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MAIN ROUTES FOR THE THERMO-CONVERSION OF BIOMASS INTO FUELS AND CHEMICALS. PART 2: GASIFICATION SYSTEMS

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Abstract:

Gasification as a thermo-chemical process is defined and limited to combustion and pyrolysis. The gasification of biomass is a thermal treatment, which results in a high production of gaseous products and small quantities of char and ash. The solid phase usually presents a carbon content higher than 76%, which makes it possible to use it directly for industrial purposes. The gaseous products can be burned to generate heat or electricity, or they can potentially be used in the synthesis of liquid transportation fuels, H2, or chemicals. On the other hand, the liquid phase can be used as fuel in boilers, gas turbines or diesel engines, both for heat or electric power generation. However, the main purpose of biomass gasification is the production of low- or medium heating value gas which can be used as fuel gas in an internal combustion engine for power production. In addition to limiting applications and often compounding environmental problems, these technologies are an inefficient source of usable energy.

Introduction

Gasification is a thermo-chemical conversion technology that carbonaceous materials (coal, petroleum coke, biomass, etc.) into a combustible gas called producer gas. The production of combustible gas from carbonaceous materials is already an old technology. The first record of its commercial application origins from so called dry distillation (or pyrolysis – heating of feedstock on absence of O2, resulting in thermal decomposition of fuel into volatile gases and solid carbon) origins from year 1812 . The first commercial gasifier was installed in 1839, when Bischaf patented a simple process for gasifying coke. The first attempt to use producer gas to fire internal combustion (IC) engine was carried out in 1881 . Gasifiers were subsequently further developed for different fuels and were in widespread use in specific industrial power and heat applications up to the 1920s, when oil fuelled systems gradually took over the producer gas fuelled systems . Before the construction of natural gas pipelines, there were many ‘‘gasworks” serving larger town and cities in Europe and the United States. During the 2nd World War (1939–1945), almost a million gasifiers were used to run cars, trucks, and buses using primarily wood as a fuel .

Since the energy crises of the 1970s, many countries have become interest in biomass as a fuel source. Biomass is the most abundant renewable energy source on earth and is considered by far the highest quality form of indirect solar energy. Biomass energy is more economic to produce and it provides more energy than other energy forms. The technology was perceived as a relatively cheap indigenous alternative for small-scale industrial and utility power generation in those developing countries that suffered from high world market petroleum prices and had sufficient sustainable biomass resources . The manufacturing took off with increased interest shown in gasification technology. A review of gasifier manufacturers in Europe, the United States, and Canada identified 50 manufacturers offering commercial gasification plants from which: (1) 75% of the designs were fixed-bed downdraft type, (2) 20% of the designs were fluidized-bed systems, (3) 2.5% of the designs were updraft type, and (4) 2.5% were of various other designs.

The remainder of this paper is organized as follows. Section 2 presents a detailed review of biomass gasification and gasification technologies. Section 3 discusses the major applications of producer gas produced from biomass gasification. Finally, Section 4 draws the main conclusions of this paper.

2. Gasification of biomass

2.1. Principles of biomass gasification

The gasification of biomass is a thermal treatment, which results in a high production of gaseous products and small quantities of char and ash . It is a well-known technology that can be classified depending on the gasifying agent: air, steam, steam–oxygen, air–steam, oxygen-enriched air, etc. . Gasification is carried out at high temperatures in order to optimize the gas production. The resulting gas, known as producer gas, is a mixture of carbon monoxide, hydrogen and methane, together with carbon dioxide and nitrogen . Yield a product gas from thermal decomposition

composed of CO, CO_2, H_2O, H_2, CH_4, other gaseous hydrocarbons (CHs), tars, char, inorganic constituents, and ash. Gas composition of product from the biomass gasification depends heavily on the gasification process, the gasifying agent, and the feedstock composition . Gasification of biomass is generally observed to follow the reaction:

$$\begin{aligned}\text{Biomass} + O_2(\text{or } H_2O) \rightarrow\ & CO, CO_2, H_2O, H_2, CH_4 + \text{other CHs} \\ & + \text{tar} + \text{char} + \text{ash} \qquad (1)\end{aligned}$$

Assuming a gasification process using biomass as a feedstock, the first step of the process is a thermochemical decomposition of the cellulose, hemicelluloses and lignin compounds with production of char and volatiles . Further the gasification of char and some other equilibrium reactions occur.

Char gasification is the rate-limiting step in the production of gaseous fuels from biomass. Arrhenius kinetic parameters have been determined for the reaction of chars prepared by pyrolysis of cottonwood and Douglas fir at 1275 K with steam and CO2

. The results indicate that both reactions are approximately zero order with respect to char; the overall reaction rate is fairly constant throughout and declines only when the char is nearly depleted. This suggests that the reaction rate depends on such factors as total available active surface area or interfacial area between the char and catalyst particles. These parameters would remain relatively constant during the gasification process. Softwood and hardwood chars exhibited similar gasification behavior. Results indicate that the mineral (ash) content and composition of the original biomass material, and pyrolysis conditions under which char is formed significantly influence the char gasification reactivity.

One of the major problems in biomass gasification is how to deal with the tar formed during the process . Tar is a complex mixture of condensable hydrogen which includes single ring to 5-ring aromatic compounds along with other oxygen containing hydrocarbons and complex the polycyclic aromatic hydrocarbons (PAHs) . Control technologies of tar production can broadly be divided into two approaches : (1) treatments inside the gasifier (primary methods) and (2) hot gas cleaning after the gasifier (secondary methods). Although secondary methods are proven to be effective, treatments inside the gasifier are gaining much attention due to economic benefits. In primary methods, the operating parameters such as temperature, gasifying agent, equivalence ratio, residence time and catalytic additives play important roles in the formation and decomposition of tar. Primary methods are not yet fully understood and have not to be implemented commercially . Pilot-scale tests have shown that catalytic cracking of tars can be very effective. Tar conversion in excess of 99% has been achieved using dolomite, nickel-based and other catalysts at elevated temperatures of typically 1075–1175 K . Coconut shell gasification by steam reforming in the presence of nickel-dolomite. They reported that the tar yield was decreased from 19.55–1.4% at temperature 1075 K, feed rate 0.5 g min_1 and steam to carbon ratio 0.95. 2.2. Types of gasifiers Several types of gasifiers have been developed; an overview is shown in Fig. 1. These gasifiers have different hydrodynamics (especially the way in which the solid fuel and the gasification agent are contacted), gasification agents (air, oxygen and/or steam) and operating conditions such as temperature and pressure . The most important types are fixed bed (updraft or downdraft fixed beds) gasifiers, fluidized-bed gasifiers, and entrained flow gasifiers.

Fixed-bed gasifiers are the most suitable for biomass gasification. Fixed-bed gasifiers involve reactor vessels in which the biomass material is either packed in or moves slowly as a plug, with gases flowing in between the particles . Fixed-bed gasifiers

are usually fed from the top of the reactor and can be designed in either updraft or downdraft configurations. With fixed-bed updraft gasifiers, the air or oxygen passes upward through a hot reactive zone near the bottom of the gasifier in a direction countercurrent to the flow of solid material . They can be scaled up; however, they produce a product gas with very high tar concentrations. This tar should be removed for the major part from the gas, creating a gas-cleaning problem. Fixed-bed downdraft gasifiers are limited in scale and require a well-defined fuel, making them not fuel-flexible . Small scale fixed-bed downdraft gasifier installations (150 kWe–1 MWe) can be employed for on-site conversion of biomass to electricity and heat .

