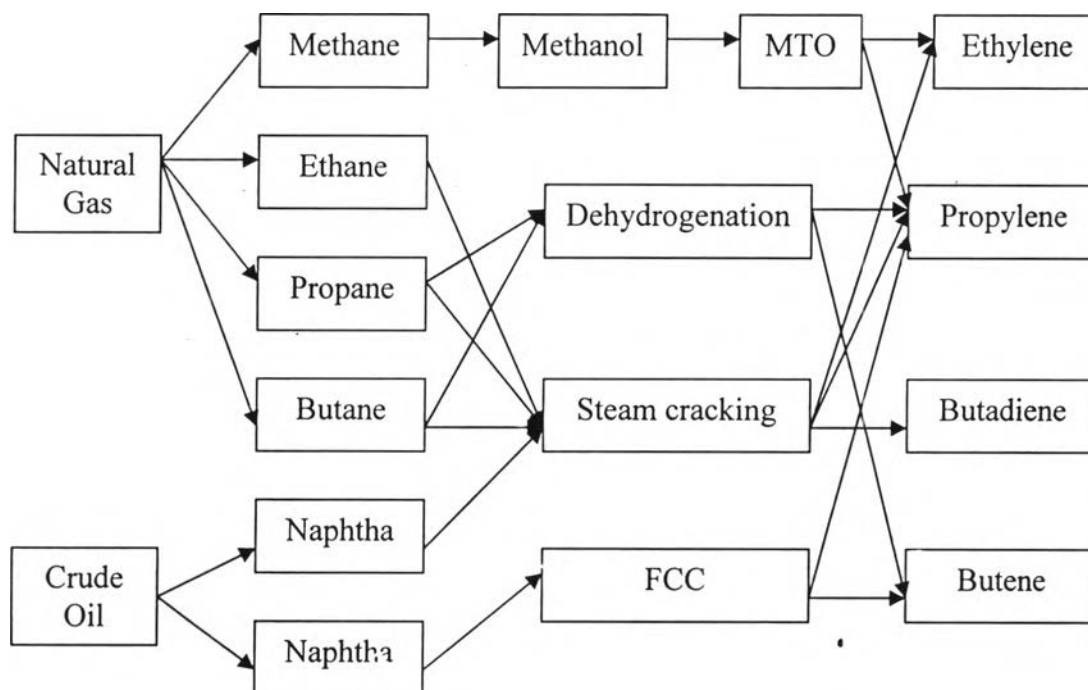


## CHAPTER II

### BACKGROUND AND LITERATURE REVIEW

#### 2.1 Olefins Production

Olefins are the largest volume chemical intermediates produced in the chemical industry, with global annual production over 300 billion lbs per year. (Deng *et al.*, 2002) Olefins are unsaturated hydrocarbons that contain one or more carbon-carbon double bonds. Ethylene and propylene are the most important of olefins. Olefins can be produced from many ways such as steam cracking of naphtha, methanol to olefins, ethane dehydrogenation, propane dehydrogenation.



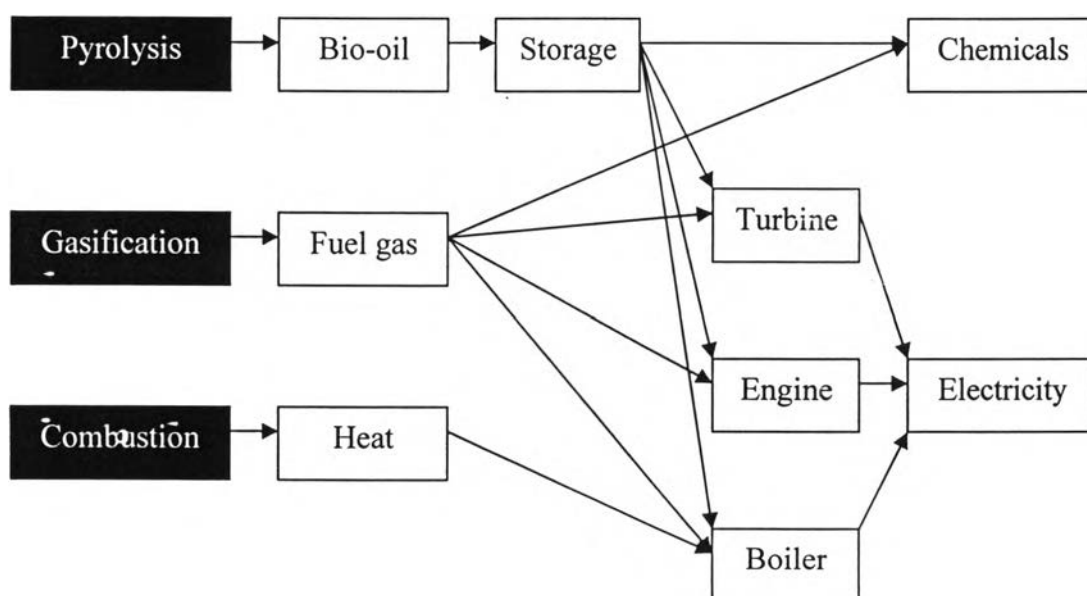
**Figure 2.1** Olefins production.

Approximately 10% of petroleum is consumed in the production of olefins and related chemicals. To reduce our reliance on fossil fuels, it would be desirable to

produce olefins from renewable fuels that produce no net CO<sub>2</sub> emissions to contribute to global warming.

Biomass is an attractive alternative to fossil fuels because it is a useful source for recycling and for fixation of CO<sub>2</sub>. If we obtain many necessary products from biomass, this would become a sustainable method to mitigate greenhouse gas because of making a closed carbon cycle. Biomass fuels and residues can be converted to energy and other chemicals via thermal, biological and physical processes. Each process area is described with the greatest emphasis on the technologies that are attracting the most attention in the research, demonstration and commercial arenas. In the thermochemical conversion technologies, biomass gasification has attracted the highest interest as it offers higher efficiencies compared to combustion and fast pyrolysis is still at a relatively early stage of development.

There are three main thermal processes available for converting biomass to a more useful energy form—combustion, gasification and pyrolysis. Their products and applications are summarized in Figure 2.2.

