

**SUNLIGHT ANCIENT AND MODERN: THE RELATIVE ENERGY
EFFICIENCY OF HYDROGEN FROM COAL AND CURRENT BIOMASS**

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**SUNLIGHT ANCIENT AND MODERN: THE RELATIVE ENERGY
EFFICIENCY OF HYDROGEN FROM COAL AND CURRENT BIOMASS**

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LIST OF SIMBOLS AND ABBREVIATIONS

B/D	Barrels per day
Boe	Barrels oil equivalent
C	°C if not other specified
Comp.	Composition
Comb.	Combustion
Ga.	Gasification
GaT	Gasification temperature
GHG	Greenhouse gas
Lb	Lower bound
Pyro.	Pyrolysis
PyT	Pyrolysis temperature
S/C	Steam-to-carbon ratio
SR	Steam reforming
T	Temperature
ΔT_{\min}	Minimal temperature difference between a heat source and a heat sink
Ub	Upper bound

SUMMARY

The significance of hydrogen production is increasing as fossil fuels are being depleted and energy security is of increasing importance to the United States. Furthermore, its production offers the potential to alleviate concerns regarding global warming and air pollution. In this paper we focused on examining the efficiency of hydrogen production from current biomass compared to that from fossil fuel coal. We explored the efficiencies of maximum hydrogen production from biomass and from coal under current technology, namely coal gasification and biomass pyrolysis, together with following-up technologies such as steam reforming (SR). Bio-oil, product from pyrolysis and precursor for steam reforming, is hard to define. We proposed a simulation tool to estimate the pyrolytic bio-oil composition from various biomasses. The results helped us understand the accuracy that is needed for bio-oil composition prediction in the case it is converted to hydrogen. Hydrogen production is energy intensive. Therefore, heat integration is necessary to raise the overall thermodynamic efficiencies for both coal gasification and biomass pyrolysis. The results showed that considering the ultimate energy source, sunlight, about 6-fold more sunlight would be required for the coal to hydrogen than that for biomass to hydrogen. The main difference is in the efficiency of conversion of the ancient biomass to coal and therefore, for modern mankind, this loss has already been incurred.

CHAPTER 1

INTRODUCTION

Hydrogen production has featured heavily as a potential energy carrier that can utilize many forms of renewable energy, such as biomass, wind and direct solar power (Hoffmann, 2001). Its significance is increasing as fossil fuels are being depleted and energy security is of increasing importance to the United States (Hoffmann, 2001; Rifkin, 2002). Furthermore, its production offers the potential to alleviate concerns regarding global warming and air pollution, either through using renewable carbon or through point source carbon sequestration (Hoffmann, 2001; Rifkin, 2002).

In this study, we focused on examining the efficiency of hydrogen production from current biomass, pinewood, compared to that from fossil fuel coal, which is closely related to current terrestrial biomass sources. We explored the efficiencies of maximum hydrogen production from biomass and from coal under current technology, namely coal gasification and biomass pyrolysis, followed by steam reforming (SR) to produce hydrogen. This will enable us to assess the ecological footprint associated with hydrogen production in terms of land area, solar energy and other external energy inputs versus the use of fossilized sunlight.

Coal gasification is a well-established technology which gasifies coal through oxygen and water as steam (Williams, et. al., 2000; Higman, et. al., 2003). Pyrolysis is chemical decomposition induced in organic materials by heat in little or no oxygen (Bridgwater,

1999), and has gain increasing attention since 1970s (Abdullayev, 1999). We studied the full life cycle from sunlight to hydrogen for biomass systems, through the pyrolysis conversion process and steam reforming, and for the competing fossil fuel system, through the gasification conversion process and steam reforming. After the whole conversion process, heat integration was conducted to raise the overall thermodynamic efficiencies for the two systems.

This study will serve as a benchmark and point of departure for our later overall examination of the two competing systems through other various combinations of technologies and for comparisons to other sources of hydrogen.

CHAPTER 2

LITERATURE REVIEW

2.1 Hydrogen Production

2.1.1 Importance of hydrogen energy

“In the twenty-first century hydrogen might become an energy carrier of importance comparable to electricity.” said by the President’s committee of Advisors on Science and Technology in 1997 (Federal Energy Research). This statement indicates the significant potential of hydrogen as an important energy carrier in the near future. But – why hydrogen?

Hydrogen is one, if not the most, efficient energy carrier. The energy stored in one gallon of gasoline is roughly equivalent to that stored in 1 kg of hydrogen (S&TR). The amount of energy produced by hydrogen is about 3 times the amount of energy produced by an equal weight of gasoline, and almost 7 times that contained in an equal weight of coal (FSEC). Fuel cells using hydrogen can be 2 – 3 times as efficient as gasoline engines (Harkin, 2001). What’s more, hydrogen is the most abundant element in the universe, making up to about 90 percent of the universe by weight. So although it is not commonly found in its pure form because it combines with other elements easily, the sources for hydrogen are abundant theoretically (DOE). NASA has already become the primary user of hydrogen as an energy carrier directly (DOE). Fuel cells can be made in any size to fit

everything from pocket-size devices to large plants, making hydrogen energy excellent for a distributed and robust energy infrastructure (Harkin, 2001).

Hydrogen is also an ecologically benign fuel since it is a carbon-free fuel with water as its only oxidization product (Gretz, 1995). The combustion of hydrogen produces no particulate or sulfur emissions as well as no carbon dioxide (DOE). As the climate change attributed to greenhouse gas emissions from anthropogenic sources is of increasing concern (Klass, 1998, P19 - 23), it is worth exploring hydrogen production to try to use its character of zero CO₂ emission. Figure 1 shows the composition and sources of the greenhouse gases (GHG) of the US (DOE, GHG). We can see that 84% of the GHG is carbon dioxide and 98% of the carbon dioxide comes from the combustion of fossil fuels. Figure 2 shows the emission trend of carbon dioxide from fuels during the year of 1970 to 2025 (DOE, World CO₂). It is worrying to see that the total anthropogenic emission of carbon dioxide has been increasing quickly, and projected to continue. This suggests alternative environmentally benign fuels should be employed if we want to reduce the risks of further potentially catastrophic climate change.

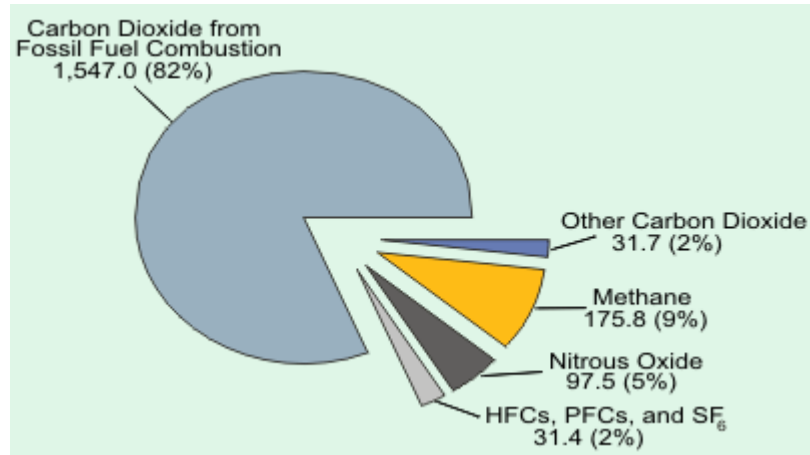


Figure 1 GHG emissions in the United States in 2001 (Million Metric Tons of Carbon Equivalent) (DOE, GHG)

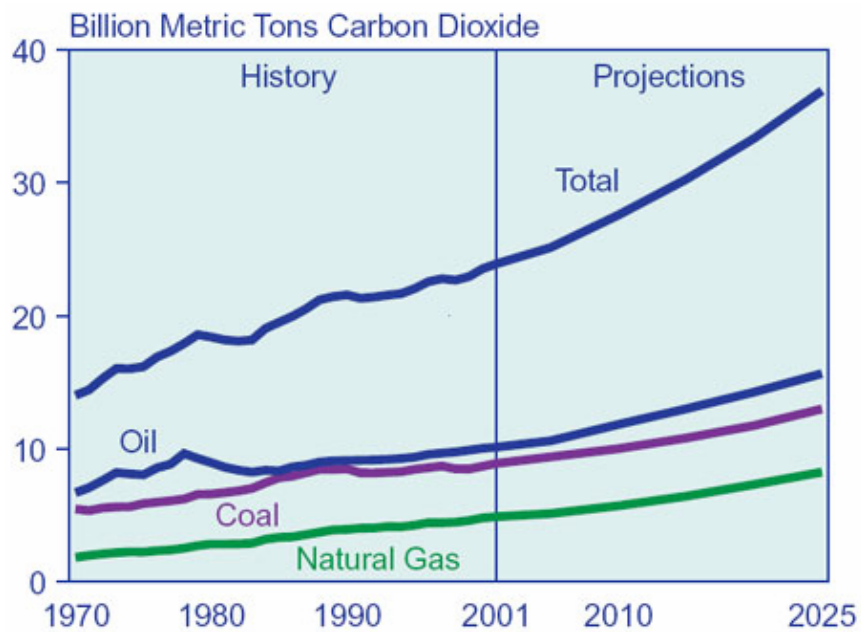


Figure 2 World energy-related carbon dioxide emissions (DOE, World CO₂)

Hydrogen energy is of increasing importance also because the liquid and gaseous fossil fuels are depleting quickly. "... our fuels were produced millions of years ago and through geological accident preserved for us in the form of coal, oil, and gas. These are essentially irreplaceable, yet we are using them up at a rapid rate. Although exhaustion of our fossil fuels is not imminent, it is inevitable." (Daniels et. al., 1955) The United States is one of the countries that are rich in coal (Klass, 1998, P13). A 258-year supply of coal is available in the US; oil and natural gas have much shorter depletion times than coal (Klass, 1998, P14-15). The same case is true with the global fossil fuels as stated above. It is only a matter of time.

Hydrogen, which could be produced in almost a dozen processes commercially (Hoffmann, 2001, P7), would also alleviate the dependence of imported energy for a country. This is especially the situation for the oil consumption of the United States. More than half of the world's total crude oil supplies are located in the Middle East and the former Soviet Union (Klass, 1998, P13). Therefore, the global oil supply, including that for the US, is influenced significantly by the global political situation as well as economic decisions. Table 1 summarizes the reasons and times for some of the global oil supply disruptions (DOE, Oil Supply), which shows clearly the dependence of the oil supply on a few countries. Currently, the US is still very dependent on importing oil as shown in Figure 3 (DOE, Oil Import). So it is really a very important task to look for another reliable and less import-dependent energy source.

Table 1 Global oil supply disruptions since 1973 (DOE, Oil Supply)

Date of <i>Net</i> Oil Supply Disruption	Duration (Months of <i>Net</i> Supply Disruption)	Average <i>Gross</i> Supply Shortfall (Million B/D)	Reason for Oil Supply Disruption
10/73-3/74	6	2.6	October Arab-Israeli War; Arab oil embargo
4/76-5/76	2	0.3	Civil war in Lebanon; disruption to Iraqi exports
5/77	1	0.7	Damage to Saudi oil field
11/78-4/79	6	3.5	Iranian revolution
10/80-12/80	3	3.3	Outbreak of Iran-Iraq War
8/90-10/90	3	4.6	Iraqi invasion of Kuwait/Desert Storm
4/99-3/00	12	3.3	OPEC (ex. Iraq) cuts production in effort to increase prices

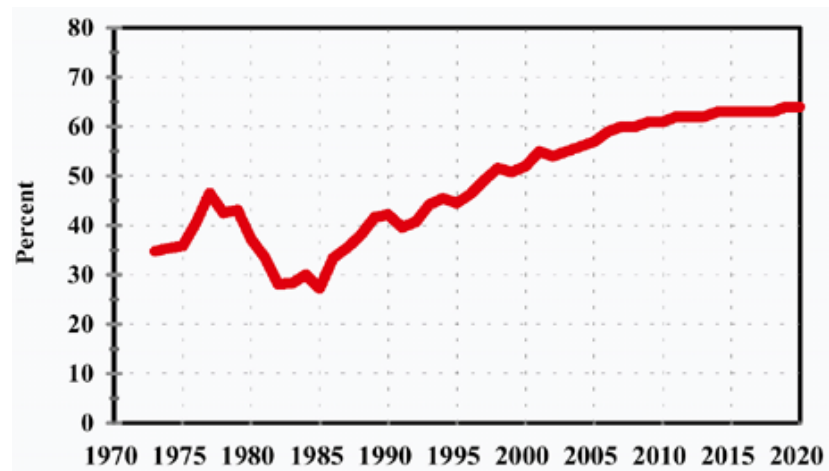
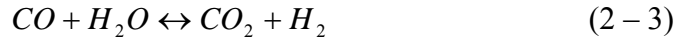
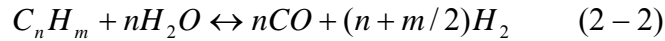
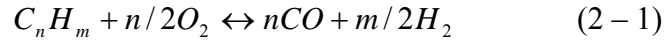


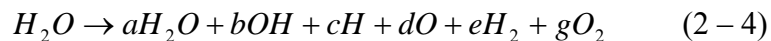
Figure 3 Net import share of petroleum consumption for the US (DOE, Oil Import)

2.1.2 Hydrogen production methods

The most efficient and least costly method of hydrogen production is the steam reforming of natural gas (Hoffmann, 2001, P7; Yürüm, 1995). Coal gasification is also a common method for hydrogen production. (The basics and the state-of-art about steam reforming and coal gasification will be discussed later in this chapter, so the specific chemistry is neglected here.) Hydrogen can also be produced through partial oxidation of heavy oil at high pressure with or without catalyst at 600 – 1315C. The major reactions are as follows.



There are sources other than hydrocarbons as sources for hydrogen production such as water electrolysis, in which water molecule is broken down into hydrogen and oxygen by the electrical current run through it. Water electrolysis is only used where electricity is cheap and where high purity is required (Hoffmann, 2001, P7). Hydrogen can be produced from water thermolysis too. The chemical reaction is



This reaction takes place at temperatures greater than 2000K (Baykara et.al., 1989). The major problems with this method are that the reactor material needs to be able to stand extremely high temperature and the separation of hydrogen from the product mixture. Other methods include water radiolysis, water photolysis (Baykara et.al., 1989).

2.1.3 Challenges

Today, most hydrogen in the United States, and about half of the world's hydrogen supply, is still produced from the non-replaceable fossil fuel – natural gas. Although it seems to be able to provide the earliest affordable feedstock for hydrogen, the costs are prohibitively expensive, and this feedstock is finite. Therefore, lower cost options for producing hydrogen from a wide variety of sources have to be aggressively pursued (DOE). Besides, hydrogen is low in energy density at its natural gaseous state (DOE), and consequently, to achieve certain distribution efficiency, the pipeline construction would require more expensive materials to stand higher pressure.