Fluidized-bed gasifiers are a more recent development that takes advantage of the excellent mixing characteristics and high reaction rates of this method of gas–solid contacting . Fluidized-bed gasifiers are typically operated at 1075–1275 K (limited by the melting properties of the bed material) and are therefore not generally suitable for coal gasification, as due to the lower reactivity of coal compared to biomass, a higher temperature is required (>1575 K) . Examples of the fluidized-bed gasifier systems are bubbling fluidized-bed gasifiers, entrained bed gasifiers, and circulating fluidized-bed gasifiers.

The bubbling fluidized-bed gasifier tends to produce a gas with tar content between that of the updraft and downdraft gasifiers. Some pyrolysis products are swept out of the fluid bed by gasification products, but are then further converted by thermal cracking in the freeboard region . The circulating fluidized-bed gasifiers employ a system where the bed material circulates between the gasifier and a secondary vessel. The circulating fluidized-bed gasifiers are suitable for fuel capacity higher than 10 MWth .

2.2. Composition of producer gas

The composition of the gas obtained from a gasifier depends on a number of parameters such as : (1) fuel composition, (2) gasifying medium, (3) operating pressure, (4) temperature, (5) moisture content of the fuels, (6) mode of bringing the reactants into contact inside the gasifier, etc. It is very difficult to predict the exact composition of the gas from a gasifier . Introduction of the water–gas equilibrium concept provides the opportunity to calculate the gas composition theoretically from a gasifier, which has reached equilibrium at a given temperature . Table 1 shows typical gas composition data as obtained from commercial wood and charcoal downdraft gasifiers operated on low to medium moisture content fuels.

3. Applications of biomass gasification

Gasification may be defined as a process by which a remnant – biomass, carbon, etc. – is converted into gases by means of a partial oxidization carried out at high temperature . At temperatures of approximately 875–1275 K, solid biomass undergoes thermal decomposition to form gas-phase products that typically include H_2, CO, CO_2, CH_4, H_2O, and other gaseous CHs. In most cases, solid char plus tars that would be liquids under ambient conditions are also formed . The solid phase usually presents a carbon content higher than 76%, which makes it possible to use it directly for industrial purposes . The gaseous products can be burned to generate heat or electricity , or they can potentially be used in the synthesis of liquid transportation fuels , H2 , or chemicals . On the other hand, the liquid phase can be used.

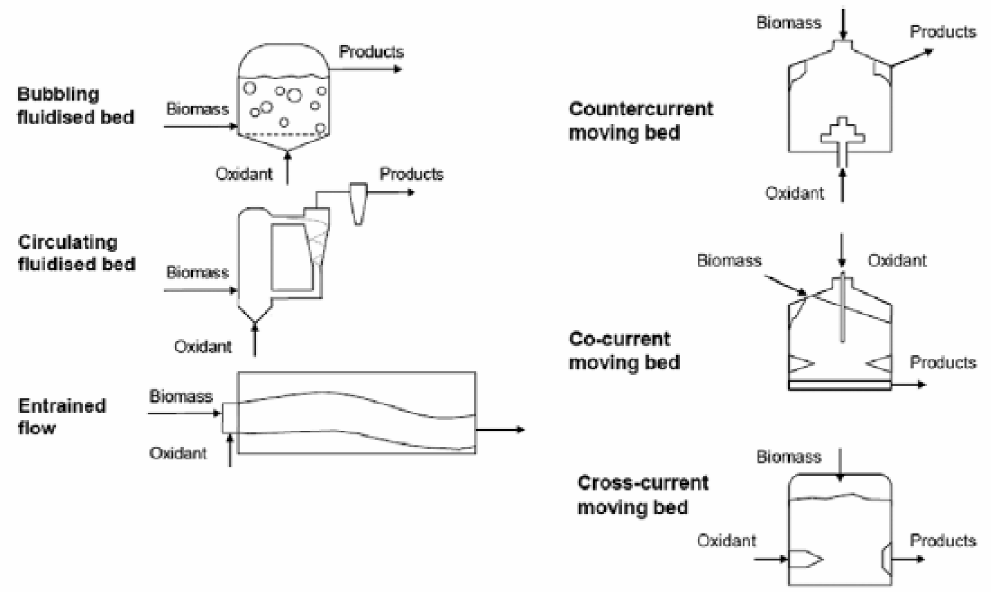

Fig. 1. Overview of gasifier types. Source: Ref. [4].

Table 1 : Typical gas composition data as obtained from commercial wood and charcoal downdraft gasifiers operated on low to medium moisture content fuels (wood 20%, charcoal 7%).

Component	H_2 (%)	CO_2 (%)	CH_4 (%)	CO (%)	N_2 (%)	Heating value (MJ/m^3)
Wood gas	12-20	9-15	2-3	17-22	50-54	5-5.9
Charcoal gas	4-10	1-3	0-2	28-32	55-65	4.5-5.6

as fuel in boilers, gas turbines or diesel engines, both for heat or electric power generation. However, the main purpose of biomass gasification is the production of low- or medium heating value (LHV, MHV) gas which can be used as fuel gas in an IC engine for power production. Possible products obtained from gasification process are given in Fig. 2.

3.1. Heat and power generation

Generating electricity and useful heat from the same power plant is called ‘‘cogeneration’’ in North America and ‘‘combined heat and power (CHP)’’ in Europe. CHP plants the product gas is fired on a gas engine. Modified gas engines can run without problems on most product gases even

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those from air-blown gasification that have calorific values of approximately 5–6 MJ/m3. Typically, the energetic output is one-third electricity and two-third heat The use of biomass for district heating and CHP has been expanding rapidly in countries such as Austria and Germany. In Finland, biomass-based fuels are used nearly completely in heat and CHP production. The number of large scale CHP plants in Finland is nearly 100MWand the total capacity is over 1500 MW. The Alholmens Kraft CHP plant in Pietarsaari, Finland, is the largest biofuelled power plant in the world. The plant produces steam for the adjacent paper mill and for a utility generating electricity and heat.

Biomass integrated gasification combined cycle (BIGCC) technology holds the promise of efficient, clean and cost-effective power generation from biomass. But, this technology is not yet commercially available. There are experiments with gasification for use in high efficiency combined-cycle power plants, which are in the demonstration phase. Several projects have been initiated for IGCC applications over the last decade, however, only two have been implemented, the SYDKRAFT plant at Värnamo based on FOSTER WHEELER technology and the ARBRE plant based on TPS technology.

