options are not
2 competitive but complementary or an alternative to each other.

3

4

5 **6.3.4.1 Milling and Screw Feeding**

6

7 The biomass-to-biosyngas and the overall system efficiency is optimized when no pre-
8 treatment is necessary, i.e. as milling wood down to 1 mm wood particles is sufficient
9 to reach complete conversion. Then the electricity consumption is not excessive and no
10 separate pre-treatment process is required with the accompanying loss in efficiency and the
11 investment and running costs. (This option is not applicable to straw, as knots in the straw
12 cuttings are not completely converted.)

13 A piston compressor is used for pressurization. Development of a new feeding and dosing
14 system is a necessity, as pneumatic feeding is not possible due to the plugging nature of
15 the fibrous biomass. This route affords higher biomass-to-biosyngas energy and system
16 efficiencies because of the low electricity and inert gas consumption. Therefore, this route
17 is the preferred option, especially for expensive biomass. However, conditionally that (i)
18 the 1 mm biomass cuttings can be fed by a screw to the gasifier and (ii) that sufficient
19 conversion is achieved in the gasifier.²⁵

20

21

22 **6.3.4.2 Torrefaction and Pneumatic Feeding**

23

24 Torrefaction is a mild heat treatment at 250–300 °C that efficiently turns solid biomass into a
25 brittle, easy to pulverize material ('bio-coal') that can be treated as coal.^{32,33} Furthermore,
26 torrefied biomass can be palletized very easily to obtain a dense and easy to transport
27 biomass fuel.³⁴ The hydrophobic nature of torrefied material further simplifies logistics.
28 Pulverized torrefied biomass can be fed like coal, thus enabling a smooth transition from
29 coal to biomass.

30 Although torrefaction is a rather common process, in e.g. the coffee industry, it has
31 never been optimized for efficient production of a brittle 'bio-coal'. Research at the Energy
32 Research Centre of the Netherlands (ECN) shows, that the conversion of wood into a
33 torrefied wood with similar milling characteristics as hard coal can have an energetic
34 efficiency of 90–97 % LHV. The gases produced during torrefaction can be used to supply
35 the thermal needs of the process.

36

37

38 **6.3.4.3 Fluidized Bed Gasification**

39

40 High overall biomass-to-biosyngas and system efficiencies can also be obtained with a
41 system in which a (pressurized) fluidized bed gasifier is used to 'pretreat' the biomass
42 (i.e. 78 and 85 %, respectively). The raw product gas, containing hydrocarbons and tars as
43 well as the unconverted char and some bed material from the bed, is directly fed into the
44 entrained flow gasifier. Upon entrained flow gasification all the organic compounds and char
45 are converted into syngas, therefore, the product gas quality and the carbon conversion of
46 the fluidized bed gasifier are irrelevant. The entrainment of bed material from the fluidized
bed gasifier is no problem and even preferred, as it will act as flux for the entrained flow

1 gasifier. Major advantage is that no pre-treatment of the biomass is necessary (chips of
2 5 cm are acceptable) and that all types of biomass can be processed (i.e. both woody and
3 straw-like biomass). However, this system is the most challenging, as the entrained flow
4 gasifier requires a very stable feed flow to guarantee safe operation, while a fluidized bed
5 gasifier typically has some variations in the product gas flow.²⁵

6

7 **6.3.4.4 Fast Pyrolysis for Bioslurry Production and Feeding**

8

9 Pyrolysis takes place at approximately 500 °C and can convert solid biomass into a liquid
10 product (bio-oil) in a process that is called flash-pyrolysis. The conversion efficiency will
11 increase to 90 % by including char in the oil to produce a bio-slurry.^{35,36} Slurries can be
12 pressurized and fed relatively easily.