2.2 Coal Production and Utilization

2.2.1 Coal basics

Coal is a combustible, brown to black sedimentary rock composed of heterogeneous components formed millions of years ago in the carbonaceous age (Karayığit, et. al.,

1994). It is one of our most important sources of energy (Van Krevelen, 1993). Combustion, gasification, liquefaction, and carbonization are the four most common processes operated on coal. The products from coal and coal itself can be used in residential purpose such as home heating, iron and steel industry which needs a lot of energy, and many other industries such as oil refineries, pulp and paper, chemical, and utility (Cimen, et. al., 1994). In countries with planned economies, 70 – 90% of the total quantity of coal consumed is burnt in the utility sector (Güney, 1994).

Among all the non-renewable resources, coal is the most abundant as shown in Table 2 (Arioglu, 1994).

Table 2 World reserves of non-renewable energy (Arioglu, 1994)

Non-renewable resources	Approximate recoverable reserves (Billions boe*)
Oil	1300
Natural gas	1500
Coal	5000
* boe: barrels oil equivalent	

After the coal is mined, it needs to go through several preparation processes before it can be used directly or to produce other products in most cases. These processes include size reduction, classification, concentration, dewatering, and waste disposal (Önal, et. al., 1994). Desulphurization of coal is of more and more importance nowadays because sulfur contributes to air pollution and may cause problems in operations on coal (Celik, et. al.,

1994).

2.2.2 Coal as a non-renewable source

Coal formation is a long and complex process which took millions of years to happen. It is the final result of the cumulative effects of climatic, geological, biological, and chemical conversions (Karayığit, et. al., 1994; Van Krevelen, 1993). Some of the chemical and biological processes of coal formation are shown in Figure 4. The peat formed from plant matter in swamps is the precursor of coal. This figure also shows the general classification of coal from low rank brown lignite through bituminous coal to high rank black bright anthracite (Van Krevelen, 1993).

Materials	Partial processes	Main chemical reactions
Decaying vegetation		
↓	Peatification	Bacterial and fungal life-cycles
Peat		
↓	Lignitification	Air oxidation, followed by decarboxylation and dehydration
Lignite		
↓	Bituminization	Decarboxylation and hydrogen disproportioning
Bituminous coal		
↓	Pre-anthracitization	Condensation to small aromatic rings systems
Semi-anthracite		
↓	Anthracitization	Condensation of small aromatic rings systems to larger ones; dehydrogenation
Anthracite		
↓	Graphitization	Complete carbonification
Meta-anthracite		

Figure 4 Coal formation process (Van Krevelen, 1993)

2.2.3 Coal properties

The physical properties of coal have a significant impact on the coal behavior in processing and reactions. These properties include pore size, porosity, surface area, and density. Coal contains a large amount of void space. It has a large pore size range, from less than 1nm to more than 10000 nm (Arikol, et. al., 1994). Porosity is defined as the fraction of the volume of a solid occupied by pores. For low rank (lignite and sub-bituminous) coals, porosity could be as high as 30% and for anthracites, it could exceed 10% (Arikol, et. al., 1994). Surface area is another important concept for solid with pores. For coal, the surface areas usually fall in 100 – 250 m²/g for lignites and sub-bituminous coals, in 50 – 100 m²/g for bituminous coals, and increase again to over 100 m²/g for anthracites (Grimes, 1982). True density of coal ranges from 1.8 g/cm³ to 4 g/cm³ (Arikol, et. al., 1994).

Coal of different rank varies a lot in chemical composition. The Table 3 summarizes the composition of some of coal samples at various ranks. Table 4 lists the proximate and ultimate analysis of coal sample after processing it to different extent.

Table 3 Chemical compositions of coal samples of different ranks (Bürküt, et. al., 1994)

Ranks of analyzed coals	Humidity %	Chemical analysis on dry, ash-free basis						
		Proximate analysis		Ultimate analysis, %				
		Volatile matter %	Fixed carbon %	C	H	N	S	O
Peat	90	65	35	58.2	5.2	1.5	0.5	34.6
Brown lignite	40	55	45	66.6	5.0	1.6	3.2	23.6
Lignite	35	42	58	69.8	5.0	1.0	2.0	22.2
Black lignite	20	40	60	70	5.3	2.3	1.9	20.5
Black bituminous coal 1	15	38	62	79	5.4	0.7	3.5	11.4
Black bituminous coal 2	10	30	70	84	5.2	1.2	0.6	9.0
Anthracite	2	7	93	92.4	3.0	0.7	0.5	3.4

Table 4 Chemical compositions of coal after different preparative steps (Higman, et. al., 2003)

	Moisture and ash free	Ash free	Moisture	As received
Proximate analysis				
Fixed carbon	0.5908	0.5109	0.5400	0.4725
Volatile matter	0.4092	0.3539	0.3741	0.3273
Moisture	0	0.1352	0	0.1250
Ash	0	0	0.0859	0.1752
Ultimate analysis				
Carbon	0.8166	0.7062	0.7464	0.6531
Hydrogen	0.0568	0.0642	0.0519	0.0594
Oxygen	0.0983	0.2050	0.0898	0.1896
Nitrogen	0.0171	0.0148	0.0157	0.0137
Sulfur	0.0113	0.0097	0.0103	0.0090
Ash	0	0	0.0859	0.0752

2.3 Biomass Production and Utilization

2.3.1 Biomass basics

“Biomass is defined as nonfossil, energy-containing forms of carbon and includes all land- and water-based vegetation such materials as municipal solid wastes, forestry and agricultural residues, municipal biosolids, and some industrial wastes.” In other words, biomass is all nonfossil organic matters that have intrinsic chemical energy content or heating value (Klass, 1998).

Throughout human survival history, biomass has been relied on as a basic source for food stuffs for people and animal, for building materials, and for energy for heating. This is still true of many Third World countries, whereas industrialized countries have substituted the biomass with fossil fuel coal, oil and natural gas as the major energy sources. The Figure 5 illustrates the trend of biomass and fossil fuels usage of the United States (Klass, 1998). The world appeared ready to resurrect biomass as a major indigenous energy resource for industrialized nations, as it had been up to the end of the nineteenth century. It now appears that biomass energy will displace increasingly larger amounts of fossil fuels as time passes (Klass, 1998).

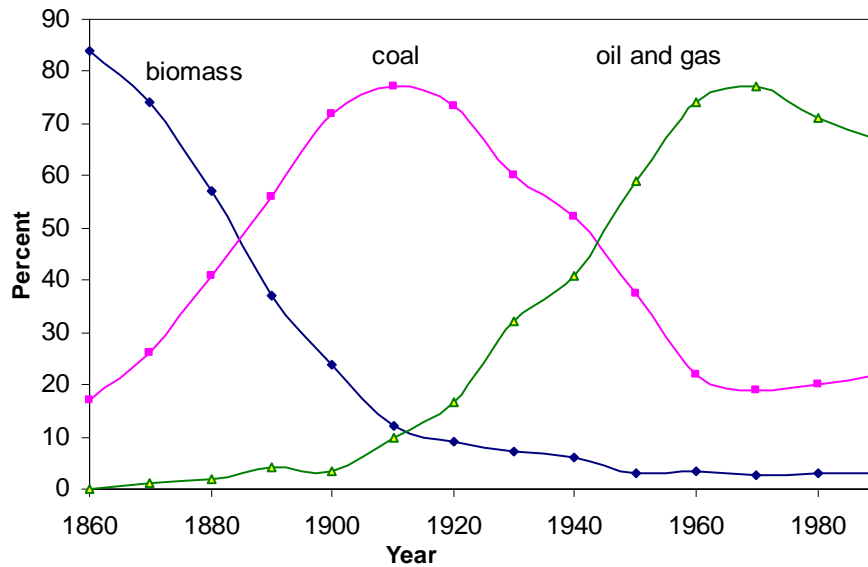


Figure 5 Utilization trends of fossil fuels and biomass over years (Klass, 1998)

2.3.2 Biomass utilization

The general processes of how biomass is used as a source of energy and fuels are shown schematically in the Figure 6 (Klass, 1998). Since the ultimate carbon release as carbon dioxide comes from the carbon dioxide in the atmosphere through photosynthesis, biomass as a direct energy source is considered not to contribute to the greenhouse gases accumulation, in other words, it is regarded as one of the few renewable, widely dispersed, resources that can be utilized to reduce both the amount of fossil fuels burned and greenhouse gases emitted from fossil fuels combustion.

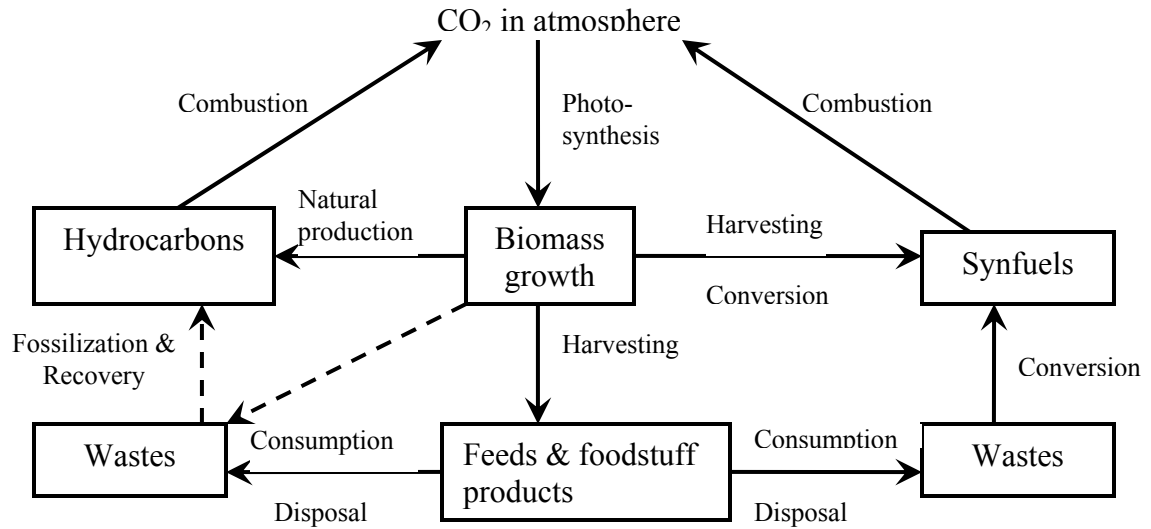


Figure 6 Biomass utilization processes (Klass, 1998)

Similarly to the coal preparation, the physical processes employed to prepare biomass for use as fuel or as a feedstock include dewatering, drying, size reduction, and concentration (Klass, 1998). The conversion processes for biomass utilization are combustion, pyrolysis, liquefaction, and gasification (Klass, 1998).

2.3.3 Biomass abundance

The average global net biomass carbon production is estimated to be 77.49 Gt annually; the standing biomass carbon (that contained in biomass above the earth's surface) is estimated to be 833.5 Gt totally (Whittaker, et. al, 1975). Table 5 summarizes the total carbon distribution, including biomass carbon, on earth. We can see that the carbon deposits that contain little chemical energy consist of lithospheric sediments, atmospheric,

and hydrospheric CO₂. Altogether, these carbon sources add up to 99.96% of the total carbon estimated to exist on the earth. The carbon in fossil fuel deposits is only about 0.02% of the total. And live and dead biomass carbon makes up the remainder, about 0.02%, the same as the carbon in the non-renewable fossil fuel. We could see that although biomass carbon is a very small fraction of the total carbon inventory of the earth, it is an extremely important fraction (Klass, 1998).

Table 5 Carbon distribution on the earth (Klass, 1998)

Carbon type	Mass (Gt)	Percent of total
Lithospheric sediments	20,000,000	99.78
Deep sea	34,500	0.172
Fossil deposits	4130	0.021
Dead organic matter in sea	3000	0.015
Dead organic matter on land	700	0.0035
Atmosphere	700	0.0035
Sea surface layers (dissolved)	500	0.0025
Live terrestrial biomass	450	0.0022
Live phytoplankton	5	0.00002
Live zooplankton	5	0.00002
Total	20,043,990	

For all the biomass carbon, forests produce about 43% of the net carbon fixed each year and contain more than 89% of the standing biomass carbon of the earth (Klass, 1998). It was found that for 1991, 26.0 million tonnes of dry bark and 74.5 million tonnes of dry wood residues were generated at primary lumber processing mills in the United States (McKeever, 1995).

2.4 Pyrolysis

2.4.1 Basic concepts

Pyrolysis is defined as chemical decomposition occurred in organic materials by heating it to a high temperature without oxygen, or with a so limited supply of oxidizing agents that gasification does not take place or only little gasification occurs (Bridgwater, 1999; Meier, et. al, 1999). Pyrolysis usually occurs under pressure higher than atmospheric pressure and at operating temperatures higher than 430°C (BTG). The mechanism of pyrolysis is that the atoms in the organic molecules of the materials vibrate apart at random positions due to the heavy vibrations at the temperature for pyrolysis (BTG). The products from pyrolysis are gases, liquid after condensation, and a solid residue containing fixed carbon (Bridgwater, 1999; Meier, et. al, 1999)..

Liquid production from fast pyrolysis has become more important than solid charcoal production (Bridgwater, et. al., 1999). In comparison to the traditional pyrolysis processes for charcoal manufacture, fast pyrolysis is an advanced process to produce a significant fraction of biomass as a liquid (Bridgwater, et. al., 1999). In fast pyrolysis, the organic materials are heated to 450 - 600 °C in the absence of air very rapidly. Similarly, the products would be organic vapours, pyrolysis gases and charcoal under these conditions. The vapours are condensed to a liquid mixture, which is called bio-oil (BTG).

2.4.2 Pyrolysis reactors

Bubbling fluid beds, circulating fluid beds and transported bed, rotating cone, and fixed bed, can all be used as the reactor for pyrolysis. The advantages of each of these reactors were given by references (Bridgwater, et. al., 1999; Gercel, 2002; Pütün, et. al., 1999; Rocha, 1999). Various reactor types can be used for fast pyrolysis too. A detailed reactor list together with the method of heating was given by Table 6 for fast pyrolysis (Bridgwater, et. al., 1999).

Table 6 Fast pyrolysis reactors and heating methods (Bridgwater, et. al., 1999)

Reactor type	Method of heating
Ablative coil	Reactor wall heating
Ablative mill	Reactor wall (disc) heating
Ablative plate	Reactor wall heating
Ablative vortex	Reactor wall heating
Circulating fluid bed	In-bed gasification of char to heat sand
Cyclone or vortex	Reactor wall heating
Entrained flow	Char combustion products; Hot sand
Fluid bed	Heated recycle gas; Hot inert gas; Partial gasification; Fire tubes
Horizontal bed	Fire tubes
Vacuum multiple hearth	Hearth heating
Rotating cone	Wall and sand heating
Stirred bed	Partial gasification of char
Transported bed	Recirculated hot sand heated by char combustion
Vacuum moving bed	Direct contact with hot surface

2.4.3 Influencing factors

The ratio of the pyrolytic products varies with the chemical composition of the biomass and the reaction conditions, such as reaction temperature, heating rate, material residence time (RWEDP; Horne, et. al., 1996) and also depends on the type of reactor (Bridgwater, 1999; Meier, et. al, 1999). To be more specific, lower reaction temperature and longer residence times benefit the production of charcoal, as in traditional pyrolysis; higher temperatures and longer residence times increase the amount of produced gases; moderate temperature and shorter residence time are optimal for liquids production (Bridgwater, et. al., 1999). For fast pyrolysis, there are more important influencing factors beyond the chemical reaction kinetics, such as the heat and mass transfer processes. This is because fast pyrolysis is usually so quick that the reaction time is only a few seconds or less. Therefore, the critical issue is to bring the biomass particle to the optimum process temperature and minimize its exposure to the intermediate/lower temperatures that favor formation of charcoal (Bridgwater, et. al., 1999). Biomass with higher lignin concentration tends to give lower liquid yields; biomass which is high in cellulose content gives higher bio-oil yields (Ensyn Group).