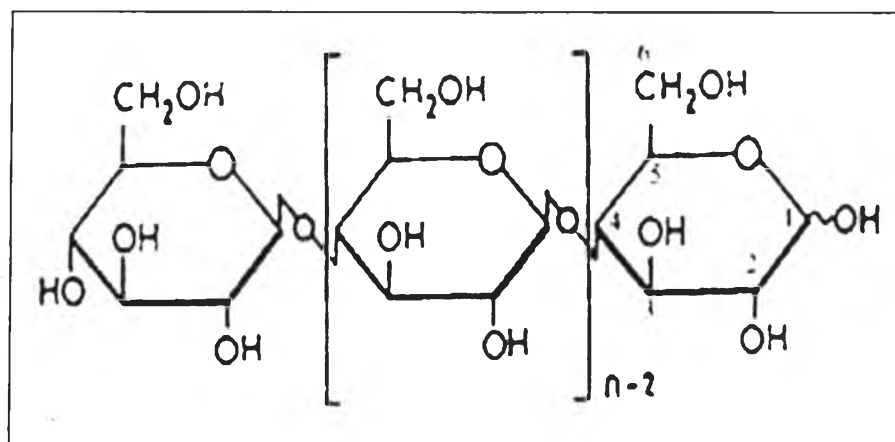


**Figure 2.2** Products from thermochemical conversion of biomass.

## 2.2 Biomass

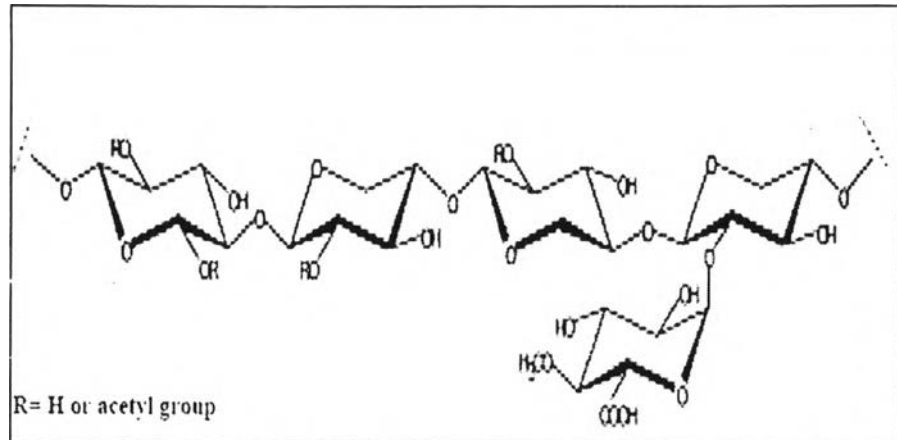
Biomass is plant matter such as trees, grasses, agricultural crops or other biological material. It can be used as a solid fuel, or converted into liquid or gaseous forms for the production of electric power, heat, chemicals, or fuels. Biomass contains varying amounts of cellulose, hemicellulose, lignin and a small amount of other extractives. (Peter, 2002)

Cellulose is a glucose polymer, consisting of linear chains of (1,4)-D-glucopyranose units, in which the units are linked 1–4 in the  $\beta$ -configuration, with an average molecular weight of around 100,000.



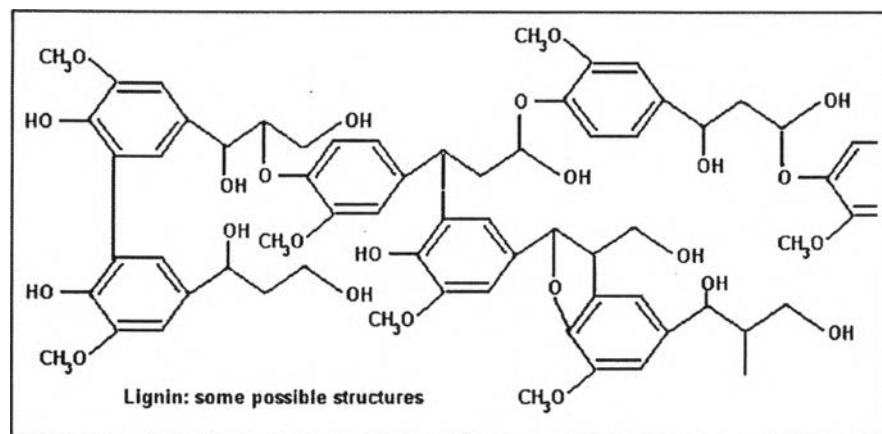
**Figure 2.3** Chemical structure of cellulose (Peter, 2002).

Hemicellulose is a mixture of polysaccharides, composed almost entirely of sugars such as glucose, mannose, xylose and arabinose and methylglucuronic and galaturonic acids, with an average molecular weight of  $<30,000$ . In contrast to cellulose, hemicellulose is a heterogeneous branched polysaccharide that binds tightly, but non-covalently, to the surface of each cellulose microfibril. Hemicellulose differs from cellulose, in consisting primarily of xylose and other five-carbon monosaccharides.



**Figure 2.4** Chemical structure of hemicellulose (Peter, 2002).

Lignin can be regarded as a group of amorphous, high molecular-weight, chemically related compounds. The building blocks of lignin are believed to be a three carbon chain attached to rings of six carbon atoms, called phenyl-propanes. These may have zero, one or two methoxyl groups attached to the rings.



**Figure 2.5** Chemical structure of lignin (Peter, 2002).

Cellulose is generally the largest fraction, representing about 40–50% of the biomass by weight; the hemicellulose portion represents 20–40% of the material by weight. Normally, cellulose is represented by an empirical formula which is  $C_6H_{10}O_5$ .

It is the inherent properties of the biomass source that determines both the choice of conversion process and any subsequent processing difficulties that may arise. Equally, the choice of biomass source is influenced by the form in which the energy is required and it is the interplay between these two aspects that enables flexibility to be introduced into the use of biomass as an energy source.

Depending on the energy conversion process selected, particular material properties become important during subsequent processing. The main material properties of biomass are divided into many sections which are:

- Moisture content
- Calorific value
- Proportions of fixed carbon and volatiles
- Ash/residue content
- Alkali metal content
- Cellulose/lignin ratio

### 2.2.1 Moisture Content

Two forms of moisture content are of interest in biomass:

- Intrinsic moisture: the moisture content of the material without the influence of weather effects.
- Extrinsic moisture: the influence of prevailing weather conditions during harvesting on the overall biomass moisture content.

In practical terms, it is the extrinsic moisture content that is of concern, as the intrinsic moisture content is usually only achieved, or applicable, under laboratory conditions. Table 2.1 lists the typical (intrinsic) moisture contents of a range of biomass materials. Also of importance in respect of the prevailing weather conditions at the time of harvesting, is the potential contamination of the harvested biomass by soil and other detritus, which can in turn have a significant deleterious impact on other 'material' properties during subsequent treatment or processing.

The parameters of interest that are affected by such contamination are the ash and alkali metal content of the material.

**Table 2.1** Proximate analysis of some biomass feedstocks (wt %) (Peter, 2002)

<b>Biomass</b>	<b>Moisture (wt %)</b>	<b>VM (wt %)</b>	<b>FC (wt %)</b>	<b>Ash (wt %)</b>	<b>LHV (MJ/kg)</b>
<b>Wood</b>	20	82	17	1	18.6
<b>Wheat straw</b>	16	59	21	4	17.3
<b>Barley straw</b>	30	46	18	6	16.1
<b>Lignite</b>	34	29	31	6	26.8
<b>Bituminous coal</b>	11	35	45	9	34

Other factors aside, such as conversion to alcohol or gas/oil, the relationship between biomass moisture content and appropriate bio-conversion technology is essentially straight forward, in that thermal conversion requires low moisture content feedstock (typically <50%), while bio-conversion can utilise high moisture content feedstocks. Thermal conversion technologies can also use feedstocks with high moisture content but the overall energy balance for the conversion process is adversely impacted.

On this basis, woody and low moisture content herbaceous plant species are the most efficient biomass sources for thermal conversion to liquid fuels, such as methanol. For the production of ethanol by biochemical (fermentation) conversion, high moisture herbaceous plant species, such as sugarcane, are more suited: such species can also be fermented via another biochemical process, anaerobic digestion (AD), to produce methane.

### 2.2.2 Calorific Value

The calorific value (CV) of a material is an expression of the energy content, or heat value, released when burnt in air. The CV is usually measured in terms of the energy content per unit mass, or volume; hence MJ/kg for solids, MJ/l for liquids, or MJ/Nm<sup>3</sup> for gases. The CV of a fuel can be expressed in two forms, the gross CV (GCV), or higher heating value (HHV) and the net CV (NCV), or lower heating value (LHV).

The HHV is the total energy content released when the fuel is burnt in air, including the latent heat contained in the water vapour and therefore represents the maximum amount of energy potentially recoverable from a given biomass source. The actual amount of energy recovered will vary with the conversion technology, as will the form of that energy i.e. combustible gas, oil, steam, etc. In practical terms, the latent heat contained in the water vapour cannot be used effectively and therefore, the LHV is the appropriate value to use for the energy available for subsequent use.