13 The Forschungs Zentrum Karlsruhe (FZK) developed a concept to produce syngas from
14 agricultural waste streams like straw.³⁶ In this concept, straw is liquefied locally by flash
15 pyrolysis into oil and char slurry, which is subsequently transported and added to a large
16 pressurized oxygen-blown entrained flow gasifier. This approach offers the advantage of
17 low transport costs of the energy dense slurry and large-scale syngas production and
18 synthesis. At the same time, the problem of pressurizing biomass is solved, since slurries
19 are pumpable. An important patented feature of the concept is formed by the fact that
20 milling of char can turn a solid mass into liquid slurry by eliminating the volume of the
21 pores of the char.³⁷ Flash pyrolysis plants typically will be 100 MW_{th} input capacity. FZK
22 developed the Lurgi-Ruhrgas concept that includes twin screws for pyrolysis. A 5–10 kg/h
23 PDU is available at the premises of FZK. Several slurries have been tested in the 500 kg/h
24 entrained flow gasifier of Future Energy in Freiberg to study its gasification and slagging
25 behaviour.³⁸ Slurries from straw have been successfully converted into syngas with high
26 conversion and near zero methane content. Biofuel costs produced by this kind of biomass-
27 to-liquid plant will be around 1 €/kg (approximately 23 €/GJ), based on a feedstock price
28 of 3 €/GJ straw.³⁶

29

30 **6.3.4.5 Slow Pyrolysis for Char and Gas Production**

31

32 Choren develops the Carbo-V concept where solid biomass is pre-treated by slow pyrolysis
33 to yield char and gases instead of the fast pyrolysis slurry.³⁹ The gases are gasified at high
34 temperature (typically 1300 °C) to generate syngas. The char is pulverized and injected
35 downstream the high-temperature reactor in order to cool the syngas by endothermic char
36 gasification reactions. This so-called chemical quench cools the syngas to approximately
37 1000 °C. The concept has been demonstrated in the 1 MW_{th} alpha plant in Freiberg,
38 Germany. Since 2003, biofuel synthesis has been added to the plant. After a short period of
39 methanol synthesis, the unit was modified to FT-synthesis. Late 2002, Choren started the
40 construction of the 45 MW_{th} 5 bar beta plant. Early 2007, this plant is projected to produce
41 FT-diesel with approximately 50 % thermal efficiency from wood.

42

43 **6.3.4.6 Black Liquor Utilization**

44

45 Existing pulp and paper industry offers unique opportunities for production of biofu-
46 els with syngas as intermediate. An important part of many pulp and paper plants is

1 formed by the chemicals recovery cycle where black liquor is combusted in so-called
2 Tomlinson boilers. Substituting the boiler by a gasification plant with additional bio-
3 fuel and electricity production is very attractive, especially when the old boiler has to
4 be replaced. The economic calculations are based on incremental costs rather than ab-
5 solute costs. This method seems generally acceptable⁴⁰⁻⁴³ and leads to e.g. methanol
6 production costs of 0.3–0.4 €/litre of petrol equivalent.⁴¹⁻⁴³ It must be realized that
7 biofuel plants, which are integrated in existing pulp and paper mills should match the
8 scale of the paper mill. The integrated capacity of the biofuel plant therefore is typi-
9 cally 300 MW_{th},⁴¹ which is at least 10 times smaller than commercial fossil fuel based
10 methanol and FT-plants. Efficiencies of biofuel plants, which are integrated in pulp-
11 and paper industry, are often reported based on additional biomass, which is needed to
12 produce the additional biofuels. This results in very high reported values of 65 % to
13 even 75 %.^{42,43}

14 Chemrec develops a technology needed to convert black liquor into initially syngas
15 and subsequently produce biofuels like DME, methanol, etc.⁴² It is a dedicated entrained
16 flow gasifier operated at temperatures as low as 1000–1100 °C. This is possible due to
17 the presence of large amount of sodium, which acts as a gas-phase catalyst in the gasifier.
18 Chemrec constructed DP1, a 3 MW_{th} entrained flow gasifier operating at 30 bar in Piteå,
19 Sweden, next to the Kappa paper mill. It includes gas cooling by water quench and gas
20 cooler. The syngas will have a composition (vol % dry) of approximately: 39 % H₂, 38 %
21 CO, 19 % CO₂, 1.3 % CH₄, 1.9 % H₂S, and 0.2 % N₂. At present, the pilot plant is being
22 commissioned. Demonstration plant DP2 will be a black liquor gasification combined cycle
23 (BLGCC) plant in Piteå. DP3 will be located in Mörrum. This will produce a biofuel. Both
24 plants will be constructed in 2006/2007. Implementation of such concept in the US paper
25 and pulp industry could produce 4.4 % of current US petroleum/diesel consumption.⁴⁰ In
26 Finland and Sweden this could be significant, as high as 51 % and 29 % of the respective
27 national use of transportation fuels.⁴³