2.4.4 Pyrolysis products

Since a large variety of biomass can be pyrolyzed to produce bio-oil or charcoal and there are a lot of factors that can influence the composition of the products, there is not a definitive composition for the product given a certain type of biomass. Ensyn Group Inc. (Ensyn Group) concluded from experiments that the yield of bio-oil from wood, paper and other biomass ranges from about 60 to 95 wt%, depending on the composition of the

feedstock. The yield of bio-oil from woody biomass ranges from 72 to 80 wt%, depending on the relative amounts and ratios of cellulose and lignin in the material (Ensyn Group). According to Stefan Czernik (Czernik, 2002), the typical product ratios for fast pyrolysis with moderate temperature and short residence time are: liquid - 75%, char - 12%, and gas - 13%.

2.4.5 Composition of bio-oil

Bio-oil typically is a dark-brown liquid with a distinctive odor. It contains varying quantities of water which forms a stable single phase free flowing mixture. The density of the bio-oil is very high, around 1.2 kg/L (Bridgwater, et. al., 1999). Chemically, bio-oil is a complex liquid mixture of oxygenated compounds containing various chemical functional groups, such as carbonyl, carboxyl, phenolic, etc (DynaMotive; Fagernas, 1995). The normal ranges of the different groups of chemicals are about: 20-25% water, 25-30% water insoluble pyrolytic lignin, 5-12% organic acids, 5-10% non-polar hydrocarbons, 5-10% anhydrosugars, and 10-25% other oxygenated compounds (DynaMotive). More than 400 organic compounds have been reported to exist in the bio-oils with a wide range of reported concentrations (Diebold, 1999). Bio-oil is obviously still a very poorly defined mixture of organics. Elemental/ultimate composition of bio-oils is important too. The average chemical composition of pyrolysis oil was $\text{CH}_{1.68}\text{O}_{0.165}\text{N}_{0.059}$ according to the work done by Gercel (Gercel, 2002). The typical range of elemental composition of fast pyrolysis is listed in Table 7.

Table 7 Typical elemental and water percentages of fast pyrolysis bio-oils (Bridgwater, et. al., 1999)

Component	Wt%
Water	20 - 30
Carbon	44 – 47
Hydrogen	6 – 7
Oxygen	46 – 48
Nitrogen	0 – 0.2

2.4.6 Advantages of bio-oil

Bio-oil has many environmental advantages over fossil fuels. Mainly, the following four advantages are the most remarkable. First of all, since bio-oil is derived from biomass or other organic materials, its production and use is considered to be neutral with respect to releasing greenhouse gases; secondly, because biomass does not contain sulfur, bio-oil produces virtually no SO_x emissions to the environment; thirdly, bio-oil fuels generate more than 50% lower NO_x emissions than diesel oil in gas turbines; and lastly, bio-oil can be produced locally where there are large quantities of organic waste (Dynamotive).

2.5 Gasification

2.5.1 Basic concepts

Gasification is one of the four “grand processes” in coal utilization; the other three are

combustion, liquefaction and carbonization (Van Krevelen, 1993). Gasification is defined as the production of gases with a usable heating value, i.e., combustible, from carbonaceous feedstock which could range from coal, oil to biomass and wastes (Higman, et. al., 2003). Gasification of coal is a well-established technology after more than 200 years' practice (Douglas Smoot, et. al., 1985). And the last ten years have seen the beginning of a renaissance of the gasification technology, as can be seen from Figure 7. Gasification is regarded as a treatment method that is able to lower the pollution caused by coal and increase the overall efficiency of the conversion of the chemical energy in the coal (Higman, et. al., 2003).

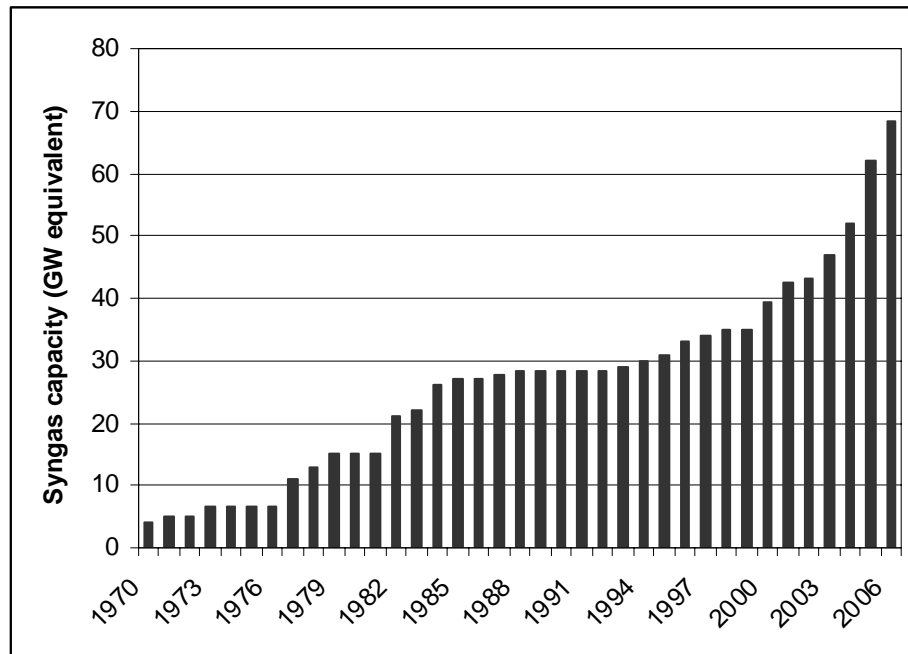
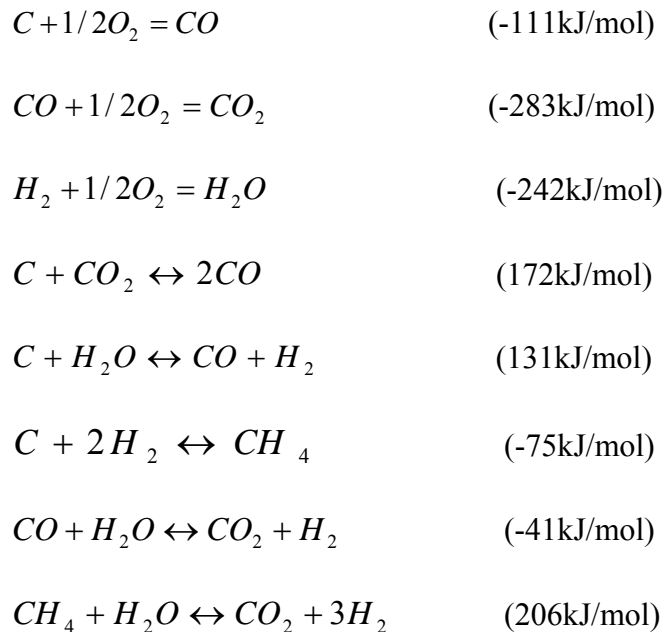


Figure 7 Cumulative worldwide gasification capacity

Note that the definition of gasification above includes the technologies of pyrolysis, partial oxidation and hydrogenation. But the dominant technology is partial oxidation, which produces from the fuel a synthesis gas (syngas) through pure oxygen, air, and/or steam as the oxidant (Higman, et. al., 2003). And we will focus on the more common process in which partial oxidation is significant.

2.5.2 Gasification reactions

For coal gasification, also for gasification for other solid carbon such as coke or char, the major chemical reactions are the following eight ones with carbon, carbon monoxide, carbon dioxide, hydrogen, water, and methane (Higman, et. al., 2003). These reactions will be referred to as 5-1 to 5-8 because they will be discussed in more detailed in Chapter 5.



The first three reactions are combustions with oxygen; they are always complete and exothermic. At the same time, the reactions with steam or carbon dioxide are always endothermic limited by thermodynamic equilibriums (Higman, et. al., 2003)

2.5.3 Gasification conditions

The gasification process takes place at temperatures in the range of 800°C to 1800°C (Higman, et. al., 2003). However, pyrolysis reactions dominate when the temperature is below 850°C, which makes it extremely complex to model the system. Besides, the partial oxidation reactions are so slow below 850°C that they become of little practical value (Higman, et. al., 2003). Over the whole temperature range described above, the reaction rates are sufficiently high that the reactions reach equilibrium fast – the products out of the gasifiers are at a composition very close to the equilibrium composition (Higman, et. al., 2003). For gasification on other carbonaceous feedstock, the temperatures are in all cases so high that, in practice, no hydrocarbons other than methane could be produced in any appreciable quantity (Higman, et. al., 2003).

Modern gasification processes are operated at pressures of at least 10 bar and up to as high as 100 bar (Higman, et. al., 2003). However, equipment reasons make it not very practical for gasification to be operated at pressures above 70 – 100 bar. And most modern gasification processes operate at pressures of 30 bar or higher (Higman, et. al., 2003).

2.5.4 Gasification products

In the practical implementation of gasification processes a broad range of reactor types has been, and continues, to be used. These reactor types can be grouped into three categories: moving-bed gasifiers, fluid-bed gasifiers, and entrained-flow gasifiers. Table 8 shows some typical products compositions from different types of gasifiers.

Table 8 Practical coal gasification products (Ünal, et. al., 1994)

Reactor	Example	Typical Product Composition (vol%)					
		CO	CO ₂	H ₂	CH ₄	N ₂ +	H ₂ O
Fixed-Bed	Lurgi	18	30	40	10	2	
Fluidized-Bed	Winkler	48	14	35	2	1	
	Westinghouse	19.2 – 23.0	5.4 – 9.3	14.4 – 19.2	2.7 – 3.4	41.5- 55.1	
	CO ₂ Acceptor	15.5	9.1	58.8	13.7	2.9	
	U-Gas	21.6	6.0	14.6		48.7	5.4
Entrained-Flow Gasifiers	Kopper-Totzek	52	10	36		2	
Molten Bath Gasifiers	Rockwell International	58	6	28	3	1	4

The desired products are usually carbon monoxide, hydrogen, and methane (Douglas Smoot, et. al., 1985), because they are the combustible, fuel-rich products. The potential uses of gasification product are for: 1) production of substitute natural gas; 2) use as a synthesis gas for subsequent production of alcohols, gasoline, plastics, etc; 3) use as a gaseous fuel for generation of electrical power; 4) use as a gaseous fuel for production of

industrial steam or heat (Higman, et. al., 2003).

2.6 Steam Reforming

2.6.1 Basic concepts

Steam reforming is the catalytic reforming of hydrocarbons under a steam atmosphere. It is the dominant technology for production of syngas and hydrogen (UOP). Most of the steam reforming practice for hydrogen production is on light hydrocarbons. Recently the steam reforming of biomass derived products has been studied and initial work has established that biomass pyrolysis oil could be steam-reformed to generate hydrogen (Wang, et. al., 1998).

Before the development of pressure swing adsorption (PSA), the syngas produced needed to go through a CO₂ wash system and a methanator to remove the carbon oxides. After the development of PSA, the purification of syngas for hydrogen is much simplified. See the following two figures for the two steam reforming processing systems.

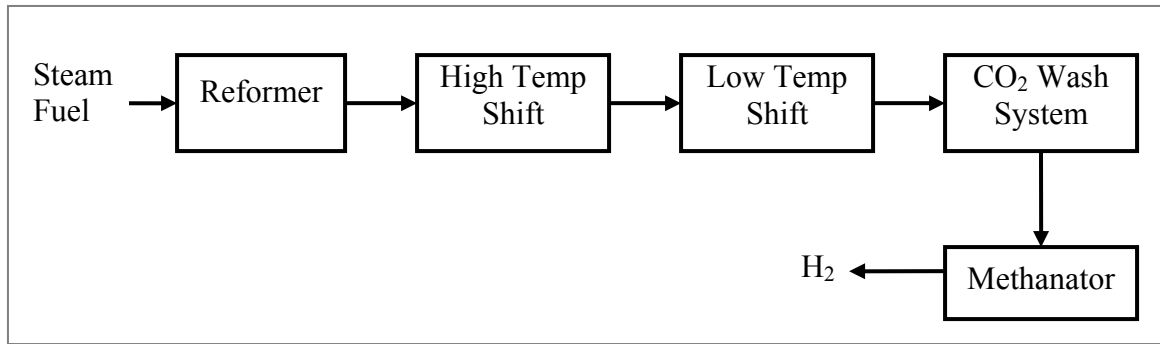


Figure 8 SR process before development of PSA (UOP)

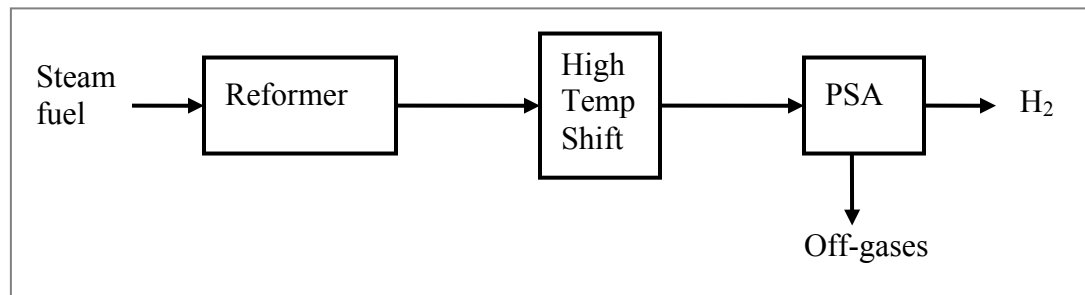
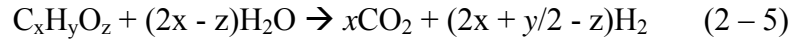


Figure 9 SR process with PSA system (UOP)

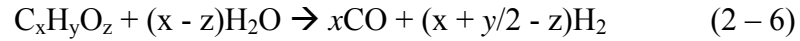
For both systems, the syngas produced by the reformer need to first pass through a shift reactor, where carbon monoxide further converts to carbon dioxide and hydrogen.

2.6.2 Reactions and conditions

The overall steam-reforming reaction of any oxygenate with a chemical formula of $C_xH_yO_z$ can be summarized as (Wang, et. al., 1998).