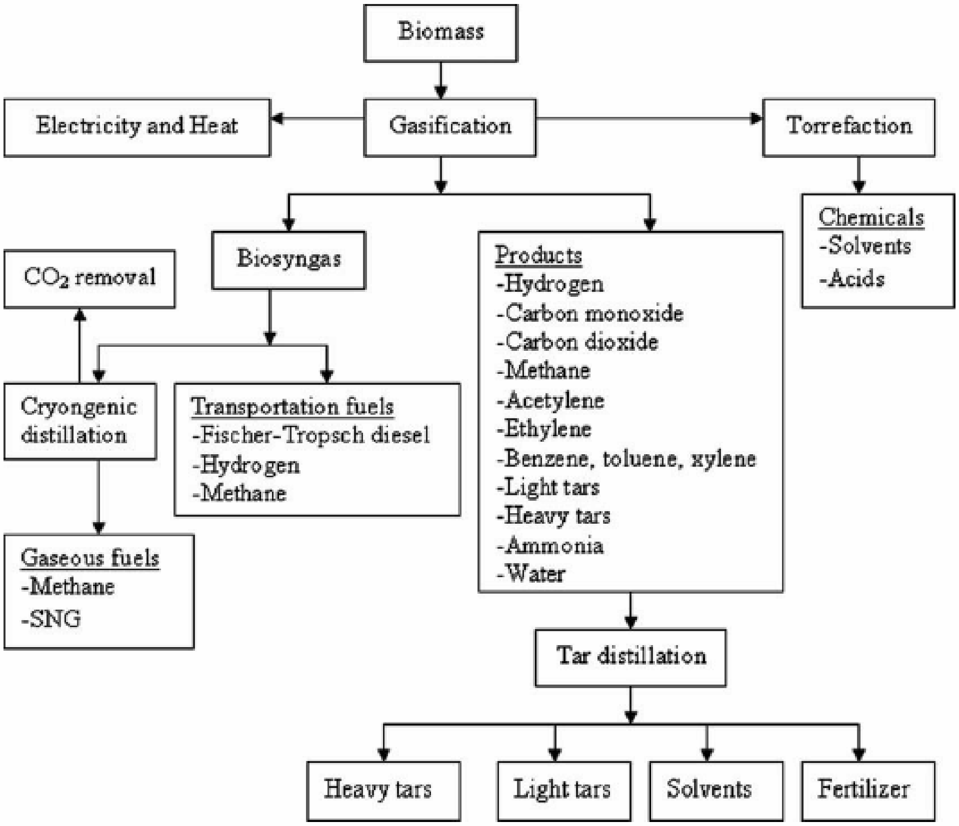

Fig. 2. Products from gasification process.

Biomass can be used as a primary energy source or as a secondary energy source to power gas turbines. As a secondary energy source, biomass is used to make a fuel, which can be used to fire a gas turbine. Biomass gasification is the latest generation of biomass energy conversion processes, and is being used to improve the efficiency, and to reduce the investment costs of bio-electricity generation through the use gas turbine technology. Biomassgasifier/gas turbines are projected to have bio-electricity efficiencies of 40–45%, or more than double those of Rankine-cycle systems. The costs of steam-Rankine systems vary widely depending on the level of sophistication. A typical installed capital cost for a 25MW unit is $1600–2100/kW. The heat produced from the electricity generating process is captured and utilized for domestic purposes and can be used in steam turbines to generate additional electricity. Fig. 3 shows the comparison between energy inputs to separate heat and power system and cogeneration system. Cogeneration is the simultaneous production of electricity and useful thermal energy from a single source.

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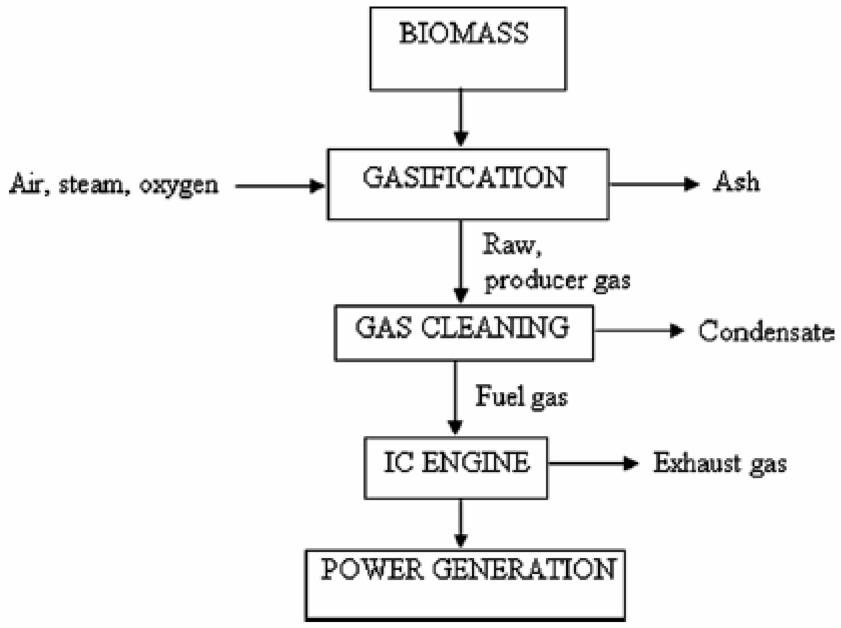

Fig. 4. System for power production by means of biomass gasification.

The gasification of biomass in fixed-bed reactors provides the possibility of combined heat and power production in the power range of 100 kWe up to 5 MWe. A system for power production by means of fixed-bed gasification of biomass consists of the main unit gasifier, gas cleaning system and engine (Fig. 4) .

Gasifiers are used to convert biomass into a combustible gas (biogas). The biogas is than used to drive a high-efficiency, combined- cycle gas turbine. Gaseous fuels consist of low and medium-calorific-value gases; the liquid is a primary-pyrolysis oil

called biocrude. A number of gasifiers have been developed to produce biogases from biomass and peat Biogas is a mixture of mainly CH4 and CO2 with very small amounts of sulfuric components. The gas generally composes of CH4 (55–65%), CO2 (35–45%), N2 (0–3%), H2 (0–1%), and H2S (0–1%) . Methane gas that is produced from manure is around 4800–6700 kcal/m3. As compare with pure methane gas contain energy of 8900 kcal/m3 . Typically between 20% and 40% of the heating value of the feedstock is contained in the biogas. For electricity generation, biogas is commonly burnt in IC engines, which may include heat recovery for

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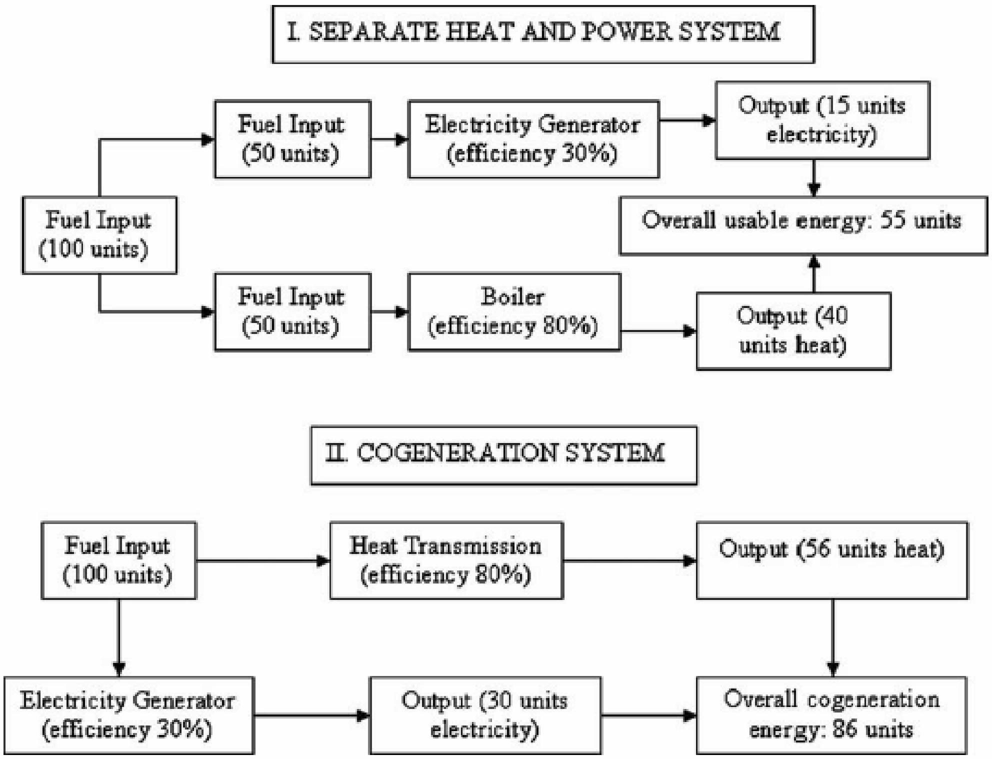
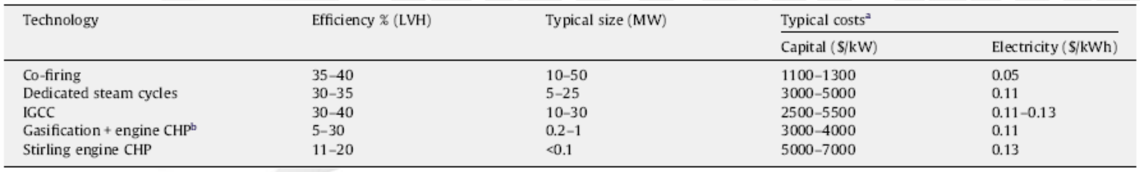


Fig. 3. Comparison between energy inputs to separate heat and power system and cogeneration system.