Table 2.1 lists the CV of a range of biomass materials. When quoting a CV, the moisture content needs to be stated, as this reduces the available energy from the biomass. It appears normal practice to quote both the CV and crop yield on the basis of dry matter tones (dmt), which assumes zero percent moisture content. If any moisture is present, this reduces the CV proportional to the moisture content.

### 2.2.3 Proportions of Fixed Carbon and Volatiles

Fuel analysis has been developed based on solid fuels, such as coal, which consists of chemical energy stored in two forms, fixed carbon and volatiles:

- The volatiles content, or volatile matter (VM) of a solid fuel, is that portion driven-off as a gas (including moisture) by heating (to 950 °C for 7 min)
- The fixed carbon content (FC), is the mass remaining after the releases of volatiles, excluding the ash and moisture contents.

Laboratory tests are used to determine the VM and FC contents of the biomass fuel. Fuel analysis based upon the VM content, ash and moisture, with the FC determined by difference, is termed the proximate analysis of a fuel. Table 2.1 gives the proximate analyses of some typical biomass sources: values for lignite and coal are given for reference.

Elemental analysis of a fuel, presented as C, N, H, O and S together with the ash content, is termed the ultimate analysis of a fuel. Table 2.2 gives the ultimate analyses for some biomass materials.

The significance of the VM and FC contents is that they provide a measure of the ease with which the biomass can be ignited and subsequently gasified, or oxidised, depending on how the biomass is to be utilized as an energy source. This type of fuel analysis is of value for biological conversion processes only once the fuel is produced, enabling a comparison of different fuels to be undertaken. Table 2.3 summarises the fuel properties of selected biomass materials.

**Table 2.2** Ultimate analyses for typical biomass materials (wt %) (Peter, 2002)

<b>Material</b>	<b>C</b>	<b>H</b>	<b>O</b>	<b>N</b>	<b>S</b>	<b>Ash</b>	<b>C:H</b>
<b>Cypress</b>	55	6.5	38.1	-	-	0.4	<b>8.5</b>
<b>Ash</b>	49.7	6.9	43	-	-	0.3	<b>7.2</b>
<b>Beech</b>	51.6	6.3	41.4	-	-	-	<b>8.2</b>
<b>Wood (average)</b>	51.6	6.3	41.5	0	0.1	1	<b>8.2</b>
<b>Miscanthus</b>	48.1	5.4	42.2	0.5	<0.1	2.8	<b>8.9</b>
<b>Wheat straw</b>	48.5	5.5	3.9	0.3	0.1	4	<b>8.8</b>
<b>Barley straw</b>	45.7	6.1	38.3	0.4	0.1	6	<b>7.5</b>
<b>Rice straw</b>	41.4	5	39.9	0.7	0.1	-	<b>8.3</b>
<b>Bituminous</b>	73.1	5.5	8.7	1.4	1.7	9	<b>13.3</b>
<b>Lignite</b>	56.4	4.2	18.4	1.6	-	5	<b>13.4</b>

#### 2.2.4 Ash/Residue Content

The chemical breakdown of a biomass fuel, by either thermo-chemical or bio-chemical processes, produces a solid residue. When produced by combustion in air, this solid residue is called 'ash' and forms a standard measurement parameter for solid and liquid fuels. The ash content of biomass affects both the handling and processing costs of the overall, biomass energy conversion cost. During biochemical conversion, the percentage of solid residue will be greater than the ash content formed during combustion of the same material



**Table 2.3** Properties of selected biomass materials (wt %) (Peter, 2002)

<b>Material</b>	<b>Moisture content (% H<sub>2</sub>O)</b>	<b>HHV (MJ/kg)</b>	<b>FC content (%)</b>	<b>VM content (%)</b>	<b>Ash content (%)</b>	<b>Alkali metal content (%)</b>
<b>Fir</b>	6.5	21	17.2	82	0.8	-
<b>Danish pine</b>	8.0	21.2	19	71.6	1.6	4.8
<b>Willow</b>	60	20	-	-	1.6	15.8
<b>Poplar</b>	45	18.5	-	-	2.1	16
<b>Cereal straw</b>	6	17.3	10.7	79	4.3	11.8
<b>Miscanthus</b>	11.5	18.5	15.9	66.8	2.8	-
<b>Bagasse</b>	45-50	19.4	-	-	3.5	4.4
<b>Switch grass</b>	13-15	17.4	-	-	4.5	14
<b>Bituminous coal</b>	8-12	26.2	57	35	8	-

For a biochemical conversion process, the solid residue represents the quantity of non-biodegradable carbon present in the biomass. This residue will be greater than the ash content because it represents the recalcitrant carbon which cannot be degraded further biologically but which could be burnt during thermo-chemical conversion.

Dependent on the magnitude of the ash content, the available energy of the fuel is reduced proportionately. In a thermo-chemical conversion process, the chemical composition of the ash can present significant operational problems. This is especially true for combustion processes, where the ash can react to form a 'slag', a liquid phase formed at elevated temperatures, which can reduce plant throughput and result in increased operating costs.

### 2.2.5 Alkali Metal Content

The alkali metal content of biomass i.e. Na, K, Mg, P and Ca, is especially important for any thermo-chemical conversion processes. The reaction of alkali metals with silica present in the ash produces a sticky, mobile liquid phase, which can lead to blockages of airways in the furnace and boiler plant. It should be noted that while the intrinsic silica content of a biomass source may be low, contamination with soil introduced during harvesting can increase the total silica content significantly, such that while the content of intrinsic silica in the material

may not be a cause for concern, the increased total silica content may lead to operational difficulties.

### 2.2.6 Cellulose/Lignin Ratio

The proportions of cellulose and lignin in biomass are important only in biochemical conversion processes. The biodegradability of cellulose is greater than that of lignin, hence the overall conversion of the carbon-containing plant material present as cellulose is greater than for plants with a higher proportion of lignin, a determining factor when selecting biomass plant species for biochemical processing. Table 2.4 gives the proportions of cellulose/hemicellulose/lignin for softwoods and hardwoods and for comparison, wheat straw and switchgrass.

**Table 2.4** Cellulose/lignin content of selected biomass (wt %) (Peter, 2002)

<b>Biomass</b>	<b>Lignin (%)</b>	<b>Cellulose (%)</b>	<b>Hemi-cellulose (%)</b>
<b>Soft wood</b>	27-30	35-40	25-30
<b>Hard wood</b>	20-25	45-50	20-25
<b>Wheat straw</b>	15.-20	33-40	20-25
<b>Switchgrass</b>	5-20	30-50	10-40

For the production of ethanol, a biomass feedstock with a high, cellulose/hemi-cellulose content is needed to provide a high, l/t, yield. While the lignin content represents a potentially large energy source, current techniques involving hydrolysis/enzymatic systems cannot convert the lignin to syngas. To illustrate the effect of cellulose content on yield, up to 280 l/t of ethanol can be produced from switchgrass, compared with 205 l/t from wood, an effect largely due to the increased proportion of lignin in wood.

## 2.2 Biomass Gasification

Normally, biomass is converted into gaseous products by thermochemical processes such as gasification and pyrolysis.

Pyrolysis is a form of incineration that chemically decomposes organic materials by heat in the absence of oxygen. Normally, pyrolysis can start at 500 °C and the obtained product from pyrolysis mainly are liquid and gases.