28
29

30 6.3.5 Syngas Cleaning and Conditioning

31

32 Generally, gasification technologies are selected for their high efficiency to produce H₂
33 and CO, with little or no hydrocarbons. The presence of minor impurities (soot, sul-
34 phur, chlorine, and ammonia) will however be inevitable. Since the concentration of
35 these components generally exceed the specification of a catalytic synthesis reactor (as
36 presented in ???), gas cleaning is necessary. It must be realized that there is an eco-
37 nomic trade off between gas cleaning and catalyst performance. Cleaning well below
38 specifications might be economically attractive for synthesis processes that use sensi-
39 tive and expensive catalytic materials. Since raw bio-syngas resembles syngas produced
40 from more conventional fuels like coal and oil residues, gas cleaning technologies will
41 be very similar. This means that it most probably will include a filter, Rectisol unit, and
42 downstream gas polishing to remove the traces. This involves e.g. ZnO and active carbon
43 filtering.

44 Because the H₂/CO-ratio generally needs adjustment, a water-gas-shift reactor will also
45 be part of gas conditioning. The Rectisol unit then combines the removal of the bulk of the
46 impurities and the separation of CO₂.

Au: Pls. update
cross reference
instead of ???.

6.4 Economics of Biomass-Based FT-Diesel Production Concepts

In the previous paragraph pressurized oxygen-blown entrained flow gasification is considered to be the heart of the optimum large-scale syngas/FT-diesel production process. In this paragraph, the production costs of the BTL diesel fuel are discussed. The fuel production costs are composed of the costs for the biomass feedstock material, transport, transshipment, and storage, pre-treatment, and the conversion (gasification, cleaning, synthesis, and product upgrading).⁴⁴ The schematic line-up of the integrated biomass gasification and Fischer-Tropsch synthesis (BTL) plant is shown in Figure 6.5.

Au: Please check cross ref. Fig. 6.5 ok here.

It is assumed that the BTL plant is located in the centre of a circular forest area. Of the area 38 % is production forest of which 50 % is exploitable with an annual biomass production yield of 10 ton dry solids per hectare. The radius of the area depends on the scale of the BTL plant, i.e. on the amount of biomass feedstock required. The biomass is assumed to be chipped and dried (7 % moisture; bulk density 202 kg/m³; calorific value LHV_{ar} 16.2 MJ/kg) in the forest, costs of which are included in the final biomass price of 4.0 €/GJ_{biomass}. The dried chips are transported by truck to a BTL plant (loading costs 0.073 €/m³; variable transport costs 0.08 €/ton/km; fixed transport costs 2.0 €/ton). The average transport distance to the BTL equals two-thirds of the area radius multiplied by 1.2 to accommodate for imperfectness of the existing road network.

Au: update § 20.

On site of the BTL plant, the biomass is intermediary stored (one week capacity; 5.3 €/m³ per year) before it is pre-treated (by torrefaction, §0) with 97 % efficiency, to yield a material that can be fed to the gasifier and allows stable gasification. The pre-treatment costs are fixed at 1.5 €/GJ of pre-treated material. In the oxygen-blown entrained flow gasifier the biomass is converted into biosyngas with 80 % chemical efficiency. The raw biosyngas is cooled, conditioned, and cleaned from the impurities. The on-specification biosyngas is used for FT synthesis to produce C₅₊ liquid fuels. Conversion efficiency from biosyngas to FT C₅₊ liquids is 71 %. All FT liquids products are equally considered as diesel fuel.

6.4.1 Capital Investment

Reliable cost data for Gas-to-Liquids projects are not available. Therefore, the investment costs for GTL as well as BTL plants are derived from the off-the-record information on the EPC cost of the 34,000 bbl/d GTL plant built by Sasol-QP in Qatar.⁴⁴ From this information the total capital investments (TCI) are determined and with a constant scale factor of 0.7, the TCI is calculated for the whole scale range from 10 to 100,000 bbl/d. However, for smaller scales this results probably in an underestimate of the TCI costs as a smaller scale-factor would be more realistic, i.e. 0.6 or even 0.5 for 'real' small GTL plants. The scale dependency of the TCI of a GTL plant as well as of a BTL plant is presented in Figure 6.7.⁴⁴

Based on assessment of the main equipments cost items of a BTL plant, it can be concluded that the TCI for a BTL plant is typically 60 % more expensive than a GTL plant with the same capacity, which is caused by the 50 % higher air separation unit (ASU) capacity, the 50 % more expensive gasifier due to the solids handling, and the requirement of a Rectisol unit for bulk gas cleaning. Although the approach followed is very simple,