This overall reaction is composed of the following three reactions:



In current steam reformers, the reaction temperature is usually above 700°C (Wang, et. al., 1998) and under a pressure from just above ambient pressure to several atmospheres (AROFE). Nickel on aluminum support is a common catalyst for steam reforming (Magrini-Bair, et. al., 2002). Many other catalysts, especially for specific steam reforming reaction, are also under intensive study (Mizuno, et. al., 2003; Wheeldon, et. al., 2003)

CHAPTER 3

PROCESS OUTLINE

Figure 10 shows the overall conversion processes from biomass or coal to produce hydrogen, respectively, in which, the processes with a “*” sign only apply to the biomass conversion system.

For biomass conversion, pyrolysis at 450°C, 500°C, and 550°C was employed at first to convert the biomass to bio-oil (condensable organics), gases (non-condensable), water, and solid carbon – char. The gases were determined to contain hydrogen, methane, steam, and carbon oxides. But the bio-oil is a poorly defined mixture, the percentage of each component varies significantly, and only a few experimental results are available to calibrate a model. Simulation tool to estimate the composition of the bio-oil is presented in Chapter 4. After this, the gases and bio-oil from pyrolysis were steam-reformed at 850°C in a steam environment to convert more hydrogen in the gaseous product and hydrogen in steam to hydrogen gas. At the temperature of the steam reforming, other gaseous products, such as methane, carbon monoxide, carbon dioxide, and extra steam, were also contained in the products from the reformer. The produced hydrogen gas was separated from the product mixture through Pressure Swing Adsorption (PSA). For the base case, it was assumed that the recovery ratio of hydrogen is 80% of the total hydrogen produced from the previous reactions. After the desired hydrogen was separated, the off-gases (gaseous products left after separation of hydrogen) were combusted to utilize the heating value of the products to improve the thermal efficiency

of the overall process. Limited by the reactor construction materials, the highest temperature for the combusted products was assumed to be 1220°C, which determined that a certain amount of steam needed to be added into the combustor for temperature control. Altogether, the products out of the reformer and the products after combustion were two hot streams from which heat could be recovered and used by other streams or reactions. Char produced from pyrolysis could also be a source for heat recovery by cooling down from pyrolysis temperature to ambient temperature. Steam reforming, biomass preheating to pyrolysis temperature, pyrolytic bio-oil/gases preheating to the reforming temperature, and water boiling and superheating are all the scenarios which require energy input in the biomass conversion system. The net energy requirement will be satisfied by external energy input.

For coal conversion, gasification at 850°C and 50 bar was employed at first to gasify the coal to a gaseous product – syngas, which contained hydrogen, methane, steam, and carbon oxides. Assuming that coal can be gasified completely with enough oxygen input, there was no solid product such as char out of coal gasification, different from that in the case in biomass pyrolysis. The gaseous product was steam-reformed at 850°C in a steam environment to convert more hydrogen in the gaseous product and hydrogen in steam to hydrogen gas. Same as the biomass conversion system, other gaseous products, such as methane, carbon monoxide, carbon dioxide, and extra steam, were also contained in the products out of the reformer. The produced hydrogen gas was separated from the product mixture through Pressure Swing Adsorption (PSA). The same recovery ratio was used in the PSA unit in coal conversion as in the biomass conversion. After the desired hydrogen

was separated, the off-gases were combusted to 1220°C to utilize the heating value of the products to provide the energy the conversion system needed. Altogether, the products out of reformer and the products after combustion were two hot streams from which heat could be recovered and used by other streams or reactions. Gasification could be exothermic or endothermic, depending on the steam-to-carbon (S/C) ratio or the oxygen-to-carbon (O/C) ratio. In the base cases we have studied, at S/C ratio lower than 0.5, the gasification was exothermic, and the heat released could be utilized to satisfy the energy requirement of other streams or reactions; at S/C ratio higher than 0.5, including 0.5, the gasification became endothermic. Steam reforming, coal preheating, water boiling and superheating are all the scenarios which require energy input in the coal conversion system. The net energy requirement will be satisfied by external energy input.

The reaction conditions will be specified in more details when one particular process is discussed. Throughout this whole calculation, a negative sign in energy means that the reaction was exothermic or heat was released; positive means endothermic reaction or heat was still required, which is the same as the convention in literature.

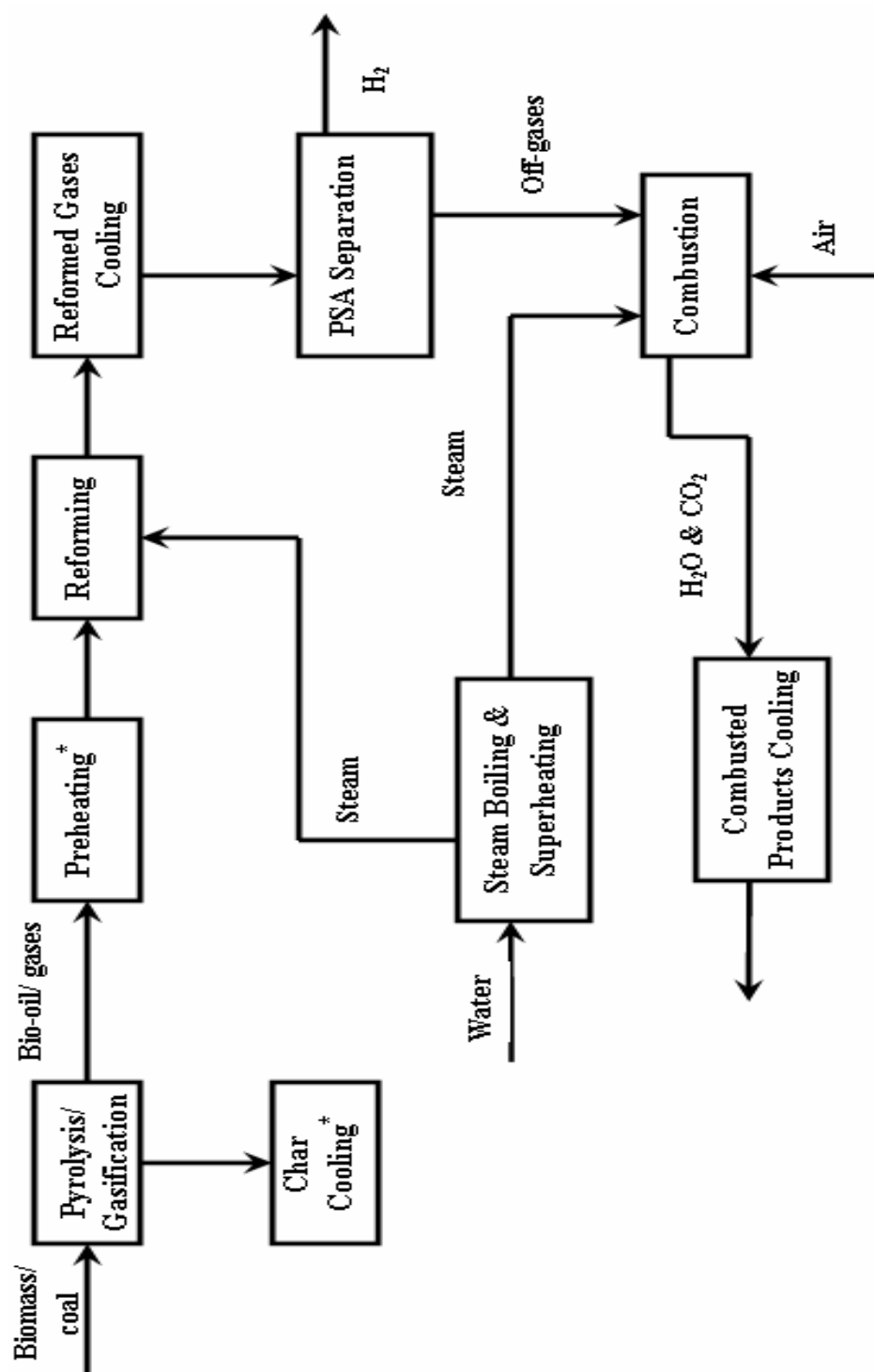


Figure 10 Conversion process outline from biomass/coal to hydrogen
 (* applies to biomass conversion system only)

CHAPTER 4

BIOMASS CONVERSION

4.1 Biomass Composition

We chose to use pinewood as the representative for current biomass in our base case because it is a very popular type of tree in the southeast United States and so could be easily obtained and is available in large quantities. The elemental compositions of the different parts of the pine wood are listed in Table 9. We neglected the element other than carbon, hydrogen, and oxygen in this study because they have relatively small concentrations.

Table 9 Elemental composition of pinewoods (TUWIEN)

	Pine wood	Pine bark	Pine chips	Pine sawdust	Average
C (wt%)	52.13	52.30	51.85	52.49	52.19
H (wt%)	6.36	5.80	6.21	6.24	6.15
O (wt%)	41.38	41.66	41.65	41.05	41.44
Other (wt%)	0.13	0.24	0.29	0.22	0.22

Another expression of composition is also important in influencing the resulted bio-oil characteristics – the chemical composition such as lignin, cellulose, etc. This composition will influence the group distribution in the pyrolytic bio-oil such as phenols concentration,

the amount of guaiacyl and syringyl products, and other compounds. This composition is listed in Table 10. However, in this study, we did not consider the influence of this composition because we used the pyrolytic data of the same type of tree, pine, and the chemical composition of the biomass was assumed to be very similar across different cases. If pyrolysis of another type of biomass is required and there is not enough experimental data on it available, analysis on its elemental and chemical composition would be indispensable for a good estimation on the bio-oil composition.

Table 10 Chemical composition of different parts of a pine tree (Oasmaa, et. al., 2003; Arpiainen, et. al., 1989)

	Stem wood	Needles	Bark
Extractives	3	12.6	4.5
Lignin (wt%)	28.1	28.4	29.2
Carbonhydrates (wt%)	67.9	54	62.4
Unknown (wt%)	1	5	4

Based on the literature data that we could find, we assumed that the pyrolysis was conducted on a mixture of the different parts of the pine wood, but mainly of pine barks and pine wood.

4.2 Biomass Pyrolysis

Pyrolysis is a very complex reaction system with the products composition depending on the reaction temperature, heating rate, residence time, biomass type and composition, and

the complex instantaneous heat and mass transfer conditions (Bridgwater, 1999; Meier, et. al., 1999; Horne, et. al., 1996). For the base case, we chose to look at the pyrolysis at 450°C, 500 °C, and 550 °C because they are common temperatures for pyrolysis and lead to high yields of bio-oil (organics plus water). Figure 11 shows the typical yields of pyrolysis products from fast pyrolysis of wood under different reaction temperatures (Bridgwater, et. al., 1999). At 450°C, 500 °C, and 550 °C, the weight percentage of the dry feed are listed in Table 11 for the organics, water, gases, and char.

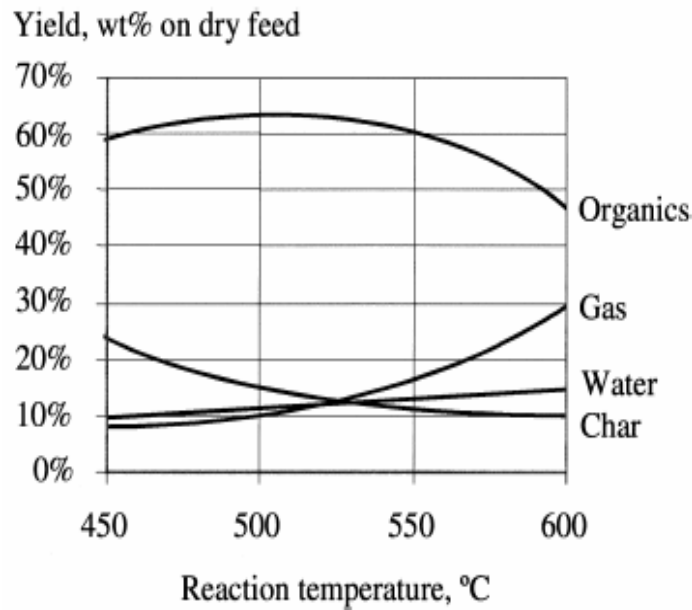


Figure 11 Typical products' yields from fast pyrolysis of wood (Bridgwater, et. al., 1999)

We will use “gases” for abbreviation to refer to the non-condensable gases and “bio-oil” to refer to the condensable organics together with water through this thesis, although the

condensable organics are also in vapor phase when they come out of the pyrolyzer. “Bio-oil organics” will refer to the bio-oil without water.

Table 11 Pyrolytic products compositions

Pyrolytic temperature	Organics (wt%)	Water (wt%)	Gases (wt%)	Char (wt%)
450°C	59	10	8	23
500°C	63	12	16	9
550°C	60	13	16	11

We based our calculation and comparison on 1kg of dry biomass and 1kg of moisture-and-ash-free coal for the two conversion systems respectively. Therefore, the mass of different products after the pyrolysis can be easily calculated. Although the bio-oil and gases are normally referred to separately, we lumped them together in the following-up processes because they are actually a single vapor phase after pyrolysis, and there is no reason to cool down and separate them for hydrogen production, which will only make the system more complex, increase the total processing cost, and waste the carbon monoxide and methane in the gases as by-product instead of as reactants for hydrogen production as well.

Before the biomass goes into the pyrolyzer, it has to be preheated to the pyrolysis temperature. Based on reference (DOE, Biomass), the heat capacity of wood-type biomass was estimated to be 2.59 kJ/kg/°C. It is self-evident that the lower the reaction

temperature is, the less energy is required to preheat the biomass. But the overall performances of the conversion from biomass to hydrogen could be very different as a result of the different reaction temperatures of pyrolysis. And the energy required for preheating the biomass will be integrated into the overall energy requirement of the conversion for comparison.

The heat required at the reaction was estimated using the enthalpy of pyrolysis, which is in the range of 1.18MJ/kg to 1.97 MJ/kg for dry wood-type biomass based on reference (Daugaard, et. al., 2003). Since there was not enough information on energy requirement of pine wood pyrolysis, we took the average as 1.58MJ/kg for base case analysis to find the optimal biomass conversion condition with respect to hydrogen production efficiency. Sensitivity analysis was conducted on the optimal case regarding the energy requirement of the pyrolysis.

Char produced in pyrolysis can provide heat during the process of being cooled down to room temperature from pyrolysis temperature. The heat capacity for char was found to be 0.67kJ/kg/°C (DOE, Biomass), with which the heat released in cooling char from pyrolysis to room temperature was calculated to be 65.48kJ, 50.91kJ, and 38.69kJ from pyrolysis at 450 °C, 500 °C, and 550 °C, respectively.

The composition of the gases was obtained from the experimental of Liu and his colleagues (Liu, et. al., 1999). We assumed that the little oxygen produced would be consumed completely during the reaction and the resulted gases would be only the four

components listed in Table 12. The gas composition is listed in Table 12. This composition is in volume percentage of the total non-condensable gases, not including the bio-oil organics or water. When the gases and bio-oils were lumped together, they were assumed to be ideally mixed.