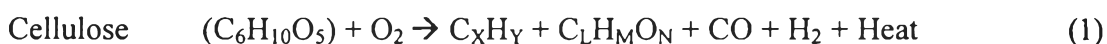
Gasification is thermal decomposition of organic materials in reducing (oxygen-deficient) atmosphere. Main product from gasification are gases. The resulting gas product contains combustible gases – hydrogen (H<sub>2</sub>) and carbon monoxide (CO) as the main constituents. Byproducts are liquids and tars, charcoal and mineral matter (ash or slag). Reducing atmosphere of the gasification stage means that only 20% to 40% of stoichiometric amount of oxygen (O<sub>2</sub>) related to a complete combustion enters the reaction. This is enough to cover the heat energy necessary for a complete gasification. In addition, gasification process can be divided into 3 stages, as follows:

**Stage I.** Gasification process starts as autothermal heating of the reaction mixture. The necessary heat for this process is covered by the initial oxidation exothermic reactions by combustion of a part of the fuel.

**Stage II.** In the second – pyrolysis stage, combustion gases are pyrolyzed by being passed through a bed of fuel at high temperature. Heavier biomass molecules distillate into medium weight organic molecules and CO<sub>2</sub>. In this stage, tar and char are also produced.

**Stage III.** Initial products of combustion, carbon dioxide (CO<sub>2</sub>) and (H<sub>2</sub>O) are reconverted by reduction reaction to carbon monoxide (CO), hydrogen (H<sub>2</sub>) and methane (CH<sub>4</sub>). These are the main combustible components of syngas. These reactions, not necessarily related to reduction, occurred at high temperature.

The net product of gasification can be found by summing up the partial reactions, as follows:



Typically, gasification process utilizes many kind of gasifying agents such as air, steam and CO<sub>2</sub> to make partial oxidation reaction and produce permanent gases of H<sub>2</sub>, CO, CO<sub>2</sub>, and hydrocarbon gases. Garcia *et al.* (1999) used steam as gasifying agent for pine sawdust using an Ni/Al coprecipitated catalyst. The catalyst improves the reaction rate of steam with char and also can participate in secondary reactions, thus leading to decrease in tar content of the gas. The high H<sub>2</sub> production during steam gasification can be attributed by the following chemical reactions:

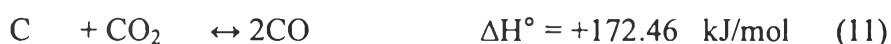


The reaction (2) represents tar reforming reaction which contributes to increment in the content of H<sub>2</sub> and CO gases.

In view of that, many researchers used steam–oxygen mixtures for biomass gasification. Aznar *et al.* (1997) reported more than 85% reduction in total tar when they increased the (steam+O<sub>2</sub>)/biomass ratio termed as gasifying ratio (GR) from 0.7 to 1.2. The researchers also reported that for low GR values in the gasifier produces light tars which can be easily destroyed using catalyst.

The use of CO<sub>2</sub> as gasifying medium is promising because of its presence in the gasification atmosphere. Tar reduction is also enhanced by dry reforming reactions of CO<sub>2</sub>, which is a gasification product. According to Minkova *et al.* (2000), a mixture of steam–CO<sub>2</sub> gives highest degree of carbonization for pyrolysis and gasification of biomass in a horizontal rotating reactor. They also mentioned that a steam–CO<sub>2</sub> mixture produced the highest activity char, which resulted in high ash content. Garcia *et al.* (2000) investigated CO<sub>2</sub> gasification in the presence of Ni/Al coprecipitated catalyst and compared the results with those of steam gasification. CO<sub>2</sub> gasification in the presence of a catalyst transformed tars and also causes a decrease of the amounts of CH<sub>4</sub> and C<sub>2</sub>-fraction (C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>) as well as an increase in H<sub>2</sub> and CO yields. Also, a significant decrease in the CO<sub>2</sub> content was

observed with a CO<sub>2</sub>/biomass ratio of 1.16 indicating that CO<sub>2</sub> itself converts to other products. Deposition of carbon in the catalyst particles can be avoided to a certain extent by feeding CO<sub>2</sub> in excess. The main chemical reactions with CO<sub>2</sub> as gasifying medium are listed below:



However, due to the emission of CO<sub>2</sub> to the atmosphere has been considered as a serious cause of the global warming or the green house effects. It is of great interest to use CO<sub>2</sub> gasification since we can simultaneously reduce the green-house gas in the atmosphere and also obtain the more valuable products from gasification.

### 2.2.1 Catalytic Gasification of Biomass

Biomass gasification is a possible alternative to the production of fuel gas and value chemicals. However, there are inefficiencies in the technology, which at present render biomass gasification economically unviable. The presence of tar and condensable organic compounds in the product gas render the gas unsuitable for specific applications. Elimination of the condensable organic compounds by a suitably cheap technology will enhance the economic viability of biomass gasification. In the mid-1980s, interest has grown on the subject of catalysis for biomass gasification. The advances in this area have been driven by the need to produce a tar-free product gas from the gasification of biomass, since the removal of tars and the reduction of the methane content increase the economic viability of the biomass gasification process. The literature in this area ranges from papers on the bench-scale reactors to those on the use of plant-scale gasifiers. Research on catalysts for use in the process is often carried out specifically in relation to gasifier design or biomass feed type. Catalytic tar reduction has been extensively reported in

the literatures. These catalysts include Ni-based catalysts, calcined dolomites and magnesites, zeolites, olivine and iron catalysts. Among all these only few have been tried as active bed additive inside the gasifier itself during gasification. There a great potential of in-bed additives in terms of tar reduction and thus avoiding complex downstream tar removal methods. These bed additives act as in situ catalysts promoting several chemical reactions in the same gasifier. The presence of additives not only influences the gas composition, but also the heating value of the product gas. The use of catalytically active materials during biomass gasification promotes the chr gasification, changes the product gas composition and reduces the tar yield. Besides these, addition of active bed materials also prevents the solid agglomeration tendencies and subsequent choking of the bed.

Among all the active materials, dolomite is the most popular and mostly studied in-bed additive. A lot of research has been done using this catalyst with regard to tar cracking in bed as well as in a secondary reactor. Karlsson *et al.* (1994) reported the successful demonstration of biomass IGCC process (VEGA Gasification with combined cycle) which involved dolomite as bed material. The tar content observed was about 1–2 g m<sup>-3</sup> of light tars (excluding benzene) and 100–300 mg m<sup>-3</sup> of heavy tars. Rapagna *et al.* (1998) also mentioned the use of calcined dolomite directly in the gasifier and observed improvements in the gas yield. Corella *et al.* (1988) reported that the use of calcined dolomite inside the gasifier could decrease the tar amount from 6.5 (without dolomite) to 1.3 wt %. Although dolomite has been proven to be a very effective bed additive in terms of tar reduction, it has some critical limitations. Dolomite is softer and thus gets eroded by the silica sand particles. Also, some dolomite particles break during the calcination and give rise to a large production of fines. So, there is a great problem of carry over of solids from the bed.