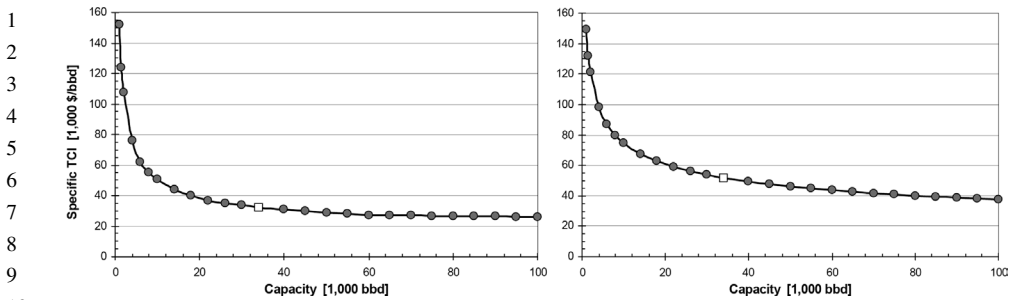


Figure 6.7 Scale-dependency of specific TCI for GTL (left) and BTL (right) plants.

the results are just as good, or probably even more accurate than in-depth studies based on detailed assessment of equipment cost items.

6.4.2 Fischer-Tropsch Biodiesel Production Costs

Based on the capital costs for the BTL plant as presented in Figure 6.8, the annual capital (CAPEX) and operational (OPEX) costs are calculated with a depreciation period of 15 years (linear), a required IRR of 12 %, operation and maintenance (O&M) costs of 5 %, and a plant availability of 8000 h per year. Based on these assumptions as well as the assumptions on biomass (logistic) costs and conversion efficiencies, the costs of the produced FT liquids can be given as a function of the plant capacity (Figure 6.8).⁴⁴ It is clear that the costs for the conversion are the dominant cost factor at plant scales below 2000 MW_{th} biomass input.

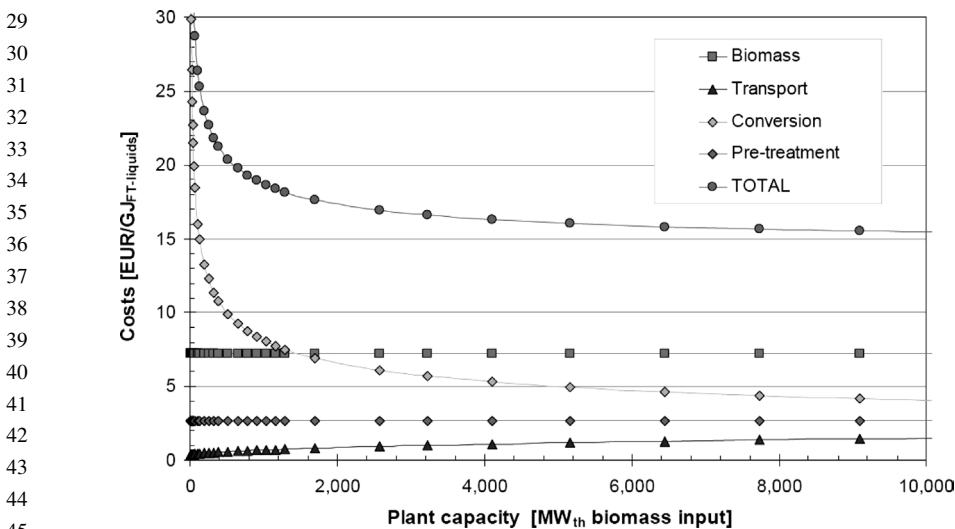


Figure 6.8 Scale dependency of Fischer-Tropsch diesel fuel production costs.