Table 12 Composition of pyrolytic gases

Component	CO	CO ₂	CH ₄	H ₂
V/V%	60.29	6.40	31.67	1.63

4.3 Bio-oil Composition Estimation

Bio-oil, product from pyrolysis and precursor for steam reforming, is hard to define because its composition depends on reaction conditions, biomass type and composition, and could contain hundreds of components (Diebold, 1999). What's more, for many components, the range of the reported concentration even exceeds a factor of 10 to 1 (Diebold, 1999). However, the current pyrolysis experiments only cover a small range of biomasses. Therefore, if the development of biomass conversion to hydrogen is to be generalized to other types of biomass, it becomes necessary to examine the potential bio-oil compositions that can be generated.

We have designed a simulation tool using MATLAB language for the purpose of estimating the pyrolytic bio-oil composition from various biomasses, using the current

available experimental bio-oil compositions and the overall empirical formula of a bio-oil. The MATLAB code is enclosed in Appendix A.

The idea of this program is to utilize a literature catalogue of biomass components and match the current overall elemental composition to it. Literature sources enabled us to identify 89 common components in bio-oil organics; each had several experimental concentrations in the bio-oil organics. We took the highest and lowest values available, relaxed them to a reasonable extent (the lowest value was further lowered to 0.5 times the original value because it is probable that not all of the components would appear in a particular bio-oil and many component could be in very small concentration; the highest value was relaxed to 1.1 times the original value), and used them as the upper and lower bound of the possible concentration of the corresponding component in our estimated bio-oil. See Table 13 for the values. In addition, Sensoz (Sensoz, 2003) conducted slow pyrolysis experiment on pinewood and gave an empirical formula of the resulted bio-oil without water, $\text{CH}_{1.43}\text{O}_{0.332}$. Assuming that fast and slow pyrolysis would result in different amount of bio-oil but would not result in much difference with respect to the bio-oil composition, we used it as the empirical formula that our estimated bio-oil would have. We also obtained some typical experimental concentrations of some components in a wood-type bio-oil under fast pyrolysis around 500C (DynaMotive Bio-oil), see Table 14. It was changed to the non-water base (third column in the table) because our estimation is on the organics in bio-oil only, not including the water (water was added in later calculations). We used it for the target concentrations for these components, and tried to minimize the difference of the estimated concentrations for these components

from the target ones, subject to the constraints of concentrations for the 89 components and the element mass balance for carbon, hydrogen, and oxygen corresponding to the empirical formula.

Table 13 Lower and upper bounds of components' concentrations in bio-oil organics (Diebold, 1999)

Component	Relaxed Lb (wt%)	Relaxed Ub (wt%)	Component	Relaxed Lb (wt%)	Relaxed Ub (wt%)
Formic	0.38	12.13	Angelicalactone	0.13	1.60
Acetic	0.63	16.00	Levoglucozan	0.50	1.87
Propanoic	0.13	2.40	Glucose	0.50	1.73
Hydroxyacetic	0.13	1.20	Fructose	0.88	3.87
Butanoic	0.13	0.67	D-Xylose	0.13	1.87
Pentanoic	0.13	1.07	D-Arobinose	0.13	0.13
4-oxypentanioc	0.13	0.53	Cellobiosan	0.75	4.27
Hexanoic	0.13	0.40	1,6 Anhrdroglucofuranose	3.88	4.13
Benzoic	0.25	0.40	2-Methoxy Phenol	0.13	1.47
Heptanoic	0.38	0.40	4-Methyl Guaiacol	0.13	2.53
Methanol	0.50	3.20	Ethyl Guaiacol	0.13	0.80
Ethanol	0.75	1.87	Eugenol	0.13	3.07
Ethylene Glycol	0.88	2.67	Isoeugenol	0.13	9.60
Acetone	3.50	3.73	4-Propylguaiacol	0.13	0.53
2-Butanone	0.38	1.20	Acetoguiacone	1.00	1.07
2,3-Pentenedione	0.25	0.53	Prpioguiacone	1.00	1.07
3Me2cyclopenten2ollone	0.13	2.53	2,6-DiOMe Phenol	0.88	6.40
2-Et-cyclopentanone	0.25	0.40	Methyl Syringol	0.13	0.40
Dimethylcyclopentanone	0.38	0.40	4-Ethyl Syringol	0.25	0.27
Trimethylcyclopentenone	0.13	0.67	Propyl Syringol	0.13	2.00
Trimethylcyclopentanone	0.25	0.53	Syringaldehyde	0.13	2.00
Formaldehyde	0.13	4.40	4-Propenyl Syringol	0.13	0.40
Acetaldehyde	0.13	11.33	4-OH-3,5-DiOMe Phenol Ethanone	0.13	0.40
2-Propenal	0.75	1.20	Furan	0.13	0.40
2-Methyl-2-butenal	0.13	0.67	2-Methyl Furan	0.13	0.27
Pentanal	0.63	0.67	2-Furanone	0.13	1.47

Table 13 Lower and upper bounds of components' concentrations in bi-oil organics (continued) (Diebold, 1999)

Component	Relaxed Lb (wt%)	Relaxed Ub (wt%)	Component	Relaxed Lb (wt%)	Relaxed Ub (wt%)
Ethanedial	1.13	6.13	Furfural	0.13	1.47
Phenol	0.13	5.07	3-Methyl-2(3h) Furanone	0.13	0.13
2-Methyl Phenol	0.13	0.80	Furfural alcohol	0.13	6.93
3-Methyl Phenol	0.13	0.53	Furoic Acid	0.50	0.53
4-Methyl Phenol	0.13	0.67	5-Methyrfurfural	0.13	0.80
2,3 Dimethyl Phenol	0.13	0.67	5-OH-Methyl-2-Furfural	0.38	2.93
2,4 Dimethyl Phenol	0.13	0.40	Hydroxyacetaldehyde	1.13	17.33
2,5 Dimethyl Phenol	0.25	0.53	Acetol	0.88	9.87
2,6 Dimethyl Phenol	0.13	0.53	Acetal	0.13	0.27
2-Ethylphenol	0.13	1.73	Acetyloxy-2-propanone	0.13	1.07
2,4,6 TriMe Phenol	0.38	0.40	2-OH-3-Me-2-cyclopentene-1-one	0.13	0.67
1,2 DiOH Benzene	0.13	0.93	Methyl Cyclopentenolone	0.13	2.53
1,3 DiOH Benzene	0.13	0.40	1-Acetyloxy-2-Propanone	0.13	1.07
1,4 DiOH Benzene	0.13	2.53	2-Methy-3-hydroxy-2-pyrone	0.25	0.53
4-Methoxy Catechol	0.75	0.80	2-Methoxy-4-metylanisole	0.13	0.53
1,2,3 Trio-OH-Benzene	0.75	0.80	4-OH-3 methoxybenzaldehyde	0.13	1.47
Methyl Formate	0.13	1.20	Dimethylcyclopentene	0.88	0.93
Butyrolactone	0.13	1.20	Lignin	31.25	40.00
Valerolactone	0.25	0.27			

Table 14 Concentrations of major components of a wood-derived bio-oil (DynaMotive, Bio-oil)

Component	Concentrations (wt%)	Non-water base (wt%)
Water	23.4	0
Lignin	24.9	32.5
Cellubiosan	1.9	2.5
Glyoxal	1.9	2.5
Hydroxyacetaldehyde	10.2	13.3
Levoglucosan	6.3	8.2
Formaldehyde	3.0	3.9
Formic Acid	3.7	4.8
Acetic Acid	4.2	5.5
Acetol	4.8	6.3

Mathematically, the problem of bio-oil component matching is formulated through the following equations.

$$\min \quad \sum \alpha_i (W_i - W_i^T)^2 \quad (4-1)$$

$$s.t. \quad Lb_i \leq W_i \leq Ub_i \quad (4-2)$$

$$x_{ref} / Mw_{bio} = \sum x_i W_i / Mw_i \quad (4-3)$$

$$y_{ref} / Mw_{bio} = \sum y_i W_i / Mw_i \quad (4-4)$$

$$z_{ref} / Mw_{bio} = \sum z_i W_i / Mw_i \quad (4-5)$$

Where $W \equiv$ wt% of component in one composition

$Mw \equiv$ molecular weight

$x \equiv$ number of carbon in the formula of some component

y \equiv number of hydrogen in the formula of some component

z \equiv number of oxygen in the formula of some component

α \equiv weight placed on component in bio-oil composition estimation

Lb \equiv lower bound

Ub \equiv upper bound

Superscript L \equiv lowest hydrogen production

Superscript U \equiv most hydrogen production

Superscript T \equiv target

Subscript i \equiv component i

Subscript ref \equiv reference

Subscript bio \equiv whole bio-oil

MATLAB returned only one composition that satisfied the constraints with the least squares error from the target. However, we consider the above optimization to be highly degenerate, in other words, there could be many compositions that have the same variance from the target and satisfy the constraints and hence are “optimal” too. These different compositions might result in very different hydrogen production levels. Therefore we tried to find another two compositions, corresponding to the highest and lowest hydrogen production ability, by posing the following two minimization problems. The two compositions that resulted are listed in Table 15 together with the first result from MATLAB, in which “conc.” refers to the concentrations corresponding to the bio-oil composition closest to the target one; “Lb conc.” refers to the concentration corresponding to the composition with the lowest hydrogen production ability; “Ub

conc.” refers to the concentration corresponding to the composition with the highest hydrogen production ability.

$$\min \quad \sum (y/2 + x - z)_i W_i^L \quad (4-6)$$

$$s.t. \quad Lb_i \leq W_i^L \leq Ub_i \quad (4-7)$$

$$x_{ref} / Mw_{bio} = \sum x_i W_i^L / Mw_i \quad (4-8)$$

$$y_{ref} / Mw_{bio} = \sum y_i W_i^L / Mw_i \quad (4-9)$$

$$z_{ref} / Mw_{bio} = \sum z_i W_i^L / Mw_i \quad (4-10)$$

$$\max \quad \sum (y/2 + x - z)_i W_i^U \quad (4-11)$$

$$s.t. \quad Lb_i \leq W_i^U \leq Ub_i \quad (4-12)$$

$$x_{ref} / Mw_{bio} = \sum x_i W_i^U / Mw_i \quad (4-13)$$

$$y_{ref} / Mw_{bio} = \sum y_i W_i^U / Mw_i \quad (4-14)$$

$$z_{ref} / Mw_{bio} = \sum z_i W_i^U / Mw_i \quad (4-15)$$

The results showed, somewhat surprisingly, that the hydrogen production would not change much with different bio-oil compositions, i.e., the hydrogen production is not very sensitive to the bio-oil composition, given the common constraints on the composition. The results of the hydrogen production capacity and the variances to the target bio-oil composition for the three compositions are listed in Table 16. From the results, we can see that even with relaxed variance constraint, the hydrogen production

ability changed little. We used the least squares solution from MATLAB for the calculations on following processes.

Table 15 Estimated bio-oil compositions

Component	Conc. (wt%)	Lb conc. (wt%)	Ub conc. (wt%)	Component	Conc. (wt%)	Lb conc (wt%)	Ub conc (wt%)
Formic	0.25	2.17	0.19	Angelicalactone	0.06	0.06	0.06
Acetic	0.86	0.31	0.31	Levoglucozan	0.25	0.25	0.25
Propanoic	0.06	0.06	0.06	Glucose	0.25	0.25	0.25
Hydroxyacetic	0.06	0.06	0.06	Fructose	0.44	0.44	0.44
Butanoic	0.64	0.57	0.73	D-Xylose	0.06	0.06	0.06
Pentanoic	1.17	1.17	1.17	D-Arobinose	0.06	0.06	0.06
4-oxyptanioc	0.06	0.06	0.06	Cellobiosan	1.05	0.38	0.38
Hexanoic	0.44	0.44	0.44	1,6 Anhrdroglucofurano se	1.94	1.94	1.94
Benzoic	0.44	0.13	0.44	2-Methoxy Phenol	1.61	1.61	1.61
Heptanoic	0.44	0.44	0.44	4-Methyl Guaiacol	2.79	2.79	2.79
Methanol	0.25	0.25	3.52	Ethyl Guaiacol	0.88	0.88	0.88
Ethanol	2.05	2.05	2.05	Eugenol	3.37	3.37	3.37
Ethylene Glycol	0.44	0.44	0.44	Isoeugenol	10.56	10.56	10.56
Acetone	4.11	4.11	4.11	4-Propylguaiacol	0.59	0.59	0.59
2-Butanone	1.32	1.32	1.32	Acetoguiacone	1.17	1.17	1.17
2,3-Pentenedione	0.59	0.59	0.48	Prpioguiacone	1.17	1.17	1.17
3Me2cyclopenten2ollo ne	2.79	2.79	2.79	2,6-DiOMe Phenol	0.44	3.76	2.30
2-Et-cyclopentanone	0.44	0.44	0.13	Methyl Syringol	0.44	0.44	0.44
Dimethylcyclopentanon e	0.44	0.44	0.19	4-Ethyl Syringol	0.29	0.29	0.29
Trimethylcyclopenteno ne	0.73	0.73	0.73	Propyl Syringol	2.20	2.20	2.20
Trimethylcyclopentano ne	0.59	0.59	0.13	Syringaldehyde	0.06	0.06	0.06
Formaldehyde	1.41	0.06	0.06	4-Propenyl Syringol	0.44	0.44	0.44
Acetaldehyde	4.14	6.92	3.83	4-OH-3,5-DiOMe Phenol Ethanone	0.06	0.06	0.06
2-Propenal	1.32	1.32	1.32	Furan	0.44	0.44	0.44
2-Methyl-2-butenal	0.73	0.73	0.73	2-Methyl Furan	0.29	0.29	0.29
Pentanal	0.73	0.73	0.34	2-Furanone	0.06	0.06	0.06
Ethanedial	0.56	0.56	0.56	Furfural	0.06	0.06	0.06
Phenol	5.57	5.57	5.57	3-Methyl-2(3h) Furanone	0.06	0.06	0.06
2-Methyl Phenol	0.88	0.88	0.88	Furfural alcohol	0.06	0.06	0.06
3-Methyl Phenol	0.59	0.59	0.59	Furoic Acid	0.25	0.25	0.25
4-Methyl Phenol	0.73	0.73	0.73	5-Methyrfurfural	0.17	0.06	0.88
2,3 Dimethyl Phenol	0.73	0.73	0.73	5-OH-Methyl-2- Furfural	0.19	0.19	0.19

Table 15 Estimated bio-oil compositions (continued)