An alternative of dolomite can be naturally occurring particles of olivine, which is a mineral containing magnesium, iron oxide and silica. Olivine is advantageous in terms of its attrition resistance over that of dolomite. Rapagna *et al.* (2000) investigated the catalytic activity of olivine and observed that it has a good performance in terms of tar reduction and the activity is comparable to calcined dolomite. They reported more than 90% reduction in average tar content, the tar

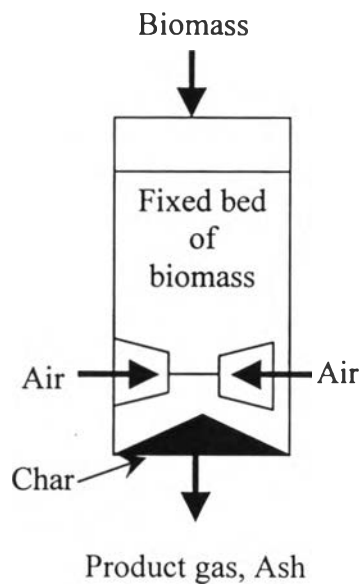
amounted  $2.4 \text{ g m}^{-3}$  compared to  $43 \text{ g m}^{-3}$  with only sand. The authors also performed experiments with olivine as the bed material and a La–Ni–Fe trimetallic perovskite catalyst in a secondary reactor. The combined action of the materials was very promising; a gas with around  $0.3 \text{ g m}^{-3}$  of tar was produced.

A number of other metal oxide catalysts such as  $\text{V}_2\text{O}_5$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CoO}$ ,  $\text{NiO}$ ,  $\text{CuO}$ ,  $\text{MoO}_3$  on  $\text{Al}_2\text{O}_3$  were tested by Yoshinori *et al.* (1984) for wood gasification to produce methanol synthesis gas. All these metal oxides produced high yields of gas, but the gas composition strongly varied depending on the type of metal oxide used.  $\text{MoO}_3$ ,  $\text{CoO}$  and  $\text{V}_2\text{O}_5$  produced higher amount of  $\text{CO}_2$ , whereas  $\text{NiO}$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  produced relatively low amounts of  $\text{CO}_2$ . The most suggested favourable gasification catalyst was  $\text{NiO}/\text{Al}_2\text{O}_3$ , which could produce a gas with a  $\text{H}_2/\text{CO}$  ratio close to 2.0, also observed to produce only traces of total olefins. Although these authors did not quantitatively measure the tar amount, their results showed that the additives greatly improve the overall product distribution and the gas heating value. Several other researchers reported in-bed use of Ni-based catalysts. Bilbao *et al.* (1998) observed that addition of 50 wt % of the Ni–Al catalyst to bed material (sand), increases hydrogen production up to 62 % with considerable decrease in the methane content. The same Ni/Al coprecipitated catalyst was also observed to be very effective for  $\text{CO}_2$  gasification of biomass. The ratio of catalyst weight and biomass flow rate significantly influences the product gas distribution.

### 2.2.2 Gasifier

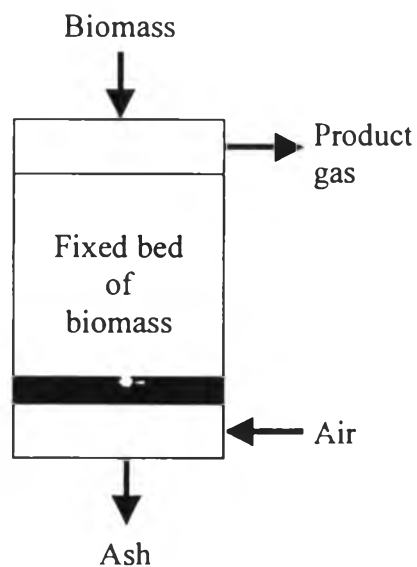
Normally, biomass solid is used as feedstocks in biomass gasification process. The gasification reactor is called gasifier. A number of reactor configurations have been developed and tested, with advantages and disadvantages and as summarized in Table 2.5. A recent survey of gasifiers found that 75% of gasifiers offered commercially were downdraft, 20% were fluid beds (including circulating fluid beds), 2.5% were updraft and 2.5% were other types. (Bridgwater, 2003)

**Table 2.5** Gasifier reactor types and characteristics (Bridgwater, 2003)



#### Downdraft-fixed bed reactor

- Co-current mode in moving down of solid and product gas
- Low tar content in product gas
- High carbon conversion
- Limited scale-up to around 500 kg/h feed rate
- Maximum feed moisture content of around 35% wet basis
- Examples: Biomass Engineering, Rural Energy, BTG&KARA, Fluidyne, Johannssen

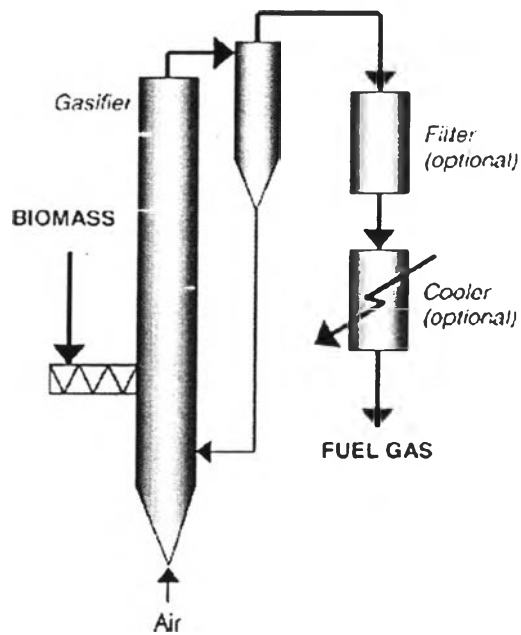


#### Updraft-fixed bed reactor

- Counter-current upward moving product gas stream
- High tar content in product gas
- Limited scale-up to around 4dry t/h feed rate
- High thermal efficiency and high carbon conversion
- Intolerant of high proportion of fines in feed
- Low temperature of effluent gas
- Good turn-down capability
- Examples: Wellman, Volund, Bioneer

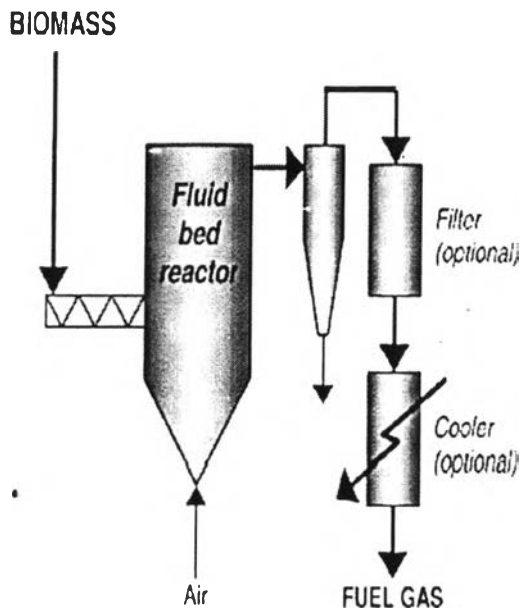


**Table 2.5** Gasifier reactor types and characteristics (continued)



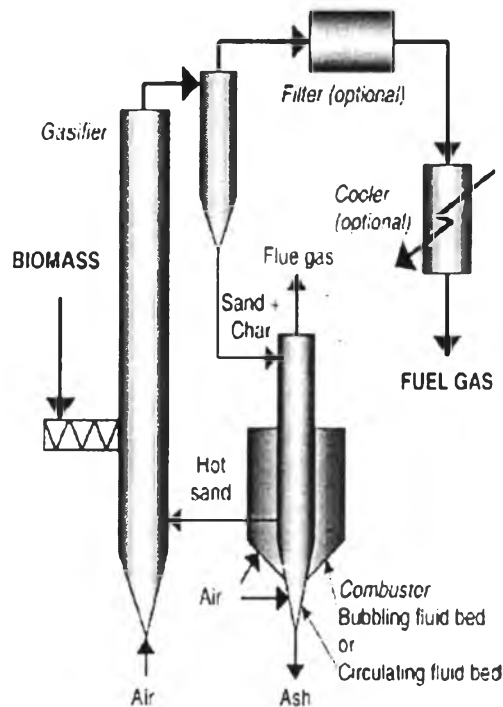
#### Bubbling fluid bed

- Good temperature control & high reaction rates
- Higher particulates in the product gas and moderate tar levels in product gas
- Good scale-up potential to 10-15 dry t/h with high specific capacity and easily started and stopped
- Greater tolerance to particle size range
- Tar cracking catalyst can be added to bed
- Limited turn-down capability
- Examples: EPI, Carbona, Dinamec