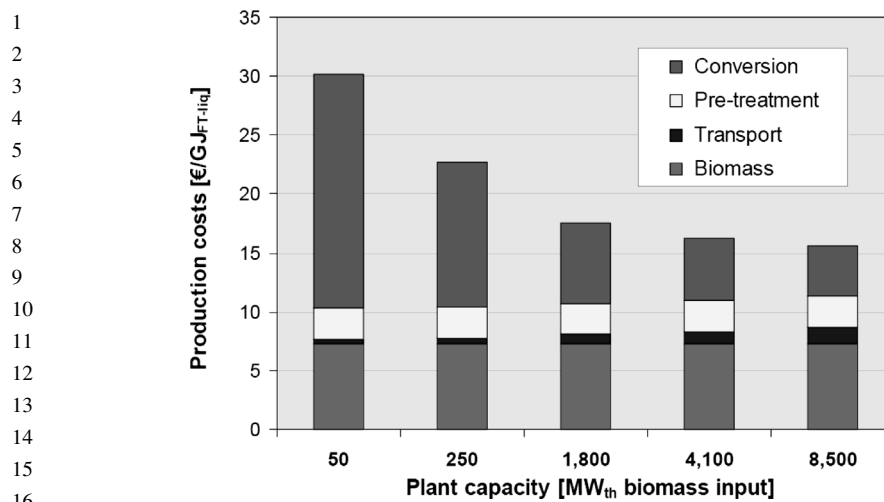


Figure 6.9 Scale dependency of FT-fuel production costs ($15 \text{ €/G}_{\text{FT}} \approx 55 \text{ €/t/L}$).

6.4.2.1 Impact of Transport Distances

The transport, transshipment, and storage costs are only a small cost item, independent of the scale and related transport distances. The results also show that, in the assessed case, no advantage can be taken from decreasing the plant size, as the decrease in transport costs is completely outweighed by the increasing investment costs. In this assessment only land transport by truck is considered. In reference [45] various scenarios based on overseas biomass import are compared. In general can be stated that overseas transport would add approximately $1 \text{ €/G}_{\text{FT}}$ to the fuel costs.

6.4.2.2 Impact of Scale

In Figure 6.9, the cumulative FT-fuel production costs are shown in an alternative way, for five specific scales. The production costs decrease from $30 \text{ €/G}_{\text{FT}}$ for a $50 \text{ MW}_{\text{th}}$ plant to just above $15 \text{ €/G}_{\text{FT}}$ (i.e. approximately 55 €/t/L) at a scale of $8500 \text{ MW}_{\text{th}}$. The latter scale of the projected Shell Qatar plant is comparable to a conventional oil refinery. At large scale the biomass costs of $7.3 \text{ €/G}_{\text{FT}}$ make up half of the fuel costs. At small scale the investments costs are the determining cost item, i.e. two-thirds of the fuel costs.

6.4.2.3 Impact of Biomass Price

The costs of the biomass add $7.3 \text{ €/G}_{\text{FT}}$ to the FT-diesel fuel costs (independent of the scale). The $7.3 \text{ €/G}_{\text{FT}}$ follows from the overall biomass-to-fuel conversion efficiency of 56% , i.e. for each GJ of FT fuel 1.8 GJ of biomass is required.⁴⁴ This illustrates the importance of systems with high biomass to fuel efficiencies. Operating a smaller BTL plant might be advantageous when cheap local biomass is available. In the case that biomass is available at $0.6 \text{ €/G}_{\text{BM}}$, FT-fuels can be produced at $15 \text{ €/G}_{\text{FT}}$ already

1 in a 150 MW_{th} biomass plant.⁴⁵ However, one can question how many of these loca-
2 tions will exist within a global biomass market. Therefore, based on economic consid-
3 erations, it is advisable to direct technology development towards large BTL facilities.
4 Additionally, it should be noted that the use of a scale factor of 0.7 for calculating the
5 investment costs, most likely results in an underestimation of the costs for scales below
6 2,500 MW_{th} (or 20,000 bbl/d). A factor of 0.6 for these smaller scales is probably more
7 accurate, while a factor of 0.5 should be used for the even smaller scales below 5,000 bbl/d
8 (600 MW_{th}).
9

10 6.5 Conclusions

11
12 To meet the longer-term market demands as mentioned in the Vision document of the
13 European Technology Platform on Biofuels, and to gradually shift to biofuels with a better
14 overall CO₂-reduction potential, the introduction of so-called second-generation biofuels is
15 a necessity. Making H₂ and CO (syngas) from biomass is widely recognized as a necessary
16 step in the production of second-generation biofuels. There are two major approaches in
17 converting biomass into a syngas.
18

19 The first approach is based on fluidized bed gasification: biomass is converted to fuel
20 gas at approximately 900 °C. This option requires almost no biomass pre-treatment, but
21 the product gas needs downstream catalytic upgrading. A catalytic reactor is needed to
22 reform the hydrocarbons to syngas. Support R&D is being performed at VTT (Finland),
23 Värnamo (Sweden), and CUTECH (Germany). The fluidized bed gasification approach has
24 the advantage that the gasification technology has already been developed and demonstrated
25 with biomass for the production of heat and/or electricity.