Component	Conc. (wt%)	Lb conc. (wt%)	Ub conc. (wt%)	Component	Conc. (wt%)	Lb conc (wt%)	Ub conc (wt%)
2,4 Dimethyl Phenol	0.44	0.44	0.44	Hydroxyacetaldehyde	0.56	0.56	0.56
2,5 Dimethyl Phenol	0.59	0.59	0.59	Acetol	3.67	0.44	0.44
2,6 Dimethyl Phenol	0.59	0.59	0.59	Acetal	0.29	0.29	0.29
2-Ethylphenol	1.91	1.91	1.91	Acetyloxy-2-propanone	0.06	0.06	0.06
2,4,6 TriMe Phenol	0.44	0.44	0.44	2-OH-3-Me-2-cyclopentene-1-one	0.73	0.73	0.73
1,2 DiOH Benzene	0.06	0.06	1.03	Methyl Cyclophenolone	2.79	2.79	2.79
1,3 DiOH Benzene	0.06	0.06	0.44	1-Acetyloxy-2-Propanone	0.06	0.06	0.06
1,4 DiOH Benzene	1.79	0.06	2.79	2-Methy-3-hydroxy-2-pyrone	0.13	0.13	0.13
4-Methoxy Catechol	0.38	0.38	0.38	2-Methoxy-4-metylanisole	0.59	0.59	0.59
1,2,3 Trio-OH-Benzene	0.38	0.38	0.38	4-OH-3 methoxybenzaldehyde	0.06	0.06	0.24
Methyl Formate	0.06	0.06	0.06	Dimethylcyclopentene	1.03	1.03	0.44
Butyrolactone	0.06	0.06	0.06	Lignin	15.63	15.63	15.63
Valerolactone	0.29	0.29	0.13				

Table 16 Sensitivity of hydrogen production to bio-oil

	W	W ^L	W ^U
Value of $\sum (y/2 + x - z)_i W_i$	136.66	135.50	138.12
Variance	5212.40	5981.70	6906.70
Variance ratio	1	1.15	1.32

4.4 Bio-oil/Gases Preheating

The bio-oil and gases from the pyrolyzer need to be preheated to the steam-reforming temperature, 850C. For this to be calculated, the specific heat capacities for all the 89 components in the bio-oil organics, together with those for the five components in the

gases, need to be known. However, many of the components do not have the specific heat capacity data available in the literature for them. In the case that there is no literature data available, the estimation method in Perry's Chemical Engineer's Handbook (Perry's) was used to calculate the heat capacity, which is an estimation method based on the contribution from different types of atoms as stated by the equation below.

$$Cp^0 = a_1 + a_2C + a_3H + a_4O + a_5N + a_6S + a_7F + a_8Cl + a_9I + a_{10}Br + a_{11}Si + a_{12}Al + a_{13}B + a_{14}P + a_{15}E \quad (4-16)$$

Where, $Cp^0 \equiv$ ideal gas heat capacity, J/mol K

$a_1 - a_{15} \equiv$ parameters

C, H, O, N \equiv number of carbon, hydrogen, oxygen, and nitrogen atoms in the molecule

S, F, Cl, I, Br \equiv number of sulfur, fluorine, chlorine, iodine, bromine atoms in the molecule, respectively

Si, Al, B, P \equiv number of silicon, aluminum, boron, phosphorus atoms in the molecule, respectively

E \equiv number of atoms in the molecule excluding the 13 atom-types listed above

So based on this method and also some literature data, the specific heat capacities of the 93 components in the bio-oil and gases were calculated and listed in Table 17.

Table 17 Specific heat capacities for components in bio-oil/gases

Component	Cp (J/mol/°C)	Component	Cp (J/mol/°C)
Formic *	83.8	Glucose	425.9
Acetic *	134.4	Fructose	425.9
Propanoic	188.3	D-Xylose	353.5
Hydroxyacetic	156.7	D-Arobinose	353.5
Butanoic	240.3	Cellobiosan	758.7
Pentanoic	292.3	1,6 Anhydroglucofuranose	375.1
4-oxyptanioc	282.3	2-Methoxy Phenol	305.1
Hexanoic	344.3	4-Methyl Guaiacol	357.1
Benzoic	274.7	Ethyl Guaiacol	409.1
Heptanoic	396.3	Eugenol	430.7
Methanol *	89.8	Isoeugenol	430.7
Ethanol	146.3	4-Propylguaiacol	461.1
Ethylene Glycol	166.7	Acetoguiacone	399.1
Acetone *	164.4	Prpioguiacone	451.1
2-Butanone	219.9	2,6-DiOMe Phenol	377.5
2,3-Pentenedione	261.9	Methyl Syringol	429.5
3Me2cyclopenten2ollone	283.5	4-Ethyl Syringol	481.5
2-Et-cyclopentanone	345.5	Propyl Syringol	533.5
Dimethylcyclopentanone	345.5	Syringaldehyde	419.5
Trimethylcyclopentenone	367.1	4-Propenyl Syringol	503.1
Trimethylcyclopentanone	397.5	4-OH-3,5-DiOMe Phenol	471.5
Formaldehyde *	62.2	Ethanone	
Acetaldehyde *	125.8	Furan	159.1
2-Propenal	137.5	2-Methyl Furan	211.1
2-Methyl-2-butenal	241.5	2-Furanone	179.5
Pentanal	271.9	Furfural	201.1
Ethanedial	105.9	3-Methyl-2(3h) Furanone	231.5
Phenol *	233.1	Furfural alcohol	231.5
		Furoic Acid	221.5

Table 17 Specific heat capacities for components in bio-oil/gases (continued)

Component	Cp (J/mol/°C)	Component	Cp (J/mol/°C)
2-Methyl Phenol	284.7	5-Methyrfurfural	253.1
3-Methyl Phenol	284.7	5-OH-Methyl-2-Furfural	273.5
4-Methyl Phenol	284.7	Hydroxyacetaldehyde	136.3
2,3 Dimethyl Phenol	336.7	Acetol	188.3
2,4 Dimethyl Phenol	336.7	Acetal	374.7
2,5 Dimethyl Phenol	336.7	Acetyloxy-2-propanone	282.3
2,6 Dimethyl Phenol	336.7	2-OH-3-Me-2-cyclopentene-1-one	283.5
2-Ethylphenol	336.7	Methyl Cyclopentenolone	283.5
2,4,6 TriMe Phenol	388.7	1-Acetyloxy-2-Propanone	282.3
1,2 DiOH Benzene	253.1	2-Methy-3-hydroxy-2-pyrone	273.5
1,3 DiOH Benzene	253.1	2-Methoxy-4-metylanisole	409.1
1,4 DiOH Benzene	253.1	4-OH-3 methoxybenzaldehyde	347.1
4-Methoxy Catechol	325.5	Dimethylcyclopentene	325.1
1,2,3 Trio-OH-Benzene	273.5	Lignin	340.7
Methyl Formate	136.3	CO *	29.8
Butyrolactone	209.9	CH4 *	70.1
Valerolactone	261.9	CO2 *	82.1
Angelicalactone	231.5	H2 *	27.2
Levoglucosan	375.1	H2O *	34.2

* data from literature (Dean, 1987; Yaws, 1997)

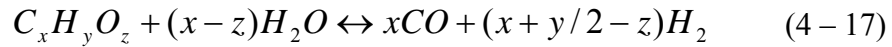
Although the bio-oil composition did not have much influence on hydrogen production, it might affect the energy for preheating before steam reforming because the average heat capacity could change. Calculations were also conducted based on the composition estimated by the upper bound and lower bound of hydrogen production (see Table 18), it turned out that the preheating energy hardly changed.

Table 18 Preheating energy and SR energy under three estimated bio-oil compositions

	W	W ^L	W ^U
Preheating Energy (kJ)	708.59	708.46	708.33
SR energy (S/C=1) (kJ)	3033.46	3041.03	3031.47

4.5 Steam Reforming of Bio-oil/Gases

Steam reforming is the process by which organics are converted into hydrogen and carbon monoxide by reaction with steam. The basic reactions are shown by the first equation below. We included the water gas shift reaction (equation 4–18 below) in this step.



The steam reforming of higher organics is irreversible (Wang, et. al., 1997). But the water gas shift reaction and the methane reforming reaction (equation 4-19 above) are both limited by the equilibrium at reaction temperature. For the base case, it was assumed the reactions took place at 850C and 1.78 atm based on the experimental conditions of reference (DOE Solicitation). Using this specification we calculated the final composition

of the products at equilibrium. The calculation was done with programming tool gPROMS and was enclosed in Appendix A.

Note that at low S/C ratio, carbon-formation reaction, $C + CO_2 \leftrightarrow 2CO$, could occur in the system at the same time. However, the equilibrium constant for this reaction at 850°C is 880.93, which indicates that the reverse carbon-formation reaction is minimal. Therefore, we neglected this reaction in the calculation.

The product composition is also a function of the steam to feed ratio. We calculated the products' composition under steam-to-carbon (S/C) ratio of 1, 2, 3, and 4, respectively. The results are listed in column 2 to column 5 in Table 19. To calculate the energy requirement for the reforming reactions, the same difficulty appeared – literature data are not available for enthalpy of formation for most of the components in the bio-oil. We used the estimation method for the enthalpy of formation in Perry's Chemical Engineer's Handbook (Perry's) to solve this problem. The idea of this estimation is stated below by equation 4-20. It is the estimation for enthalpy of formation based on the contribution from various characteristic structural groups. So for this to be calculated, the atomic structures of all the components need to be known. The components' formula and structures are both listed in appendix B. After the enthalpy of formation was known for each component, the energy requirement for the steam reforming could then be calculated. Based on the equilibrium composition, the reactant extent of the steam reforming, water-gas shift, and methane formation/reforming were known. The results of energy requirements are summarized in the next section.

$$\Delta H_{f,298}^0 = 68.29 + \sum_{i=1}^n N_i \Delta H_i \quad (4-20)$$

Where, $\Delta H_{f,298}^0 \equiv$ enthalpy of formation at 298.15 K, kJ/mol

$n \equiv$ number of different atomic groups contained in the molecule

$N_i \equiv$ number of atomic groups i contained in the molecule

$\Delta H_i \equiv$ numeric value of atomic group i obtained (listed in Appendix C)

Table 19 Product compositions after SR of bio-oil/gases

	CO (mol)	CO ₂ (mol)	CH ₄ (mol)	H ₂ (mol)	H ₂ O (mol)
Pyrolysis at 450°C					
S/C=1	28.4	3.8	2.1	44.0	11.1
S/C=2	24.6	9.3	0.5	54.4	38.6
S/C=3	21.1	13.1	0.2	59.1	69.2
S/C=4	18.4	15.9	0.1	62.2	100.7
Pyrolysis at 500 °C					
S/C=1	30.5	4.1	2.3	47.2	11.9
S/C=2	26.4	10.0	0.5	58.3	41.4
S/C=3	22.6	14.1	0.2	63.4	74.1
S/C=4	19.7	17.1	0.1	67.0	108.1
Pyrolysis at 550 °C					
S/C=1	31.2	4.5	2.2	48.3	13.0
S/C=2	26.8	10.5	0.5	59.3	43.5
S/C=3	23.0	14.7	0.2	64.5	77.3
S/C=4	20.1	17.7	0.1	67.8	112.4

4.6 Heat Integration of Biomass Conversion System

4.6.1 Summary of energy requirements at specific positions

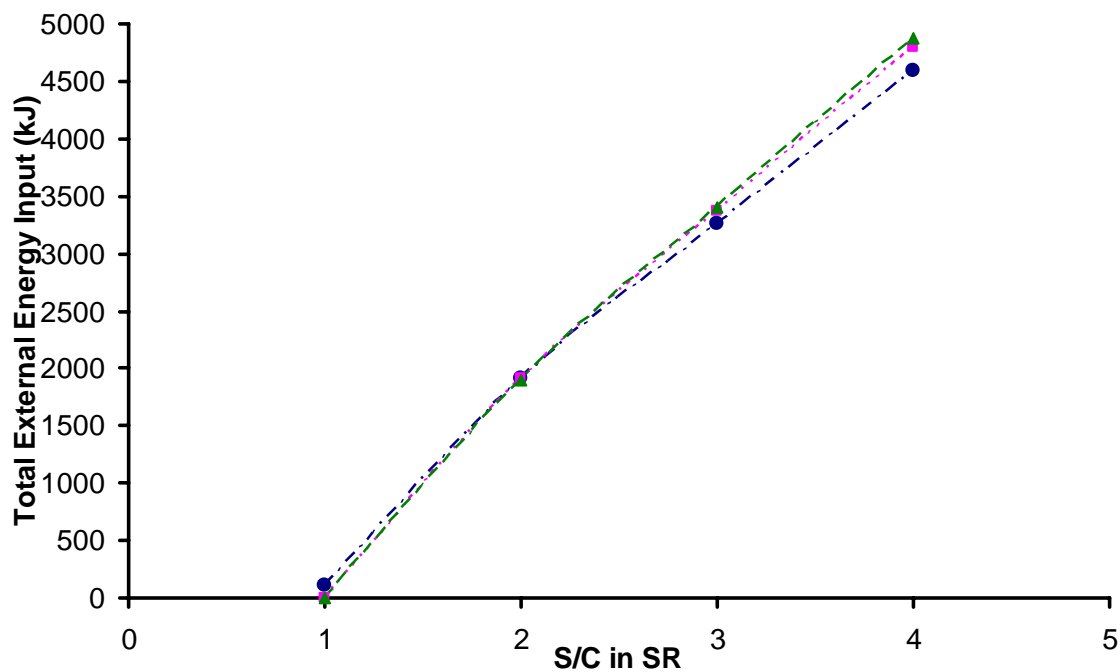
The following table (Table 20) summarizes the energy requirement at each specific position of the whole conversion process of biomass. We can see that the most significant energy requirement is water boiling to make the steam and the steam superheating. And the most energy recovery comes from the cooling of the products after combustion. Both of these parts involve a large quantity of water, which releases or requires a lot of energy when condensed or vaporized, respectively.