#### Circulating fluid bed (CFB)

- Large minimum size for viability, above around 15 t/h dry feed rate
- High cost at low capacity
- In-bed catalytic processing not easy
- Examples: Technical University of Vienna, TPS, Lurgi, Foster and Wheeler

**Table 2.5** Gasifier reactor types and characteristics (continued)**Twin fluid bed**

- Complex process with two close-coupled reactors with difficult scale-up and high cost
- Complexity requires capacities of >10 t/h for viability
- MHV gas produced with air and without requiring oxygen
- Low carbon conversion to gas as carbon in char is lost to reheat sand for recycling
- Higher tar levels in gas
- Examples: Ferco, Vermont

Atmospheric circulating fluidised bed gasifiers have proven very reliable with a variety of feedstocks and are relative easy to scale up from a few MWth up to 100 MWth. Even for capacities above 100 MWth, there is confidence that the industry would be able to provide reliable gasifiers. This appears to be the preferred system for large-scale applications and is used by most industrial companies and these systems therefore have high market attractiveness and are technically well proven.

Atmospheric bubbling fluidised bed gasifiers have proven to be reliable with a variety of feedstocks at pilot scale and commercial applications in the small to medium scale up to about 25 MWth. They are limited in their capacity size range as they have not been scaled up significantly and the gasifier diameter is significantly larger than that of circulating fluid beds for the same feedstock capacity. On the other hand, they are more economic for small to medium range capacities. Their market attractiveness is thus relative high as well as their technology strength.

Pressurised fluidised bed systems either circulating or bubbling are considered of more limited market attractiveness due to the more complex operation of the installation and the additional costs related to the construction of pressurized vessels. However, pressurised fluidised bed systems have the advantage in integrated combined cycle applications as the need to compress the fuel gas prior its utilisation in the combustion chamber of the gas turbine is avoided.

Atmospheric downdraft gasifiers are attractive for small scale applications up to about 1.5 MWth as there is a very big market in both developed and developing economies. However, the problem of efficient tar removal is still a major problem and a higher level of automation is needed especially for small-scale industrial applications. Nevertheless, recent progress in catalytic conversion of tar gives more credible options and these systems can therefore be considered of average technical strength.

Atmospheric updraft gasifiers seem to have little market attractiveness for power applications. While this may be due to the high tar levels in the fuel gas, recent developments in tar cracking have shown that very low levels can be achieved from dedicated thermal/catalytic cracking reactors downstream of the gasifier. Another possible reason is that the upper size of a single unit is around 2.5MWe so larger plant capacities require multiple units.

Atmospheric cyclonic gasifiers have only recently been tested for biomass feedstocks and although they have medium market attractiveness due to their simplicity, they are still unproven. Finally, atmospheric entrained bed gasifiers are still at a very early stage of development and since they require feedstock of a very small particle size, their market attractiveness is very low. No company is known to be developing pressurised systems for downdraft, updraft, cyclonic or entrained bed gasifiers for biomass feedstocks and it is difficult to imagine that such a technology could ever be developed into a commercial product due to the inherent problems of scale, tar removal and cost.

In conclusion, for large-scale applications the preferred and most reliable system is the circulating fluidised bed gasifier while for the small-scale applications the downdraft gasifiers are the most extensively studied. Bubbling fluidised bed gasifiers can be competitive in medium scale applications. Large-scale fluidised bed

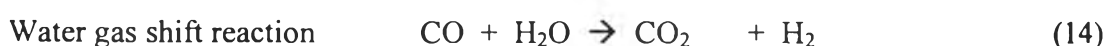
systems have become commercial due to the successful co-firing projects (see below), while moving bed gasifiers are still trying to achieve this.

### 2.3 Fischer-Tropsch Synthesis

Most of gaseous products from biomass gasification mainly are H<sub>2</sub>, CO and trace amount of hydrocarbons such as CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub> and etc. A mixture of H<sub>2</sub> and CO is called Synthesis gas or syngas. Synthesis gas is the important feedstock for many chemical processes. Synthesis gas can be converted to liquid fuels using Fischer-Tropsch technology.

The Fischer-Tropsch process is an example of the application of a catalytic process on a large industrial scale. The conversion of the synthesis gas to aliphatic hydrocarbons over metal catalysts was discovered by Franz Fischer and Hans Tropsch at the Kaiser Wilhelm Institute for Coal Research in Mullheim in 1923. They proved that CO hydrogenation over iron, cobalt or nickel catalysts at 180-250 °C and atmospheric pressure results in a product mixture of linear hydrocarbons. The Fischer-Tropsch product spectrum consists of a complex multicomponent mixture of linear and branched hydrocarbons and oxygenated products. Main products are linear paraffins and α-olefins. The hydrocarbon synthesis is catalyzed by metals such as cobalt, iron, and ruthenium. Both iron and cobalt are used commercially these days at a temperature of 200 to 300 °C and at 10 to 60 bar pressure. The overall reactions of the Fischer-Tropsch synthesis are summarized below.

#### Main reactions



#### Side reactions



Based on the syngas ( $\text{CO}+\text{H}_2$ ) production from biomass gasification. There is an increasing interest in the design of a suitable catalyst for conversion of syngas to light olefins ( $\text{C}_2\text{-C}_4$ ). It has been known for a long time that iron (Fe) and cobalt (Co) catalysts can convert syngas to olefin in the Fischer-Tropsch synthesis. Das *et al.* (1997) investigated conversion of syngas to light olefins over silicalite-1 supported iron and cobalt catalysts promoted with manganese. The addition of manganese to iron catalysts improves the olefin selectivity in syngas conversion higher than cobalt catalyst. Because manganese reduces the particle size of iron oxide and thereby makes carburization difficult. The addition of manganese to silicalite-1 supported cobalt catalyst was found to improve the CO conversion but the olefin selectivity was slightly decreased by the presence of manganese. In addition high selectivity for  $\text{C}_3$  olefin was obtained with catalyst having 10 wt.% iron and 5 wt.% manganese.

Riedel *et al.* (1999) studied the comparative of Fischer-Tropsch synthesis with  $\text{H}_2/\text{CO}$  and  $\text{H}_2/\text{CO}_2$  syngas using Fe and Co-based catalysts. Iron catalysts (Fe- $\text{Al}_2\text{O}_3\text{-Cu-K}$ ) and cobalt catalysts (Co-MnO-Aerosil-Pt) behaved differently in  $\text{CO}_2$  hydrogenation. With the alkalized iron catalyst the same hydrocarbon product composition was obtained from a  $\text{H}_2/\text{CO}_2$  and from a  $\text{H}_2/\text{CO}$  synthesis gas in spite of the CO partial pressure remaining low, specifically due to water gas shift equilibrium constraints. With the cobalt catalyst at increasing  $\text{CO}_2$  and respectively decreasing CO content of the syngas, the product composition shifted from Fischer-Tropsch type (mainly higher hydrocarbons) to almost exclusively methane. Investigation of the various modified iron catalysts showed alumina to be the best support for  $\text{CO}_2$  hydrogenation and potassium to act as a powerful promotor.