26 The second approach is based on entrained flow gasification: fuel is converted at high
27 temperature (1000–1300 °C) into a syngas with little or no methane and other hydrocarbons.
28 The entrained flow gasification processes have already been developed and demonstrated
29 on large-scale for coal. In some cases even mixtures of coal and specific biomass have
30 been tested successfully. Most biomass feedstocks, however, are not suitable to be directly
31 injected into an entrained flow gasifier because the fuel size needs to be small. Additional
32 extensive pre-treatment (e.g. pyrolysis, torrefaction) is therefore required.

33 It should be realized that the above-mentioned options are not necessarily competing
34 processes. The preference very much depends on boundary conditions, based on fuel
35 type and fuel availability. Furthermore, the potential scale of the plants is an important
36 issue. The back-end of the process generally needs to be as large as possible because of
37 the dominant economy-of-scale effect in biofuel synthesis and upgrading. The front-end
38 however involves biomass supply. This generally means that increasing plant size means
39 higher feedstock costs because longer transport distances are involved.

40 There is however an attractive way to deal with this scale ‘mismatch’ by splitting the two
41 parts: biomass is pre-treated in relatively small-scale plants close to the geographical origin
42 of the biomass and the intermediate is transported to a central large-scale plant where it
43 is converted into a biofuel. The pre-treatment should preferably result in a densified and
44 easy to transport material. Conventional pelletization is an option, but more attractive is
45 the use of dedicated pre-treatment that also produces a feedstock that can be used directly
46 in the large-scale syngas plant, e.g. torrefaction or pyrolysis. Loss of efficiency due to pre-
treatment then in general is compensated for by the logistic advantages of densification.

References

- 1
- 2
- 3 1. M.E. Dry, The Fischer-Tropsch Synthesis, in *Catalysis-Science and Technology*, J.R. Anderson;
- 4 M. Boudart (Eds), Springer-Verlag, New York, USA, 159–255, 1981.
- 5 2. H. Boerrigter, H. den Uil and H.P. Calis, Green diesel from biomass via Fischer-Tropsch
- 6 synthesis: new insights in gas cleaning and process design, in *Pyrolysis and Gasifica-*
- 7 *tion of Biomass and Waste*, A.V. Bridgwater (Ed.), CPL Press, Newbury, UK, 371–383,
- 8 2003.
- 9 3. H. Boerrigter and H. den Uil, Green diesel from biomass by Fischer-Tropsch synthesis: new
- 10 insights in gas cleaning and process design, RX–03-047, ECN, Petten, the Netherlands, 1–15,
- 11 2003.
- 12 4. (a) D. Hunt, *Synfuels Handbook*, Industrial Press Inc., McGraw-Hill Inc., New York, 1983 and
- 13 (b) *Encyclopaedia of Science and Technology*, 7th ed., McGraw-Hill Inc., New York., USA,
- 14 1992.
- 15 5. E.D. Larson (2006) Advanced Technologies for Biomass Conversion to Energy, in *Proceedings*
- 16 *of the 2nd Olle Lindström Symposium on Renewable Energy*, Bio-Energy, Royal Institute of
- 17 Technology, Stockholm, Sweden, 2006.
- 18 6. (a) K. Hedden. A. Jess and T. Kuntze, From Natural Gas to Liquid Hydrocarbons, in *Edröl*
- 19 *Erdgas Kohle, part 1*, **110**, 318–321, 1999, (b) Idem, *part 2*, **110**, 365–370, 1994, (c) Idem, *part*
- 20 *3*, **111**, 67–71, 1995 and (d) Idem, *part 4*, **113**, 531–540, 1997.
- 21 7. C. Higman and M. van der Burgt, *Gasification*, Elsevier Science, USA, 2003.
- 22 8. H. Boerrigter, A. van der Drift and R. van Ree, Biosyngas; markets, production technologies,
- 23 and production concepts for biomass-based syngas, RX–04-013, ECN, Petten, the Netherlands,
- 24 1–37, 2004.
- 25 9. H.J. Veringa and H. Boerrigter, De syngas-route . . . van duurzame productie tot toepassingen,
- 26 RX–04-014, ECN, Petten, the Netherlands, 2004.
- 27 10. (a) A. van der Drift, R. van Ree, H. Boerrigter and K. Hemmes, Bio-syngas: key intermediate
- 28 for large scale production of green fuels and chemicals, in *proceedings of 2nd World Conference*
- 29 *and Technology Exhibition on Biomass for Energy, Industry and Climate Protection*, **Vol. II**,
- 30 2155–2157, Rome, Italy, 2004 and (b) Idem, RX–04-048, ECN, Petten, the Netherlands, 1–4,
- 31 2004.
- 32 11. H. Boerrigter, A. van der Drift and E.P. Deurwaarder, Biomass-to-liquids: Opportunities &
- 33 challenges within the perspectives of the EU Directives, in *5th Annual GTL (Gas-to-Liquids)*
- 34 *Technology & Commercialization Conference & Exhibition*, 2006.
- 35 12. M. Kaltschmitt and H. Hartmann, *Energie aus Biomasse, Grundlagen, Techniken und Verfahren*,
- 36 Springer-Verlag, Berlin, 770.
- 37 13. Conclusion from the Congress on Synthetic Biofuels – Technologies, Potentials, Prospects,
- 38 Wolfsburg, Germany, 2004.
- 39 14. H. Boerrigter and A. van der Drift, Large-scale production of Fischer-Tropsch diesel from
- 40 biomass: optimal gasification and gas cleaning systems., RX–04-119, ECN, Petten, The Nether-
- 41 lands, 2004.
- 42 15. H. Boerrigter, H.P. Calis, D.J. Slort, H. Bodenstaff, A.J. Kaandorp, H. den Uil and L.P.L.M.
- 43 Rabou, Gas cleaning for integrated Biomass Gasification (BG) and Fischer-Tropsch (FT) sys-
- 44 tems, C–04-056, ECN, 2004.
- 45 16. M.A. Paisley, R.P. Overend, M.J. Welch and B.M. Igoe, FERCO’s SilvaGas biomass gasification
- 46 process commercialisation opportunities for power, fuels, and chemicals, in *The 2nd World*
- Conference on Biomass for Energy, Industry, and Climate Protection*, Rome, Italy, 2004.
17. K. Whitty, State-of-the-art in black liquor gasification technology, in *IEA Annex XV meeting*,
- Piteå, Sweden, 2002.
18. A. van der Drift, An overview of innovative biomass gasification concepts, in *12th European*
- Conference on Biomass for Energy*, Amsterdam, the Netherlands, 381-11384, 2002.