Table 20 Energy required or released at specific positions of biomass conversion

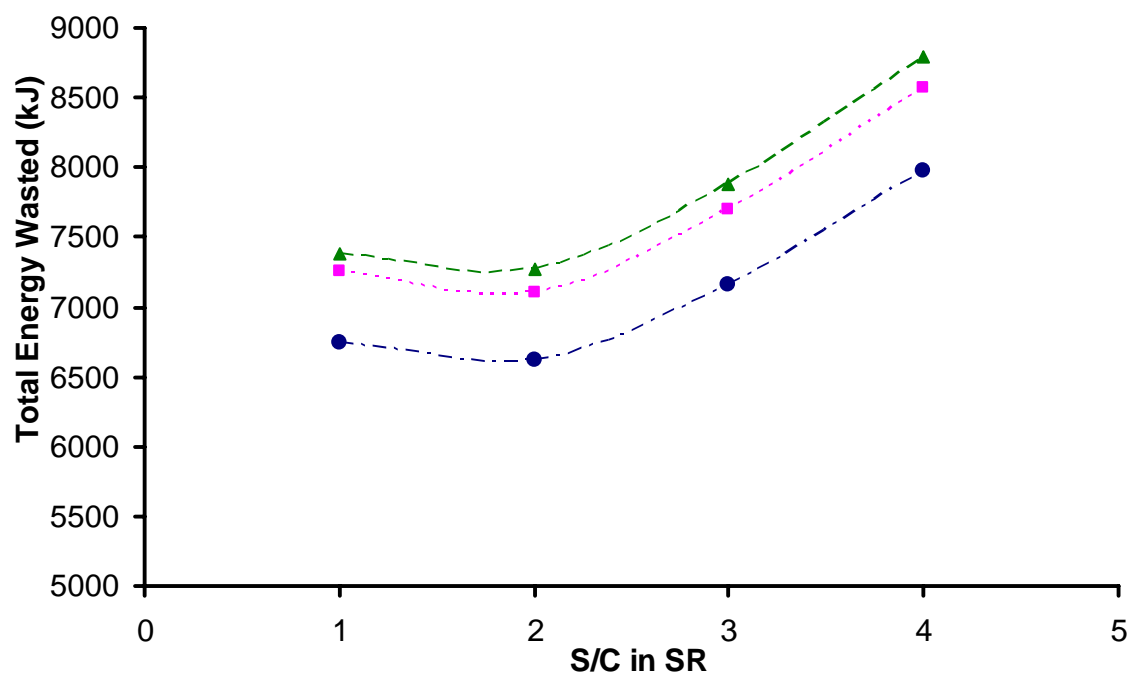
kJ	Biomass heating	Pyro.	Pyro. products heating	SR	Water boiling & heating	SR products cooling	Comb. products cooling	Char cooling
T range (°C)	25– PyT	PyT	PyT -850	850	25-163-850	850 – 25	1220-25	PT-25
Pyrolysis at 450°C								
S/C=1 in SR	1102	1580	653	2831	8415	- 2776	- 18167	- 65
S/C=2 in SR	1102	1580	653	2946	9643	- 5092	- 15153	- 65
S/C=3 in SR	1102	1580	653	2853	11389	- 7473	- 13485	- 65
S/C=4 in SR	1102	1580	653	2759	13377	- 9882	- 12339	- 65
Pyrolysis at 500°C								
S/C=1 in SR	1231	1580	709	3033	8968	- 2980	- 19471	- 51
S/C=2 in SR	1231	1580	709	3154	10287	- 5466	- 16243	- 51
S/C=3 in SR	1231	1580	709	3055	12162	- 8021	- 14455	- 51
S/C=4 in SR	1231	1580	709	2954	14295	- 10606	- 13225	- 51
Pyrolysis at 550°C								
S/C=1 in SR	1361	1580	733	3059	9081	- 3110	- 19720	- 39
S/C=2 in SR	1361	1580	733	3155	10466	- 5674	- 16481	- 39
S/C=3 in SR	1361	1580	733	3049	12408	- 8308	- 14667	- 39
S/C=4 in SR	1361	1580	733	2946	14614	- 10972	- 13418	- 39

4.6.2 Heat integration

There were three heat sources in the biomass system that could be used to provide heat where needed, namely, cooling the steam reformed products (1), from the combustion of the off-gases (gases out of the reformer except 80% of the hydrogen that had been separated) from the PSA unit (2), and from cooling the by-product, charcoal (3). We used the “heat sinks” to stand for the streams or reaction systems that require energy. The heat sinks for the biomass system were: biomass preheating (4), pyrolysis (5), bio-oil/gases preheating (6), steam reforming (7), and water boiling and superheating (8). We used Pinch Analysis for the heat integration with ΔT_{\min} between 10°C and 20°C depending on the phases of the streams (gases streams are separated by a ΔT_{\min} of 20°C; liquid streams are separated by a ΔT_{\min} of 10°C, streams of gases and solid/liquid are separated by a ΔT_{\min} of 15°C). Figure 12 illustrates the summarized results of the heat integration for the total external energy input and total wasted energy (energy that could not be used by the system itself), correlated with pyrolysis temperature and S/C ratios in steam reforming.



(a)



(b)

Figure 12 Total external energy input (a) and energy wasted (b) after heat integration for biomass conversion (Blue circle– 450°C; Purple square - 500 °C; Green triangle - 550 °C)

4.6.3 Heat integration discussion

It can be seen that the total energy input (Figure 12a) after heat integration did not vary much with different pyrolysis temperatures, with less than 300kJ to be the maximum difference at the same S/C ratio in SR. However, it increased significantly with increasing S/C ratio in SR. The total energy input did not vary much with pyrolysis temperature because all of the externally energy needed was to satisfy the energy requirement at high temperatures, at which heat integration within the system could not meet the needs. In addition, the energy requirements at high temperatures were at steam reforming, pyrolytic products preheating, and water superheating, and they did not change much with different pyrolysis temperatures. On the other hand, with increasing S/C ratio in SR, the energy requirement for water superheating increased significantly. This is why the total energy input increases significantly with increasing S/C ratio in SR.

From Figure 12b, we can see that the wasted energy increased apparently with increasing pyrolysis temperature. This is because as the temperature of pyrolysis increases, the energy it requires will be at higher temperature. And part of the energy which could be utilized at lower pyrolysis temperature became useless and wasted. As to the influence of S/C ratio in SR, when $S/C = 2$ in steam reforming, the wasted energy was least for all the cases studied. It is the result of the balance between energy available from heat sources, combusted products especially, and the extent of utilization of the energy. To be more specific, the wasted energy was mainly the result of the heat released at lower

temperatures, in which water condensation was the dominant part. Water condensation released a lot of energy, whereas it was at the temperature of 100°C, a large portion of it can not be utilized by the heat sinks. For the cases where external energy input required was zero, the energy from heat sources was enough to satisfy the requirement of the heat sinks. On the other hand, for the cases where the external energy inputs required were positive, it indicated that the energy from heat sources had been utilized to the maximum extent, and temperature constraint determined external energy must be put in to satisfy the balance requirement.

4.6.4 Detailed results and grand composite curve

See Table 21 as an example and Table 40 – 50 Appendix D for more detailed heat integration analysis on biomass conversion. The shaded area or bolded line stands for the temperature range of the corresponding heat sources or heat sinks. The different shading in the heat sinks (8) was a result that the amount of water vapor changed at the temperature 163°C, at which the water is vaporized (DOE Solicitation). In other words, only part of the steam had to continue to be heated to 850°C. See section 4.6.2 for definitions of number 1 – 8 for heat sources/sinks.

Table 21 Heat integration for biomass conversion through pyrolysis at 450 °C and S/C = 2 in SR)

Pyrolysis at 450 °C; S/C=2 in SR															
Subunit	Streams and Temperature										Defi- cit (kJ)	Accumulated (kJ)		Adjusted (kJ)	
	Heat sources				Heat sinks							Input	Output	Input	Output
	1	2	3	T /°C		4	5	6	7	8					
				1220											
1				870	850						-3329	0	3329	1905	5234
2				850	830						2846	3329	483	5234	2388
3				470	450						-3394	483	3878	2388	5783
4				450	435						1401	3878	2477	5783	4382
5				178	163						-2037	2477	4514	4382	6419
6				100	90						6419	4514	-1905	6419	0
7				35	25						-6441	-1905	4536	0	6441
				25							-180	4536	4715	6441	6620

Note that in the heat integration tables, the convention set by Linnhoff et. al. (Linnhoff, et. al., 1983) was followed. The “deficit” column shows the amount of energy the hot streams still need to provide to the cold streams. In the “accumulated” column, the initial external energy input (input to subunit 1) was assumed to be zero; the heat from higher subinterval could be transferred to the lower interval. In the column of “adjusted”, the initial external energy was set to be the largest absolute value of the numbers in “accumulated” because a heat input can not be negative. This gives the minimum external heat input while making all the inputs positive or zero. The first input in the “adjusted” column is the energy that has to be put in by an external means; the last output in the “adjusted” column is the energy wasted by the system.

The following figure, Figure 13, is the grand composite curve for the heat integration shown in Table 21. The temperatures were adjusted to those for heat sources by adding ΔT_{\min} to the heat sinks' temperatures so that both the heat sinks and heat sources were brought to a common reference of temperature. Based on the data from Table 21, it shows schematically the temperatures at which external energy is required or energy is wasted from the system. The shaded area is where part of the energy required by the heat sinks of the system could be satisfied from the energy of heat sources. The upper thin horizontal line shows the temperature and amount of externally required energy. We can see from it that the extra energy that has to be put in externally is around 163°C, which is the temperature that water is boiled to make steam to be superheated under higher pressure. The lower thin horizontal line shows the temperature and amount of the energy wasted from the system, which is from the condensation temperature of steam to ambient temperature.

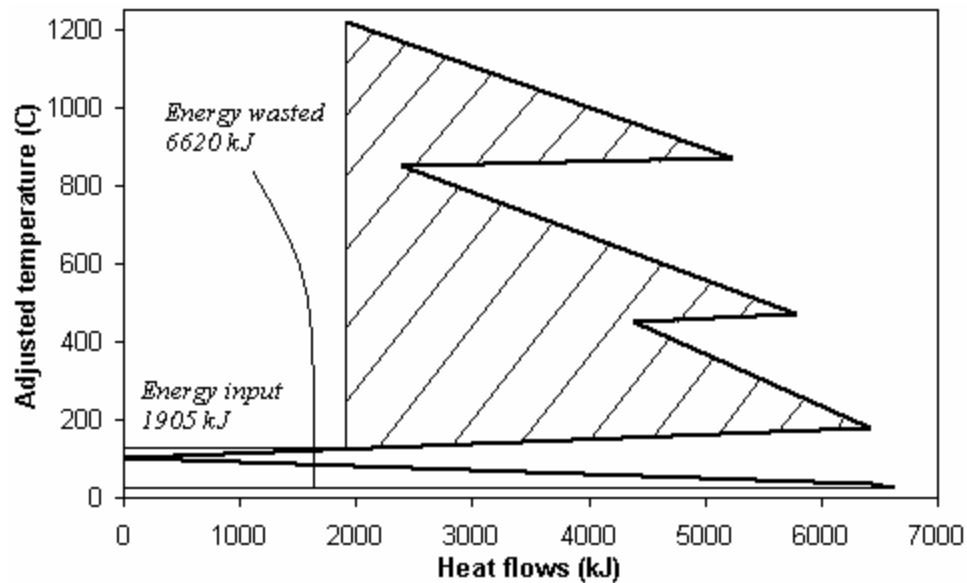


Figure 13 Grand composite curve for heat integration in Table 21 for biomass conversion

However, instead of using a constant heat capacity throughout the whole temperature changing process of the streams, we used stage-wise constant heat capacities data to make up the disadvantage of the original Pinch Analysis method to improve the accuracy of the calculation. To do this, the specific heat capacities of the streams at different mixing ratios as a result of different reaction temperature and different amounts of steam input were calculated. The calculation results are summarized in Table 22 - 24. The heat capacities of steam increased with increasing temperature.

Table 22 Specific heat capacities for heat sources/sinks in biomass conversion through pyrolysis at 450°C

Pyrolysis at 450°C										
Biomass (kJ/g/°C)			2.59E-03							
Bio-oil & Gases (J/mol/°C)			125.0							
Char (kJ/g/°C)			0.00067							
	Temperature		1050	850	680	500	330	140	70	30
Products stream after SR (J/mol/°C)	S/C=1	All			32.1	31.5	30.9	30.2		
		No water							29.5	29.3
	S/C=2	All			33.8	32.9	32.1	31.3		
		No water							30.1	29.9
	S/C=3	All			34.7	33.8	32.9	31.9		
		No water							30.5	30.2
	S/C=4	All			35.2	34.2	33.3	32.3		
		No water							30.9	30.5
Products stream after comb. (J/mol/°C)	S/C=1	All	40.6	38.9	37.6	36.1	34.7	33.2		
		No water							32.3	31.7
	S/C=2	All	42.3	40.4	38.8	37.4	35.4	33.6		
		No water							32.9	32.2
	S/C=3	All	43.6	41.4	39.6	37.7	35.9	33.8		
		No water							33.2	32.5
	S/C=4	All	44.6	42.2	40.3	38.2	36.2	34.0		
		No water							33.5	32.7
Water (J/mol/°C)				34.4	34.1	33.7	33.4	33.4/75.6	75.6	

Table 23 Specific heat capacities for heat sources/sinks in biomass conversion through pyrolysis at 500 °C

Pyrolysis at 500 °C										
	Temperature		1050	850	680	500	330	140	70	30
Products stream after SR (J/mol/°C)	S/C=1	All			32.1	32.1	30.9	30.2		
		No water							29.5	29.3
	S/C=2	All			33.8	32.9	32.2	32.2		
		No water							30.1	29.9
	S/C=3	All			34.7	33.8	32.9	31.9		
		No water							30.6	30.2
	S/C=4	All			35.2	34.2	33.3	32.3		
		No water							30.9	30.5
Products stream after comb. (J/mol/°C)	S/C=1	All	40.6	39.0	37.6	36.1	34.7	33.2		
		No water							32.3	31.7
	S/C=2	All	42.3	40.4	38.8	37.0	35.4	33.6		
		No water							32.9	32.2
	S/C=3	All	43.6	41.4	39.6	37.7	35.9	33.8		
		No water							33.2	32.5
	S/C=4	All		44.6	42.3	40.3	38.2	36.2		
		No water							33.5	32.7

Table 24 Specific heat capacities for heat sources/sinks in biomass conversion through pyrolysis at 550 °C

Pyrolysis at 550 °C										
	Temperature		1050	850	680	500	330	140	70	30
Products stream after SR (J/mol/°C)	S/C=1	All			32.2	31.5	30.9	30.2		
		No water							29.5	29.4
	S/C=2	All			33.9	33.0	32.2	31.3		
		No water							30.1	29.9
	S/C=3	All			34.8	33.9	33.0	32.0		
		No water							30.6	30.3
	S/C=4	All			35.3	34.3	33.4	32.3		
		No water							30.9	30.6
Products stream after comb. (J/mol/°C)	S/C=1	All	40.7	39.1	37.7	36.2	34.8	33.2		
		No water							32.4	31.7
	S/C=2	All	42.5	40.5	38.9	37.1	35.5	33.6		
		No water							32.9	32.2
	S/C=3	All	43.7	41.5	39.7	37.7	35.9	33.9		
		No water							33.3	32.5
	S/C=4	All	44.7	42.4	40.4	38.3	36.3	34.1		
		No water							33.5	32.7

4.7 Summary of Biomass Conversion Process

In summary, the amount of mass and energy involved in the biomass conversion process, especially the amount of hydrogen produced and total energy requirement, are listed in Table 25. The calculations were based on 1 kg pinewood as the current biomass.