However, the crucial problems of these catalysts are on the one side the carbon formation which causes the break up of the catalysts, and on the other side, their attrition due to carbide formation. It has been shown that the  $\text{Fe}_2\text{MnO}_4$  spinel is efficient to reduce these phenomena. Therefore, Co/Fe based materials containing a spinel phase (cobalt ferrite) and metal phase (Co-Fe alloy) for producing light olefins from  $\text{CO}/\text{H}_2$ . Tihay *et al.* (2000) reported that new metal/oxide (Co-Fe) catalysts (with no reduction or thermal pre-treatment) are efficient to produce light hydrocarbons with a low selectivity in  $\text{CO}_2$  by the Fischer-Tropsch synthesis. The

low selectivity in CO<sub>2</sub> is due to the occurrence of the CO<sub>2</sub>/H<sub>2</sub> reaction. These materials are stable under reaction conditions, and only few carbides are formed during the FT reaction. Best Co/Fe ratio is 0.5, it has an effect on the reactivity and give percentage of olefins in the C<sub>2</sub>-C<sub>4</sub> about 79.

Recently, Jun *et al.* (2004) investigated Fischer-Tropsch synthesis from bio-mass derived syngas. The Fischer-Tropsch reaction has been carried out using CO/CO<sub>2</sub>/H<sub>2</sub>/Ar mixture as a model for bio-syngas on co-precipitated Fe/Cu/K, Fe/Cu/Si/K and Fe/Cu/Al/K catalysts in a fixed bed reactor. The reaction with the model bio-syngas showed that only CO was converted to hydrocarbons while, in the reaction with a balanced (i.e. H<sub>2</sub>-enriched) feed gas, CO<sub>2</sub> was converted to hydrocarbons as well as CO. Alumina as a structural promoter gave much higher activity for hydrocarbon production than silica. Potassium addition promoted the catalytic activity and the selectivities toward olefins (84.92 %) and long-chain hydrocarbons, but too high K promotion caused the gradual deactivation of the catalysts. The suitable catalyst is Fe/Cu/Al/K (100/6/16/4 %wt).

## 2.4 Pyrolysis and Upgrading Bio-oil

Another way for biomass conversion is pyrolysis. Pyrolysis is thermal decomposition occurring in the absence of oxygen. It is always also the first step in combustion and gasification processes where it is followed by total or partial oxidation of the primary products. Lower process temperature and longer vapour residence times favour the production of charcoal. High temperature and longer residence time increase the biomass conversion to gas and moderate temperature and short vapour residence time are optimum for producing liquids. Table 2.6 indicates the product distribution obtained from different modes of pyrolysis process. Nowadays, fast pyrolysis for liquids production is of particular interest currently.

Fast pyrolysis occurs in a time of few seconds or less. Therefore, not only chemical reaction kinetics but also heat and mass transfer processes, as well as phase transition phenomena, play important roles. The critical issue is to bring the reacting biomass particle to the optimum process temperature and minimise its exposure to the intermediate (lower) temperatures that favour formation of charcoal. One way,

this objective can be achieved is by using small particles. Another possibility is to transfer heat very fast only to the particle surface that contacts the heat source.

In fast pyrolysis, biomass decomposes to generate mostly vapours and aerosols and some charcoal. After cooling and condensation, a dark brown mobile liquid is formed which has a heating value about half that of conventional fuel oil. While it is related to the traditional pyrolysis processes for making charcoal, fast pyrolysis is an advanced process, with carefully controlled parameters to give high yields of liquid. The essential features of a fast pyrolysis process for producing liquids are:

- Very high heating and heat transfer rates at the reaction interface, which usually requires a finely ground biomass feed.
- Carefully controlled pyrolysis reaction temperature of around 500 °C and vapour phase temperature of 400-450 °C,
- Short vapour residence times of typically less than 2 s,
- Rapid cooling of the pyrolysis vapours to give the bio-oil product.

The main product, bio-oil, is obtained in yields of up to 75 wt% on dry feed basis, together with by-product char and gas which are used within the process so there are no waste streams other than flue gas and ash.

A fast pyrolysis process includes drying the feed to typically less than 10% water in order to minimise the water in the product liquid oil (although up to 15% can be acceptable), grinding the feed (to around 2 mm in the case of fluid bed reactors) to give sufficiently small particles to ensure rapid reaction, pyrolysis reaction, separation of solids (char), and collection of the liquid product (bio-oil).

**Table 2.6** Typical product yields (dry wood basis) obtained by different mode of pyrolysis of wood (Bridgwater, 2003)

Mode	Description	Liquid (%)	Char (%)	Gas (%)
Fast Pyrolysis	Moderate temperature, short residence time, particularly vapour	75	12	13
Carbonisation	Low temperature, very long residence time	30	35	35
Gasification	High temperature, long residence time	5	10	85

Fast pyrolysis liquid has a higher heating value of about 17 MJ/kg as produced with about 25 wt% water that cannot readily be separated. The liquid is often referred to as ‘oil’ or ‘bio-oil’ or ‘bio-crude’, although it will not mix with any hydrocarbon liquids. It is composed of a complex mixture of oxygenated compounds that provide both the potential and challenge for utilisation. There are some important characteristics of this liquid that are summarised in Table 2.7 and discussed briefly in Table 2.8.

#### 2.4.1 Upgrading bio-oil

Pyrolysis and high pressure liquefaction (HPL) of biomass are the two main thermochemical conversion methods used for the production of bio-oils. Currently, the HPL process has been superseded by the fast pyrolysis process. Generally, both bio-oil types are corrosive, polar, viscous and thermally unstable. On the other hand, a number of striking differences exist between these bio-oil types. First, the oxygen contents of pyrolysis oils (40-50 wt%) are higher than the oxygen contents of HPL oils (9-25 wt%). Secondly, the water contents of pyrolysis oils (20-50 wt%) are higher than most HPL oils (1-25 wt%) [7,8]. Thus, bio-oil yields obtained from pyrolysis are of the order of 70-80 wt% of wood (including water) compared to 30 wt% from HPL. On account of these low yields, the production of bio-oils by the HPL method has received limited attention. Hence, current emphasis



has been focused on the production of bio-oils by the pyrolysis method. These properties along with its unstable nature has made the direct use of bio-oils as conventional fuel impossible, except for boilers or as turbine fuel. As such in most cases, bio-oils need to be upgraded. One of the methods of upgrading is catalytic conversion.

The catalytic conversion, i.e. upgrading, of pyrolytic oils to fuels and chemicals has been studied by a number of workers. Upgrading has been carried out mostly with typical hydrotreating catalysts and HZSM-5 catalyst. On the other hand, information on bio-oil upgrading with catalysts other than HZSM-5 is sparse. In an earlier work of Adjaye and Bakhshi (1995), the upgrading of an HPL bio-oil was studied over a number of catalysts. The catalysts were HZSM-5, silicalite, H-mordenite, H-Y and silica-alumina. These catalysts were selected on the basis of their pore size, acidity, and molecular sieving property. The yield of hydrocarbons as well as the extent of deoxygenation, coke formation and conversion of the non-volatile portion of the bio-oil were investigated. The maximum hydrocarbon yield with HZSM-5 occurred at 370°C and was 39.3 wt% of bio-oil feed. With the other catalysts, the hydrocarbon yields increased with temperature and were up to 22.1 wt% for silicalite, 27.5 wt% for H-mordenite, 21 wt% for H-Y, and 26.2 wt% for silica-alumina at 410°C. Toluene, xylenes and trimethylbenzenes were some of the major hydrocarbon compounds produced.