- 1 19. A. van der Drift, C.M. van der Meijden and H. Boerrigter, MILENA gasification technology
2 for high efficient SNG production from biomass, in *14th European Biomass Conference &*
3 *Exhibition*, Paris, France, 2005.
- 4 20. EREC (European Renewable Energy Council): Renewable energy scenario to 2040, **16**, 2004.
- 5 21. L. Waldheim, Status of Chrisgas project; production of hydrogen-rich synthesis gas, in *Synbios,*
6 *the syngas route to automotive biofuels*, Stockholm, Sweden, 2005.
- 7 22. E. Kurkela, Novel ultra-clean concepts of biomass gasification for liquid fuels, in *Synbios, the*
8 *syngas route to automotive biofuels*, Stockholm, Sweden, 2005.
- 9 23. M. Claussen and S. Vodegel, The CUTEC concept to produce BtL-fuels for advanced power
10 trains, in *International Freiberg Conference on IGCC and Xtl technologies*, Freiberg, Germany,
2005.
- 11 24. A.G. Collot, Matching gasifiers to coals, ISBN 92-9029-380-2, IEA Clean Coal Centre, 63,
12 2002.
- 13 25. A. van der Drift, H. Boerrigter, B. Coda, M.K. Cieplik and K. Hemmes, Entrained flow gasifi-
14 cation of biomass; ash behaviour, feeding issues, and system analyses, C-04-039, ECN, Petten,
15 the Netherlands, 2004.
- 16 26. M. Schingnitz, Möglichkeiten zur Vergasung von Biomasse im Flugstrom, in: *Foerdergemein-*
17 *schaft Oekologische Stoffverwertung e.V.*, Halle, Germany, 47-57, 2003.
- 18 27. B. Sander, G. Daradimos and H. Hirschfelder, Operating results of the BGL gasifier at the
19 Schwarze Pumpe, in *Gasification Technologies*, San Francisco, USA, 2003.
- 20 28. M. Kanaar and C. Wolters, Fuel flexibility NUON Power Buggenum, in *Gasification, a versatile*
21 *solution*, Brighton, UK, 2004.
- 22 29. F. Kamka, A. Jochmann and L. Picard, Development status of BGL gasification, in *International*
23 *Freiberg Conference on IGCC and Xtl technologies*, Freiberg, Germany, 2005.
- 24 30. R. Bain, Overview of US biomass gasification projects and fuel tax exemptions, in *Synbios, the*
25 *syngas route to automotive biofuels*, Stockholm, Sweden, 2005.
- 26 31. A. van der Drift and H. Boerrigter, Synthesis gas from biomass for fuels and chemicals, C-06-
27 001, ECN, Petten, the Netherlands, 2006.
- 28 32. P.C.A. Bergman, A.R. Boersma, R.W.R. Zwart and J.H.A. Kiel, Torrefaction for biomass co-
29 firing in existing coal-fired power stations (BIOCOAL), C-05-013, ECN, Petten, the Nether-
30 lands, 1-72, 2005.
- 31 33. P.C.A. Bergman, A.R. Boersma, J.H.A. Kiel, M.J. Prins, K.J. Ptasinski and F.J.J.G. Janssen,
32 Torrefaction for entrained flow gasification of biomass, C-05-067, ECN, Petten, the Netherlands,
33 1-51, 2005.
- 34 34. P.C.A. Bergman, Combined torrefaction and pelletisation – the TOP process, C-05-073, ECN,
35 Petten, the Netherlands, 1-29, 2005.
- 36 35. A.V. Bridgwater, Fast pyrolysis of biomass: a handbook – Volume 2, CPL press, Newbury, UK,
37 2002.
- 38 36. E. Henrich, Clean syngas from biomass by pressurised entrained flow gasification of slurries
39 from fast pyrolysis, in *Synbios, the syngas route to automotive biofuels*, Stockholm, Sweden,
40 2005.
- 41 37. E. Henrich and K. Raffelt, Two-stage rapid pyrolysis-entrained bed gasification of coal and solid
42 wastes to synthesis gas, Patent EP1586621, 1-9, 2005.
- 43 38. E. Dinjus, E. Henrich, T. Kolb and L. Krebs, Synthesegas aus Biomasse, Verfahren des
44 Forschungszentrums Karlsruhe, in *Pyrolyse- und Vergasungsverfahren in der Energietechnik*
45 *Bio-Fuel-Konzepte*, Freiberg, Germany, 2004.
- 46 39. M. Rudloff, Operation experiences of Carbo-V process for FTD production, in *Synbios, the*
syngas route to automotive biofuels, Stockholm, Sweden, 2005.
- 40 40. E.D. Larson, Potential of biorefinery as large-scale production plant for liquid fuels in the forest
41 and pulp industry, in *Synbios, the syngas route to automotive biofuels*, Stockholm, Sweden,
42 2005.