Table 2 : Typical data and figures for power generation from biomass.



Technology	Efficiency % (LVH)	Typical size (MW)	Typical costs^a	
			Capital ($/kW)	Electricity ($/kWh)
Co-firing	35–40	10–50	1100–1300	0.05
Dedicated steam cycles	30–35	5–25	3000–5000	0.11
IGCC	30–40	10–30	2500–5500	0.11–0.13
Gasification + engine CHP^b	5–30	0.2–1	3000–4000	0.11
Stirling engine CHP	11–20	<0.1	5000–7000	0.13

combined heat and power production. Electrical capacities range from tens of kW to several MW. Biogas may also be burnt in gas turbines; at larger scales, combined-cycle systems may be economically justified .

The capital cost of power plants with biomass gasification in the United States is about 2000–3000/kW and generation cost is in the order of 90/MWh. Such plants may be cost-effective in CHP mode if connected to district heating schemes. The cost of biomass combustion steam cycle and CHP plants can be lower, with 1000/ kW as the cost target. In Europe, the investment cost of biomass plants varies considerably from 1000 to 5000/kW, depending on plant technology, level of maturity and plant size . Data regarding investments required and the cost of bio-electricity with utilization of different technologies are presented in Table 2.

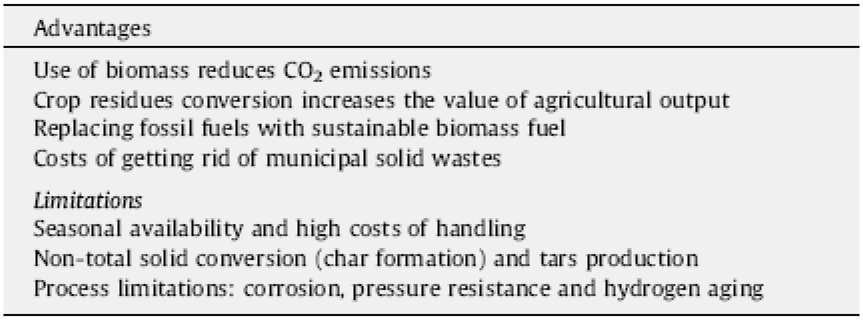
3.2. Transportation fuels via biomass gasification

3.2.1. Hydrogen

Many experts think that hydrogen has a major role to play as an energy carrier in future energy supply. Hydrogen can be used as a transportation fuel, whereas neither nuclear nor solar energy can be used directly. It has good properties as a fuel for IC engines in automobiles. Hydrogen can be used as a fuel directly in an IC engine not much different from the engines used with gasoline. Hydrogen has very special properties as a transportation fuel, including a rapid burning speed, a high effective octane number, and no toxicity or ozone-forming potential. It has much wider limits of flammability in air (4–75% by volume) than methane (5.3– 15% by volume) and gasoline (1–7.6% by volume). A stoichiometric hydrogen–air mixture has very low minimum ignition energy of 0.02 mJ. A hydrogen engine is easy to start in cold winter because hydrogen remains in a gaseous state until it reaches a low temperature
such as 20 K. With proper measurements it is believed that this amount of NOx can be reduced, even attaining 1/200 as low as diesel engines . The advantage is that hydrogen stores approximately 2.6 times more energy per unit mass than gasoline, meaning that hydrogen is more energy efficient than gasoline. The disadvantage is that it needs an estimated four times more volume than gasoline to store that energy .

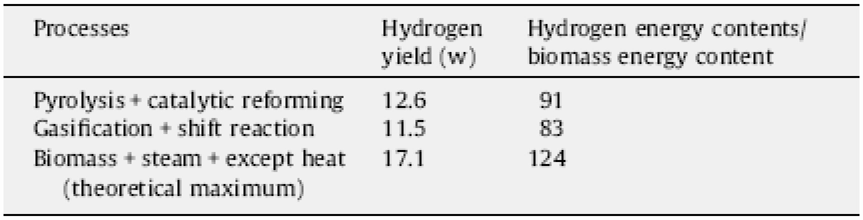
The methods available for the hydrogen production from biomass can be divided into two main categories: thermo-chemical

Table 3 : Main advantages and limitations of biomass to hydrogen.



Advantages
Use of biomass reduces CO_2 emissions
Crop residues conversion increases the value of agricultural output
Replacing fossil fuels with sustainable biomass fuel
Costs of getting rid of municipal solid wastes
Limitations
Seasonal availability and high costs of handling
Non-total solid conversion (char formation) and tars production
Process limitations: corrosion, pressure resistance and hydrogen aging

Table 4 : Comparison of hydrogen yields were obtained by use of three different processes.



Processes	Hydrogen yield (w)	Hydrogen energy contents/ biomass energy content
Pyrolysis + catalytic reforming	12.6	91
Gasification + shift reaction	11.5	83
Biomass + steam + except heat (theoretical maximum)	17.1	124

and biological routes. The production of hydrogen from renewable biomass has several advantages and limitations compared to that of fossil fuels, as shown in Table 3. The yield of hydrogen that can be produced from biomass is relatively low, 12–14% based on the biomass weight .

Hydrogen can be produced from biomass by pyrolysis , gasification , steam gasification , steam-reforming of bio-oils , and enzymatic decomposition of sugars . Table 4 shows comparison of hydrogen yields were obtained by use of three different processes. A certain numbers of efforts have been made by researchers to test gasification of various types of biomass for the production of hydrogen. Biomass gasification has been identified as a possible system for producing renewable hydrogen, which is beneficial to exploit biomass resources, to develop a highly efficient clean way for large-scale hydrogen production, and has less dependence on insecure fossil energy sources.

In the pyrolysis and gasification processes, water–gas shift is used to convert the reformed gas into hydrogen, and pressure swing adsorption is used to purify the product. The cost of hydrogen production from supercritical water gasification of wet biomass was several times higher than the current price of hydrogen from steam methane reforming. The price of hydrogen obtained by direct gasification of lignocellulosic biomass, however, is about three times higher than that for hydrogen produced by steam reforming of natural gas . Estimated cost comparison of hydrogen production by biomass gasification and natural gas steam reforming is shown in Fig. 5 .