Since bio-oils are currently being produced mainly from pyrolysis, it was of interest to investigate the upgrading of a pyrolysis oil with these catalysts and to compare the results with those obtained with HPL oil.

**Table 2.7** Typical properties of wood derived crude bio-oil (Bridgwater, 2003)

Physical	Typical	Characteristics
Moisture content	15–30%	Liquid fuel
pH	2.5	Ready substitution for conventional fuels in many static applications such as boilers, engines, turbines
Specific gravity	1.20	Heating value of 17 MJ/kg at 25 wt% water, is about 40% that of fuel oil diesel
Elemental analysis C	55–58%	Does not mix with hydrocarbon fuels
H	5.5–7.0%	Not as stable as fossil fuels
O	35–40%	Quality needs definition for each application
N	0–0.2%	
Ash	0–0.2%	
HHV as produced	16–19 MJ/kg	
Viscosity (at 40 °C & 25% water)	40–100 cp	
Solids (char)	1%	
Vacuum distillation residue up to	50%	

**Table 2.8** Typical properties and characteristics of wood derived crude bio-oil  
(Bridgwater, 2003)

Appearance	<p>Pyrolysis oil typically is a dark brown free flowing liquid. Depending upon the initial feedstock and the mode of fast pyrolysis, the colour can be almost black through dark red-brown to dark green, being influenced by the presence of micro-carbon in the liquid and by the chemical composition. Hot vapour filtration gives a more translucent red-brown appearance due to the absence of char. High nitrogen contents in the liquid can give it a dark green tinge.</p>
Odour	<p>The liquid has a distinctive odour—an acrid smoky smell, which can irritate the eyes if exposed for a prolonged period to the liquids. The cause of this smell is due to the low molecular weight aldehydes and acids. The liquid contains several hundred different chemicals in widely varying proportions, ranging from formaldehyde and acetic acid to complex high molecular weight phenols, anhydrosugars and other oligosaccharides.</p>
Miscibility	<p>The liquid contains varying quantities of water which forms a stable single phase mixture, ranging from about 15 wt% to an upper limit of about 30–50 wt% water, depending on how it was produced and subsequently collected. Pyrolysis liquids can tolerate the addition of some water, but there is a limit to the amount of water, which can be added to the liquid before phase separation occurs, in other words the liquid cannot be dissolved in water. It is miscible with polar solvents such as methanol, acetone, etc. but totally immiscible with petroleum-derived fuels</p>

**Table 2.8** Typical properties and characteristics of wood derived crude bio-oil  
(continued)

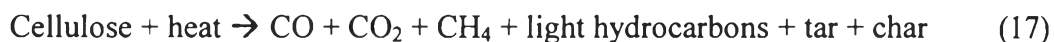
Density	The density of the liquid is very high at around 1.2 kg/l compared to light fuel oil at around 0.85 kg/l. This means that the liquid has about 42% of the energy content of fuel oil on a weight basis, but 61% on a volumetric basis. This has implications on the design and specification of equipment such as pumps
Viscosity	The viscosity of the bio-oil as produced can vary from as low as 25 cSt to as high as 1000 cSt (measured at 40 °C) or more depending on the feedstock, the water content of the oil, the amount of light ends that have been collected and the extent to which the oil has aged. Viscosity is important in many fuel applications
Distillation	Pyrolysis liquids cannot be completely vaporised once they have been recovered from the vapour phase. If the liquid is heated to 100 °C or more to try to remove water or distil off lighter fractions, it rapidly reacts and eventually produces a solid residue of around 50 wt% of the original liquid and some distillate containing volatile organic compounds and water. The liquid is, therefore, chemically unstable, and the instability increases with heating, so it is preferable to store the liquid at room temperature. These changes do also occur at room temperature, but much more slowly and can be accommodated in a commercial application
Ageing	The complexity and nature of bio-oil causes some unusual behaviour, specifically that the following properties tend to change with time: viscosity increases, volatility decreases, phase separation and deposition of gums can occur

## 2.5 Biomass Conversion to Olefins

Biomass can be converted into synthesis gas and bio-oil via gasification and pyrolysis, respectively. Both of synthesis gas and bio-oil are possible to convert into olefins by catalytic process. In order to produce olefins from biomass in single reactor, gasification process is proposed for olefins production from biomass. Three assumptions are proposed, as follows:

1. Olefins generate from biomass decomposition.
2. Olefins generate from CO hydrogenation over catalyst (Fischer-Tropsch synthesis).
3. Olefins generate from catalytic cracking of bio-oil.

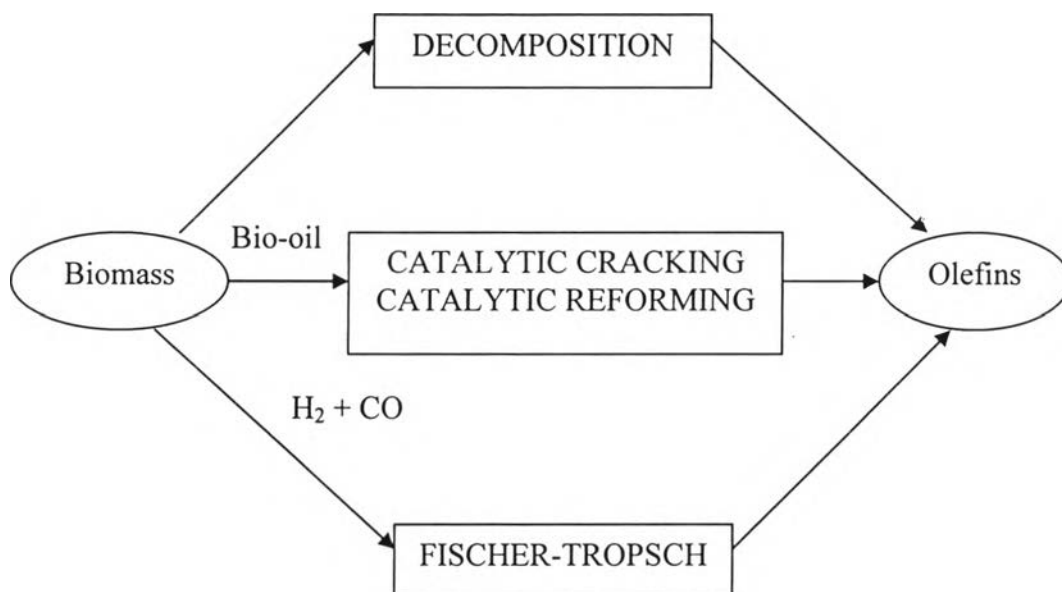
During biomass gasification, biomass can be decomposed to solid char, condensable hydrocarbons or tar, and gases [Eq. (17)]. This process is called pyrolysis.



Due to H<sub>2</sub> and CO are major products from biomass gasification. As mention ealier, H<sub>2</sub> and CO can be converted into olefins by Fischer-Tropsch synthesis. Therefore, it is possible to use catalyst for olefins production from biomass derived syngas.

Some liquid product or bio-oil is produced as by-product in gasifier. Based on the upgrading bio-oil, bio-oil is possible to convert into olefins by catalytic conversion process.

From these proposed assumptions, it is possible to integrate all possible ways in single gasifier. All reaction pathways are showed in Figure 2.3.



**Figure 2.6** Possible reaction pathways of olefins production from biomass gasification.

The aim of this work is to evaluate possible products from CO<sub>2</sub> gasification of biomass by using cellulose as a representative of biomass. The effect of catalyst and gasification temperature were studied. CO<sub>2</sub> gasification process is operated at 600, 700, and 800 °C. In addition, steam gasification of cellulose was also compared with CO<sub>2</sub> gasification.