116 *Biofuels*

- 1 41. K. Sipilä, T. Mäkinen and P. McKeough, Raw material availability to synfuels production
2 and remarks on RTD goals, results of the BioFuture project, in *Synbios, the syngas route to*
3 *automotive biofuels*, Stockholm, Sweden, 2005.
- 4 42. I. Landälv, Status and potential of CHEMREC black liquor gasification, in *Synbios, the syngas*
5 *route to automotive biofuels*, Stockholm, Sweden, 2005.
- 6 43. T. Ekbom, Techno-economics of biomass and black liquor gasification for automotive fuel
7 production, in *Synbios, the syngas route to automotive biofuels*, Stockholm, Sweden, 2005.
- 8 44. H. Boerrigter, Economy of Biomass-to-Liquids (BTL) plants, C-06-019, ECN, Petten, the
9 Netherlands, 1–29, 2006.
- 10 45. R.W.R. Zwart, H. Boerrigter and A. van der Drift, Integrated Fischer-Tropsch diesel production
11 systems, *Energy & Fuels*, **20**, 2192–2197, 2006.
- 12
- 13
- 14
- 15
- 16
- 17
- 18
- 19
- 20
- 21
- 22
- 23
- 24
- 25
- 26
- 27
- 28
- 29
- 30
- 31
- 32
- 33
- 34
- 35
- 36
- 37
- 38
- 39
- 40
- 41
- 42
- 43
- 44
- 45
- 46