Hydrogen is produced from the steam gasification of beech wood, olive waste, and wheat straw, hazelnut shell, wood sawdust, and waste wood. Modeling of biomass steam gasification to synthesis gas is a challenge because of the variability (composition, structure, reactivity, physical properties, etc.) of the raw material and because of the severe conditions (temperature, residence time, heating rate, etc.) required .This is well-illustrated in a fluidized gasification system as shown in Table 5.

the production of hydrogen gas on a pilot scale by steam gasification of charred lignocellulosic waste material. In the study, the hydrogen gas was freed from moisture and CO2. They investigated the beneficial effect of some inorganic salts such as chlorides, carbonates and chromates on

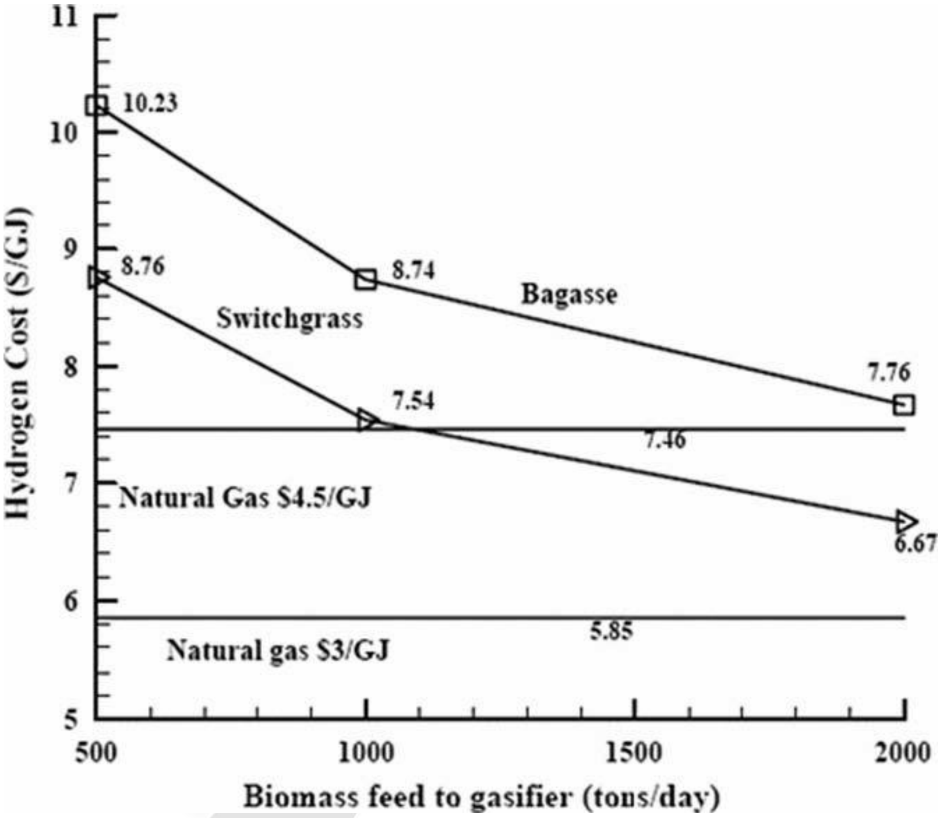
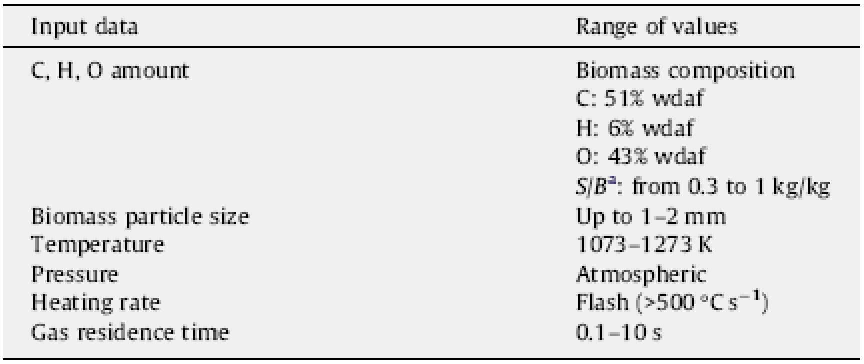


Fig. 5. Estimated cost comparison of hydrogen production by biomass gasification and natural gas steam reforming..

Table 5 : Biomass and process characteristics..



Input data	Range of values
C, H, O amount	Biomass composition C: 51% wdaf H: 6% wdaf O: 43% wdaf S/B^a: from 0.3 to 1 kg/kg
Biomass particle size	Up to 1–2 mm
Temperature	1073–1273 K
Pressure	Atmospheric
Heating rate	Flash (>500 °C s^{-1})
Gas residence time	0.1–10 s

the reaction rate and production cost of the hydrogen gas. Steam reforming C1–C5 hydrocarbons, nafta, gas oils, and simple aromatics are commercially practiced, well-known processes. Steam reforming of hydrocarbons; partial oxidation of heavy oil residues,

selected steam reforming of aromatic compounds, and gasification of coals and solid wastes to yield a mixture of H2 and CO (syngas), followed by water–gas shift conversion to produce H2 and CO2, are well-established processes. When the objective is to maximize the production of H2, the stoichiometry describing the overall process is

$$C_nH_m + 2nH_2O \rightarrow nCO_2 + [2n + (m/2)]H_2 \qquad (2)$$

The simplicity of Eq. (2) hides the fact that, in a hydrocarbon reformer, the following reactions take place concurrently:

$$C_nH_m + nH_2O = nCO + [n + (m/2)]H_2 \qquad (3)$$

At normal reforming conditions, steam reforming of higher hydrocarbons (CnHm) is irreversible (Eq. (2)), whereas the methane reforming (Eq. (2)) and the shift conversion (Eq. (3)) reactions approach equilibrium. A large molar ratio of steam to hydrocarbon will ensure that the equilibrium for Eqs. (2) and (3) is shifted toward H2 production.

As a part of the European research project AER-GAS, the Absorption Enhanced Reforming (AER) technique is being utilized for the unpressurized steam gasification of biomass (Eq. (4)). Through simultaneous CO2 absorption (with CaO as the sorbent in the example, Eq. (6)), the equilibrium of the homogenous water gas shift reaction (Eq. (5)) is shifted towards H2 and CO2 and all of the parallel reforming/gasification reactions are also influenced in favour of the desired products. Accordingly, a hydrogen-rich product gas results with reduced CO and CO2 concentration. Eq. (7)

represents the idealized sum reaction for AER gasification – the formations of secondary products (like methane, coke, and tars) are neglected here

$$CH_xO_y + (1-y)H_2O \rightarrow CO + (0.5x + 1 - y)H_2 \Delta H_R > 0 \tag{4}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \Delta H_R < 0 \tag{5}$$

$$CaO + CO_2 \rightarrow CaCO_3 \Delta H_R < 0 \tag{6}$$

$$CH_xO_y + (2-y)H_2O + CaO \rightarrow CaCO_3 + (0.5x + 2 - y)H_2 \tag{7}$$

The yield of H2 from steam gasification increases with increasing water-to-sample (W/S) ratio . The yields of hydrogen from the pyrolysis and the steam gasification increase with increasing of temperature. the yields of H2 from pyrolysis and steam gasification of hazelnut shell at different temperatures. Steam gasification runs were carried out over a temperature range from 925 to 1225 K. W/S ratios were 0.7 and 1.9 in steam gasification runs. The highest H2 yield (59.5%) was obtained from the gasification run (W/S = 1.9) at 1225 K. In general, the gasification temperature is higher than that of pyrolysis and the yield of hydrogen from the gasification is higher than that of the pyrolysis. the yield of hydrogen from supercritical fluid (water) extraction (SFE), pyrolysis and steam gasification of wheat straw and olive waste at different temperatures. The highest yields (% dry and ash free basis) were obtained from the pyrolysis (46%) and steam gasification (55%) of wheat straw while the lowest yields from olive waste. the yield of hydrogen from SFE, pyrolysis and steam gasification of beech wood at different temperatures. Distilled water was used in the SFE (the critical temperature of pure water is 647.7 K). From Fig. 6, the yield of hydrogen from SFE was considerably high (49%) at lower temperatures. The pyrolysis was carried out at the moderate temperatures and steam gasification at the highest temperatures.

The effect of catalyst on gasification products is very important. Catalysts not only reduce the tar content, but also improve the gas product quality and conversion efficiency. Dolomite, Ni-based catalysts and alkaline metal oxides are widely used as gasification catalysts Alumina, aluminosilicate material, and nickelsupported catalysts were tested by Corte et al. [72]. K2CO3 catalyst shows a destructive effect on the organic compounds, and H2 and CO2 form at the end of the steam gasification (catalytic steam reforming) process. Lv and co-workers investigated the yield of hydrogen from biomass with the use of dolomite in the fluidized- bed gasifier and the use of nickel-based catalysts in the fixed-bed reactor downstream from the gasifier. They obtained a

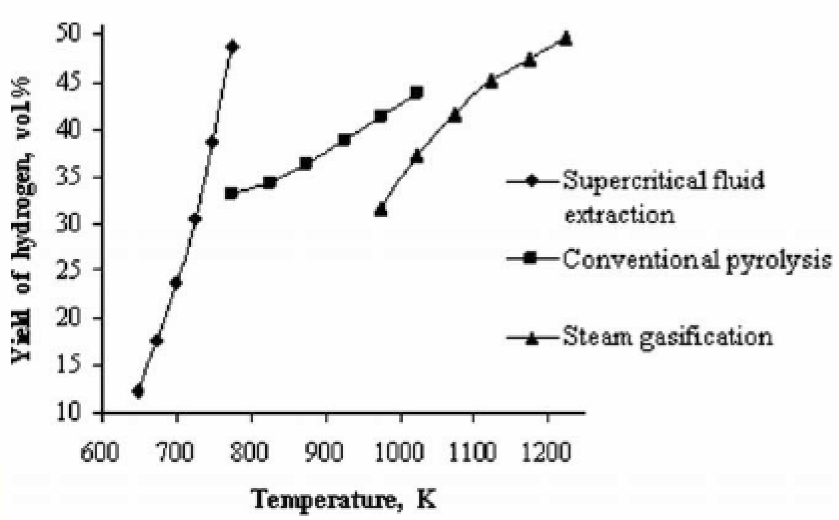
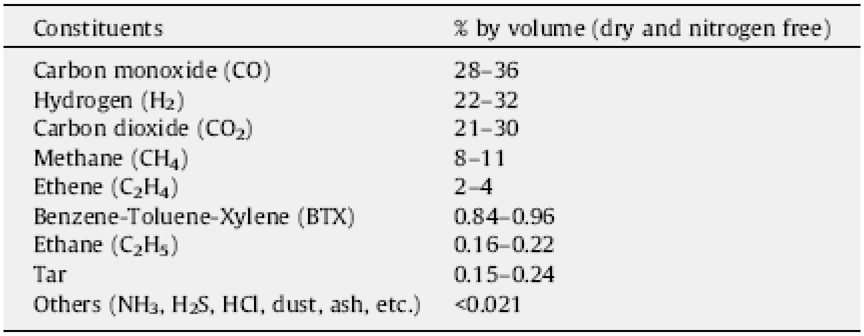


Fig. 6. Plots for yield of hydrogen from supercritical fluid (water) extraction, pyrolysis and steam gasification. [(Water/Solid) = 2] of beech wood at different temperatures..

Table 6 Composition of bio-syngas from biomass gasification.



Constituents	% by volume (dry and nitrogen free)
Carbon monoxide (CO)	28–36
Hydrogen (H_2)	22–32
Carbon dioxide (CO_2)	21–30
Methane (CH_4)	8–11
Ethene (C_2H_4)	2–4
Benzene-Toluene-Xylene (BTX)	0.84–0.96
Ethane (C_2H_5)	0.16–0.22
Tar	0.15–0.24
Others (NH_3, H_2S, HCl, dust, ash, etc.)	<0.021

maximum hydrogen yield (130.28 g H2/kg biomass) over the temperature range of 925–1125 K. Rapagna et al. studied catalytic steam gasification of biomass in a bench-scale plant containing a fluidized-bed gasifier and a secondary fixed-bed. The influence of the operating conditions in the catalytic converter on the production of gases, especially H2, was investigated over the temperature range of 935–1105 K. They obtained a maximum hydrogen yield (60 vol.%) by utilizing the fresh catalyst at the highest temperature level.

3.2.2. Fisher–Tropsch diesel via bio-syngas

Gasification technologies provide the opportunity to convert renewable biomass feedstocks into clean fuel gases or synthesis gases. The synthesis gas includes mainly hydrogen and carbon monoxide (H2 + CO) which is also called as bio-syngas [75–78]. Biomass can be converted to bio-syngas by non-catalytic, catalytic, and steam gasification processes.

In the steam-reforming reaction, steam reacts with hydrocarbons in the feed to predominantly produce bio-syngas. Steam reforming can be applied various solid waste materials including, municipal organic waste, waste oil, sewage sludge, paper mill sludge, black liquor, refuse-derived fuel, and agricultural waste . Bio-syngas is a gas rich in CO and H2 obtained by gasification of biomass. Table 6 shows the composition of bio-syngas from biomass gasification. Bio-syngas can be used in turbines and boilers or as feed gas for the production of liquid alkanes by Fischer–Tropsch Synthesis (FTS).

The production of liquid fuels from syngas has a long history, which goes back to the pioneering work of Fisher and Tropsch to synthesize hydrocarbon fuels in Germany in the 1920s. The first FTS plants began operation in Germany in 1938 but closed down after the Second World War. Then in 1955, Sasol, a worldleader in the commercial production of liquid fuels and chemicals from coal and crude oil, started Sasol I in Sasolburg, South Africa. Following the success of Sasol I, Sasol II and III, located in Secunda, South Africa, came on line in 1980 and 1982, respectively.

The FTS is a process by which gasoline, diesel oil, wax, and alcohols are produced from CO and H2 gas mixture. Basic FTS reactions are:

$$nCO + (2n+1)H_2 \leftrightarrow C_nH_{2n+2} + nH_2O \qquad (8)$$

Olefins synthesis

$$nCO + 2nH_2 \leftrightarrow C_nH_{2n} + nH_2O \qquad (9)$$

Alcohols synthesis

$$nCO + 2nH_2 \leftrightarrow C_nH_{2n+1}OH + (n-1)H_2O \qquad (10)$$

where n is the average length of the hydrocarbon chain and m is the number of hydrogen atoms per carbon. All reactions are exothermic and the product is a mixture of different hydrocarbons in that paraffin and olefins are the main parts.

The distribution of products is described by so called Schulz–Flory equation:

$$X_n = \alpha n^{1-\alpha} \qquad (11)$$

where Xn is the mole fraction of the product n. The composition of the synthesis gas, temperature, pressure, and the composition of the catalyst affect on the value of the parameter a. The effect of the parameter a on the composition of the FTS products is given in Table 7. The catalyst activation affects the reaction rate and synthesis gas conversion.

FTL processes use catalysts based mainly on iron (Fe), cobalt (Co), ruthenium (Ru), and potassium (K), and have been extensively characterized. They operate at high pressures between 2.5 and 4.5 MPa, and temperatures between 495 K and 725 K . In the FTS one mole of CO reacts with two moles of H2 in the presence Co-based catalyst to afford a hydrocarbon chain extension (–CH2–). The reaction of synthesis is exothermic (DH = –165 kJ/mol) [75– 77]:

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$$CO + 2H_2 \rightarrow -CH_2 - + H_2O \qquad (12)$$

The –CH2– is a building stone for longer hydrocarbons. A main characteristic regarding the performance of the FTS is the liquid selectivity of the process. For this reaction given with Eq. (12) is necessary a H2/CO ratio of at least two for the synthesis of the hydrocarbons. The reaction of synthesis is exothermic (DH = –42 kJ/ mol). When the ratio is lower it can be adjusted in the reactor with the catalytic water–gas shift (WGS) reaction.

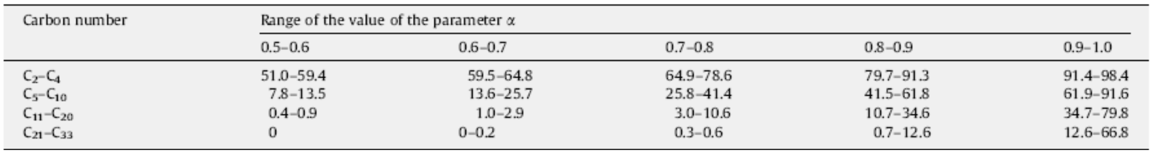
$$CO + H_2O \rightarrow CO_2 + H_2 \Delta H = -42\ \text{kJ/mol} \qquad (13)$$

When Fe-based catalysts are used with WGS reaction activity the water produced in the reaction (13) can react with CO to form additional H2. The reaction of synthesis is exothermic (DH = –204 kJ/ mol). In this case a minimal H2/CO ratio of 0.7 is required:

$$2CO + H_2 - CH_2 - + CO_2 \Delta H = -204\ \text{kJ/mol} \qquad (14)$$

Compared to other metal catalysts for FTS, a Fe-based catalyst is distinguished by higher conversion, selectivity to the lower olefins, and flexibility to the process parameters . The lifetime of the Febased catalysts is short and in commercial installations generally limited to 8 weeks . Co-based catalysts have the advantage of a higher conversion rate a longer life (over 5 years). These catalysts are in general more reactive for hydrogenation and produce.

Table 7 : Effect of the parameter a on the composition of the FTS products (% by mole).



Carbon number	Range of the value of the parameter α				
	0.5–0.6	0.6–0.7	0.7–0.8	0.8–0.9	0.9–1.0
C_2–C_4	51.0–59.4	59.5–64.8	64.9–78.6	79.7–91.3	91.4–98.4
C_5–C_{10}	7.8–13.5	13.6–25.7	25.8–41.4	41.5–61.8	61.9–91.6
C_{11}–C_{20}	0.4–0.9	1.0–2.9	3.0–10.6	10.7–34.6	34.7–79.8
C_{21}–C_{33}	0	0–0.2	0.3–0.6	0.7–12.6	12.6–66.8

therefore less unsaturated hydrocarbons and alcohols compared to Fe-based catalysts. Ni-based catalysts are also very active but their high hydrogenation activity leads to a higher level of CH4 selectivity. Ru-based catalysts are equally good but their high cost tends to exclude them; thus, the use of Ru is considered only as a promoter in support of the more economic Fe and Co catalysts [88]. Although a number of catalysts for FT process are developed, the new effective catalysts of various chemical compositions and geometric shapes are foreseen. The efficiency of a number of catalytic reactions and hence the catalytic performance, among other important factors, depend on the capability of the catalyst for heat transfer and diffusion.

The products from FTS are mainly aliphatic straight-chain hydrocarbons (CxHy). Besides the CxHy also branched hydrocarbons, unsaturated hydrocarbons, and primary alcohols are formed in minor quantities. The product distribution obtained from FTS includes the light hydrocarbons methane (CH4), ethene (C2H4) and ethane (C2H5), LPG (C3–C4, propane and butane), gasoline (C5–C12), diesel fuel (C13–C22), and light and waxes (C23–C33). The products from the FTS vary depending on the catalyst formulation and process conditions. Typical product distributions obtained with iron based for low temperature Fischer–Tropsch (LTFT) and high temperature Fischer–Tropsch (HTFT) are shown in Table 8.

The Fischer–Tropsch catalytic conversion process can be used to synthesize diesel fuels from bio-syngas. Fig. 7 shows the production of diesel fuel from bio-syngas by FTS. The design of a biomass gasifier integrated with a FTS reactor must be aimed at achieving a high yield of liquid hydrocarbons. For the gasifier, it is important to avoid methane formation as much as possible, and convert all carbon in the biomass to mainly CO and CO2. Bio-syngas can be cleaned to meet FT specifications with proven and commercial available technologies. There are no biomass-specific impurities that require a totally different gas cleaning approach. Synthetic FT diesel fuels can have excellent autoignition characteristics.

The synthetic FT diesel fuel can provide benefits in terms of both PM and NOx emissions. The FT process is particularly suitable for the production of high-quality diesel, since the products are mainly straight-chain paraffins that possess a high cetane number. A high cetane number results in a cleaner burning of the diesel with reduced harmful emissions. Physical properties of synthetic FT diesel fuel are very similar to No. 2 diesel fuel, and its chemical properties are superior in that the FT process yields middle distillates that, if correctly processed (as through a Co-based catalyst), contain no aromatics or sulfur compounds. Properties of FT diesel fuel and No. 2 diesel fuels are given in Table 9.

3.2.3. Biomethanol

Methanol is mainly produced from natural gas, but biomass can also be gasified to methanol (biomethanol). Table 10 shows main production facilities of methanol and biomethanol. Biomethanol.

Table 8 : FT product distribution for Fe-based catalyst (per 100 carbon atoms).

Product	Low temperature 493–523	High temperature K603–623 K
CH_4	4	7
C_2 to C_4 olefins	4	24
C_2 to C_4 paraffins	4	6
Gasoline	18	36
Middle distillate	19	12
Heavy oils and waxes	48	9
Water soluble Oxygenates	3	6

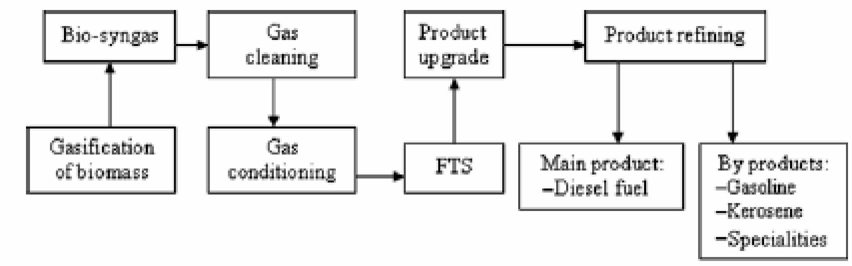
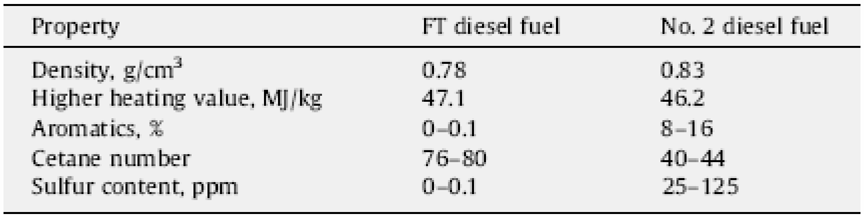


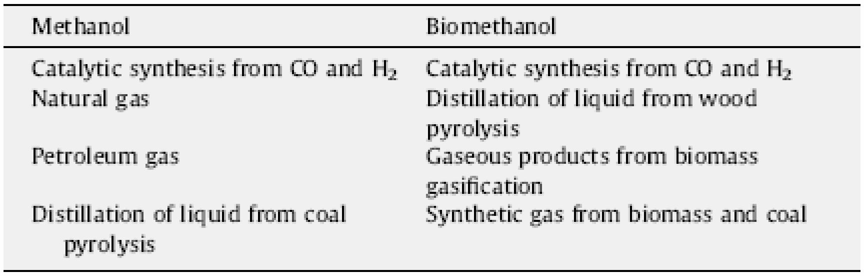
Fig. 7. Production of diesel fuel from bio-syngas by Fisher–Tropsh synthesis.

Table 9 : Properties of FT diesel fuel and No. 2 diesel fuel..



Property	FT diesel fuel	No. 2 diesel fuel
Density, g/cm^3	0.78	0.83
Higher heating value, MJ/kg	47.1	46.2
Aromatics, %	0–0.1	8–16
Cetane number	76–80	40–44
Sulfur content, ppm	0–0.1	25–125

Table 10 : Main production facilities of methanol and biomethanol.



Methanol	Biomethanol
Catalytic synthesis from CO and H_2	Catalytic synthesis from CO and H_2
Natural gas	Distillation of liquid from wood pyrolysis
Petroleum gas	Gaseous products from biomass gasification
Distillation of liquid from coal pyrolysis	Synthetic gas from biomass and coal

can be produced from H2/CO2 mixtures by means of the catalytic reaction of CO and some CO2 with hydrogen. The requirements for bio-syngas production from biomass for the subsequent methanol synthesis are not fulfilled by conventional gasification processes. In contrast to gasification processes for electricity production, the bio-syngas for the methanol generation process is limited by inert gas components (CH4, N2), which are not converted during methanol synthesis. A second requirement for the bio-syngas composition is a high hydrogen content, because a main part of the biomass carbon is converted to CO2 in the gasification step (CO2 needs 3 mol of H2 for hydrogenation to methanol). The preferable H2/CO ratio in the gasifier raw gas has to be >2 In this case, a shift reactor and therefore the additional appliances are not required. The gasification of biomass always results in a gas containing a too low hydrogen portion, respective of a too high carbon portion (CO2) for the methanol synthesis, even if the requirement mentioned above is fulfilled.

The gases produced can be steam reformed to produce H2 and followed by WGS reaction to further enhance H2 production. When the moisture content of biomass is higher than 35%, it can be gasified in a supercritical water condition. The gas is converted to methanol in a conventional steam-reforming/WGS reaction followed by high-pressure catalytic methanol synthesis:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (15)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (16)$$

$$CO + 2H_2 \rightarrow CH_3OH \qquad (17)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad (18)$$

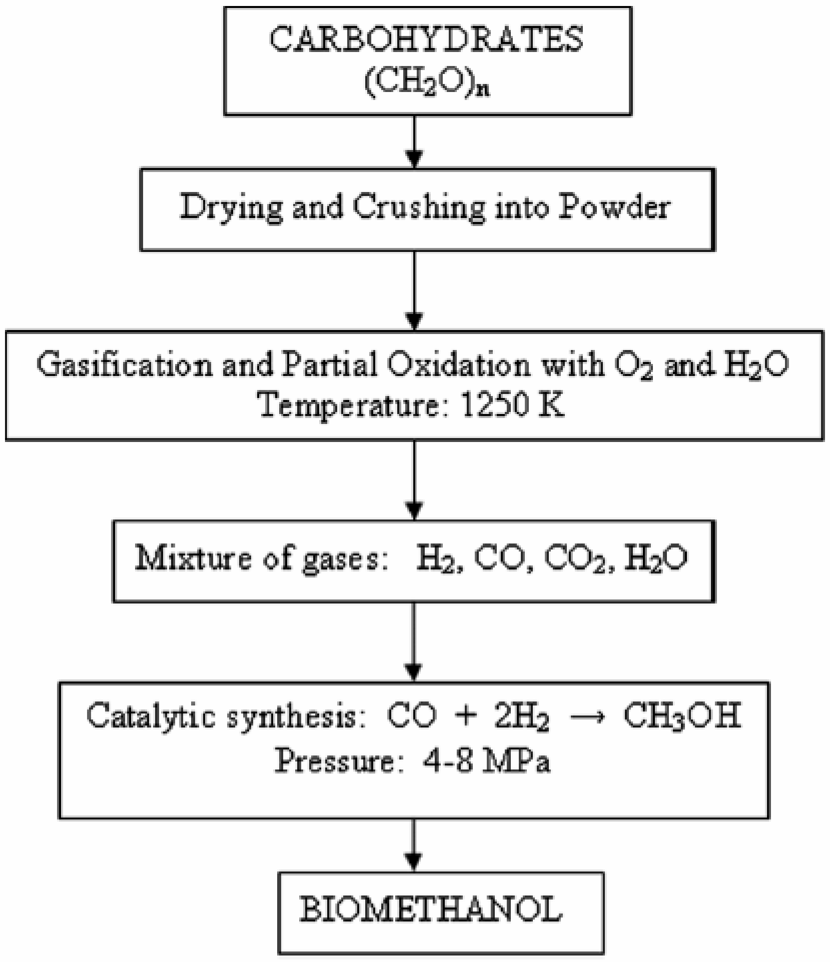


Fig. 8. Biomethanol from carbohydrates by gasification and partial oxidation with O2 and H2O. reaction [103]. Fig. 8 shows production of biomethanol from carbohydrates by gasification and partial oxidation with O2 and H2O.

A variety of catalysts are capable of causing the conversion, including reduced NiO-based preparations, reduced Cu/ZnO shift preparations, Cu/SiO2 and Pd/SiO2, and Pd/ZnO. Typical synthesis conditions are a pressure of 50–100 bar and a temperature of 495–575 K using a Cu/Zn/Al catalyst. An ideal synthesis gas should have a ratio H2/(2CO + 3CO2) at about 1.05, and a low CO2 content of approximately 3%.

In comparison with gasoline, methanol is a superior engine fuel. Thermal efficiency values for the engine are higher, and there are no emission problems. Because of a high octane number (1 0 6), methanol is an excellent fuel for high-compression engines. Methanol benefits the environment, economy and consumers. Its physical and chemical characteristics result in several inherent advantages as an automotive fuel. Some methanol benefits include low emissions, high-performance, and less flammable than gasoline. On the basis of the mass unit, methanol has a lower energy value than gasoline. The lower heating value of the liquid fuel is 19.9 MJ/kg for methanol and 44.4 MJ/kg for C8H18. As a fuel, methanol is most often used as a blend with gasoline called M85 (85% methanol and 15% gasoline), although the fuel can also be used in an almost pure form (M100). M85 vehicles tend to emit 30–50% less ozone-forming compounds. And while formaldehyde emissions tend to be higher with methanol than gasoline, M85 vehicles would likely be able to meet new emissions standards

Conclusions

The term gasification stands for a sequence of the sub-processes drying, pyrolysis, oxidation, and char gasification. Gasification is accompanied by chemical reactions that proceed at high temperature with gasifying agent and (occasionally) with steam as moderating agent. In general, the gasifying agent can be air, oxygen or oxygen-enriched air. The main product of gasification is a mixture of gases (‘‘producer gas”) with the main components H2, CO, CO2, H2O, CH4 and air nitrogen.

Renewable biomass has been considered as potential feedstock for gasification to produce syngas, the economics of current processes favor the use of light hydrocarbons (in natural gas) and coal. Gasification converts biomass to a low to medium calorific value gaseous fuel, which can be used to generate heat and electricity by direct firing in engines, turbines and boilers. Alternatively, the product gas can be reformed to produce fuels such as methanol or hydrogen, which could then be used in fuel cells. An alternative approach to the production of H2 from biomass begins with gasification of biomass. The production of hydrogen from renewable biomass has several advantages and limitations compared to that of fossil fuels.

Bio-fuels as well as green diesel produced from biomass by Fischer–Tropsch Synthesis (FTS) are the most modern biomassbased transportation fuels. The FTS produces hydrocarbons of different length from a gas mixture of H2 and CO (syngas) from biomass gasification called as bio-syngas. The FTS process is a process capable of producing liquid hydrocarbon fuels from biosyngas. The large hydrocarbons can be hydrocracked to form mainly diesel of excellent quality. The process for producing liquid fuels from biomass, which integrates biomass gasification with FTS, converts a renewable feedstock into a clean fuel. Physical properties of synthetic FT diesel fuel are very similar to No. 2 diesel fuel, and its chemical properties are superior in that the FT process yields middle distillates that, if correctly processed, contain no aromatics or sulfur compounds.

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