Table 25 Summary of biomass conversion

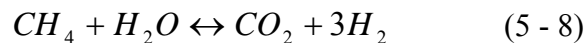
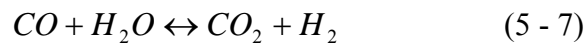
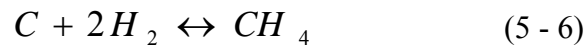
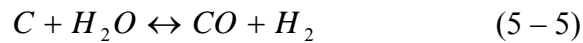
S/C in SR	S/C = 1	S/C = 2	S/C = 3	S/C=4
Pyrolysis at 450°C				
H ₂ output (mol)	35.2	43.5	47.3	49.8
H ₂ O input (mol)	160.5	167.0	184.5	207.0
H ₂ O output (mol)	155.7	153.9	167.6	187.6
Net Usage of water (mol)	4.8	13.1	16.9	19.4
O ₂ input (mol)	22.9	18.7	16.8	15.6
CO ₂ output (mol)	34.4	34.4	34.4	34.4
Total Energy Input (kJ)	113	1905	3263	4588
Total Energy Waste (kJ)	6743	6620	7164	7981
Pyrolysis at 500°C				
H ₂ output (mol)	37.7	46.7	50.7	53.4
H ₂ O input (mol)	171.3	178.4	197.1	221.3
H ₂ O output (mol)	166.9	165.1	179.7	201.2
Net Usage of water (mol)	4.4	13.3	17.4	20.0
O ₂ input (mol)	24.5	20.1	18.1	16.7
CO ₂ output (mol)	36.9	36.9	36.9	36.9
Total Energy Input (kJ)	0	1912	3373	4796
Total Energy Waste (kJ)	7250	7111	7695	8571
Pyrolysis at 550°C				
H ₂ output (mol)	38.7	47.5	51.6	54.2
H ₂ O input (mol)	173.4	181.2	200.8	225.8
H ₂ O output (mol)	169.6	168.6	184.0	206.4
Net Usage of water (mol)	3.9	12.7	16.8	19.4
O ₂ input (mol)	24.8	20.4	18.3	17.0
CO ₂ output (mol)	37.8	37.8	37.8	37.8
Total Energy Input (kJ)	0	1902	3402	4870
Total Energy Waste (kJ)	7387	7266	7882	8794

CHAPTER 5

COAL CONVERSION

5.1 Coal Gasification

In a gasification system, the reactions are basically the following eight ones (Higman, et. al., 2003). The first three reactions are combustions, so they are all essentially complete. While the last two reactions can be deduced from the reaction 5-4 to 5-6, we thus only used the reversible reactions 5-4 to 5-6 to determine the product composition under different reaction conditions.



The temperature at which gasification is practiced in industry varies from 850 to 1800 (Higman, et. al., 2003). Furthermore, the equilibrium composition also depends on the S/C ratio. We calculated the potential hydrogen production ability and the energy requirement of the gasification under temperature from 850C to 1800C and S/C ratio within 0.1 – 0.6 (hydrogen production capability is defined as the amount of hydrogen that could be produced from the gasification product using steam reforming under 100% conversion efficiency of the gasified products). It turned out that hydrogen production capability changed little, although increased, with increasing temperature, while energy requirement increased significantly with increasing temperature. Besides, S/C ratio starting from 0.6 to higher values would make oxygen input negative in the calculation, which means that oxygen was not needed at all. We eliminated such cases because in these cases, carbon would not be gasified completely. The results calculated by MATLAB (code enclosed in Appendix A) for temperature in 850 – 1000°C and S/C ratio in 0.1 – 0.6 are listed in Table 26. The coal composition chosen is on moisture-and-ash-free base as in Table 4.

Table 26 Gasification performances under different conditions

Item	S/C in Ga.	T/°C			
		850	900	950	1000
Hydrogen Production Ability (mol)	0.1	106.6	106.3	106.1	106.1
	0.2	117.9	118.0	118.2	118.2
	0.3	130.0	130.4	130.3	130.3
	0.4	142.1	142.4	142.4	142.5
	0.5	153.9	154.4	154.5	154.6
	0.6	165.8	166.3	166.6	166.7
Energy Requirement (kJ)	0.1	-4697	-3998	-3698	-3652
	0.2	-2979	-2487	-2358	-2315
	0.3	-1621	-1243	-1022	-979
	0.4	-266	122	314	358
	0.5	1207	1535	1652	1695
	0.6	2664	2968	2988	3031
Oxygen Usage (mol)	0.1	17.6	15.6	14.7	14.5
	0.2	13.0	11.6	11.3	11.2
	0.3	9.5	8.5	7.9	7.8
	0.4	6.1	5.1	4.5	4.4
	0.5	2.2	1.4	1.1	1.0
	0.6	-1.6	-2.3	-2.3	-2.4

The base case of gasification at 850°C was chosen, at which the energy requirement was the smallest and the hydrogen production ability was not reduced significantly. However, it was sensitive to different S/C ratios. Oxygen usage data suggested that with decreasing steam input, the oxygen requirement increased quickly. Therefore, we determined to look at the conversion process with S/C parameterized between 0.2 and 0.5. The gasification products under these S/C ratios and 850°C are listed in Table 27.

Table 27 Product compositions from gasification of coal under different conditions

S/C in Ga.	CO (mol)	CO ₂ (mol)	CH ₄ (mol)	H ₂ (mol)	H ₂ O (mol)
0.2	50.3	1.8	15.9	10.1	0.1
0.3	47.6	1.6	18.8	11.1	0.1
0.4	44.9	1.4	21.8	12.0	0.1
0.5	42.1	1.2	24.8	12.8	0.1

5.2 Steam Reforming of Gasification Products

Similar to steam reforming in the biomass conversion system, the S/C ratio here can also be varied. And again, we considered the cases where the S/C was 1, 2, 3, and 4 respectively. At equilibrium, the compositions of the reformed product were calculated and listed in Table 28.

Table 28 Product compositions from SR of gasification products of coal

S/C in SR	CO (mol)	CO ₂ (mol)	CH ₄ (mol)	H ₂ (mol)	H ₂ O (mol)
S/C=0.2 in gasification					
S/C=1	51.3	15.7	1.1	68.5	39.3
S/C=2	41.6	26.2	0.3	81.3	96.1
S/C=3	35.0	33.0	0.1	88.6	157.1
S/C=4	30.2	37.8	0.1	93.7	220.1
S/C=0.3 in gasification					
S/C=1	52.5	14.1	1.4	75.8	38.2
S/C=2	43.2	24.4	0.4	89.2	94.8
S/C=3	36.6	31.3	0.2	96.8	155.6
S/C=4	31.8	36.2	0.1	101.9	218.6
S/C=0.4 in gasification					
S/C=1	53.5	12.7	1.9	83.0	36.9
S/C=2	44.7	22.8	0.5	97.2	93.3
S/C=3	38.1	29.8	0.2	105.0	154.1
S/C=4	33.2	34.8	0.1	110.4	217.0
S/C=0.5 in gasification					
S/C=1	54.3	11.4	2.4	90.2	35.5
S/C=2	46.0	21.4	0.7	105.3	91.8
S/C=3	39.5	28.3	0.3	113.4	152.4
S/C=4	34.7	33.3	0.1	118.8	215.3

5.3 Heat Integration of Coal Conversion System

5.3.1 Summary of energy requirements at specific positions

The following table (Table 29) summarizes the energy requirement at each specific position of the whole conversion process of coal. Again, we can see that the most significant energy requirement is at water boiling to make the steam and the steam superheating. And the most energy recovery comes from the cooling of the products after combustion. Both of these parts involve a large quantity of water, which releases or requires a lot of energy when condensed or vaporized, respectively.

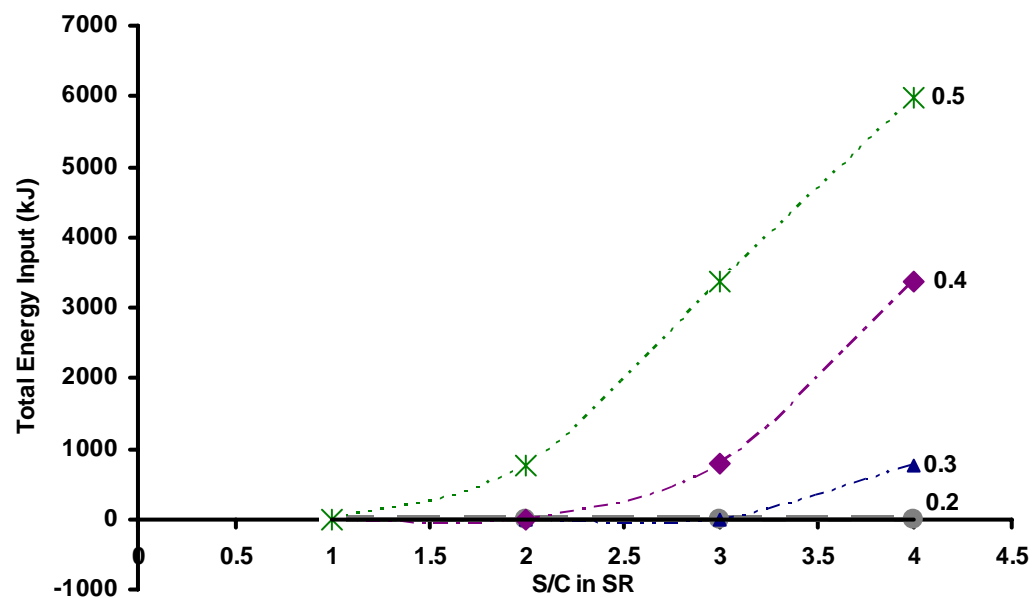
Table 29 Energy required or released at specific positions of coal conversion

	Coal preheating	SR	Water boiling & superheating	Ga.	Reformed products cooling	Comb. products cooling
T range (°C)	25-GaT	850	25-163-850	850	850-25	1220-25
S/C = 0.2 in Gasification						
S/C=1 in SR	1089	2489	14415	-4218	-6464	-28338
S/C=2 in SR	1089	2216	17223	-4218	-11075	-23806
S/C=3 in SR	1089	1974	20856	-4218	-15780	-21025
S/C=4 in SR	1089	1789	24908	-4218	-20531	-19089
S/C = 0.3 in Gasification						
S/C=1 in SR	1089	3075	15047	- 2407	-6512	-29911
S/C=2 in SR	1089	2861	17846	- 2407	-11120	-25294
S/C=3 in SR	1089	2628	21458	- 2407	-15822	-22459
S/C=4 in SR	1089	2444	25494	- 2407	-20571	-20487
S/C = 0.4 in Gasification						
S/C=1 in SR	1089	3645	15655	- 599	-6556	-31454
S/C=2 in SR	1089	3502	18445	- 599	-11161	-26742
S/C=3 in SR	1089	3282	22041	- 599	-15861	-23858
S/C=4 in SR	1089	3099	26051	- 599	-20606	-21829
S/C = 0.5 in Gasification						
S/C=1 in SR	1089	4199	16245	1207	-6599	-32981
S/C=2 in SR	1089	4140	19025	1207	-11200	-28159
S/C=3 in SR	1089	3936	22607	1207	-15898	-25227
S/C=4 in SR	1089	3760	26617	1207	-20643	-23192

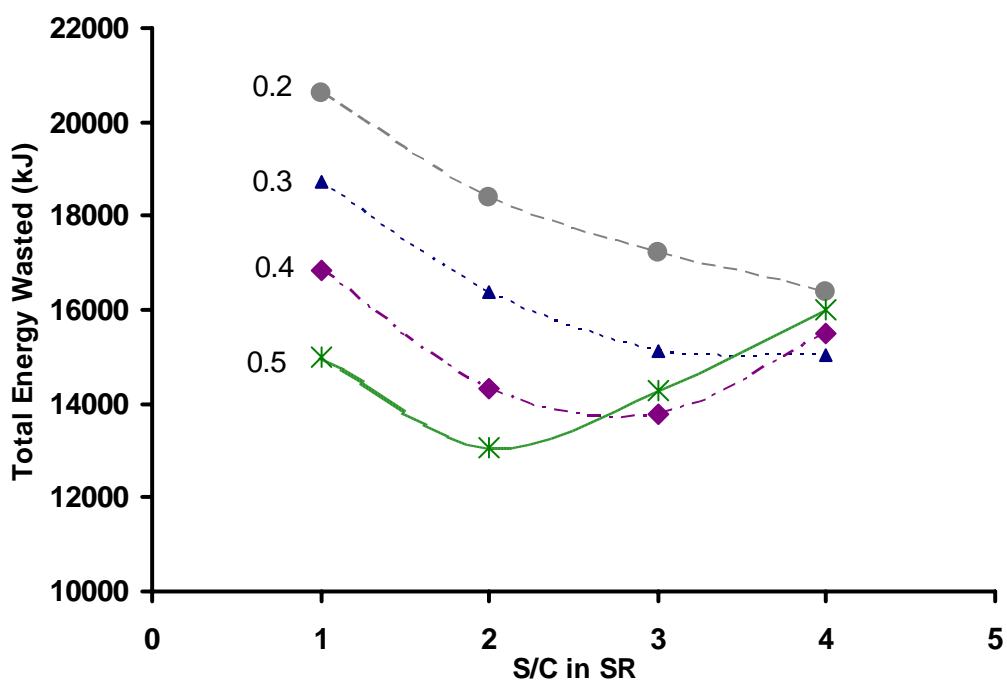
5.3.2 Heat integration

The heat integration scenarios for the coal system were different from those of the biomass system. There were two general cases: when the S/C was 0.5 in the gasification, the gasification system was a heat sink; when S/C was 0.2 to 0.4, gasification itself became a heat source because the combustion became dominant and provided more energy than required for other reactions. Among other streams or reaction systems, there were two heat sources in the coal system that could be used to provide heat where needed, namely, from cooling the steam reformed products (1), from the combustion of the off-gases (gases out of the reformer after 80% of the hydrogen were separated) from the PSA unit (2). The heat sinks for the coal system were: coal preheating (3), steam reforming (4), and water boiling and superheating (5). We used Ga as the heat source name to refer to heat released or required during gasification.

Similarly to biomass conversion, we used Pinch Analysis for the heat integration with ΔT_{\min} between 10°C and 20°C depending on the phases of the streams. Figure 14 illustrates the summarized results of the heat integration for the total external energy input and total wasted energy, correlated with S/C ratios in gasification and S/C ratios in steam reforming.



(a)



(b)

Figure 14 Total external energy input (a) and energy wasted (b) after heat integration for coal conversion (Numbers besides lines are the S/C ratios in gasification.)

5.3.3 Heat integration discussion

We can see that the total external energy (Figure 14a) input for coal conversion increased significantly with increasing S/C ratios both in gasification and in steam reforming. The trend of total energy input with respect to S/C in SR is similar to the situation in the biomass conversion. For the increase in external energy input with increasing S/C in gasification, the reason lies in the energy contribution from the gasification system. With increasing S/C in gasification, the energy released decreased significantly, even from exothermic to endothermic at S/C of 0.5. Thus with decreasing contribution from heat sources within the system, more external energy was required to satisfy the overall needs. For all the cases after gasification at S/C of 0.2, there was no external energy input required, because a lot of energy was released when the coal was gasified at S/C ratio of 1. This energy was at a high temperature, 850°C, therefore, together with the other two heat sources, it could satisfy all the energy requirements of the heat sinks. Smaller S/C ratios in other gasification cases also resulted in no requirement on external energy input.

For the wasted energy (Figure 14b), the figure shows that there are minimum points of wasted energy with respect to S/C in SR among the cases studied. As was the same to the situation in the biomass conversion, these points all appeared at where external energy input started to be required, because when external energy input was required, it meant that the heat sources could not meet the total energy requirement of the system. And when this occurred, it was the point where the energy from these heat sources had been utilized to the maximum extent. Also from Figure 4b, the energy wasted increased with decreasing S/C ratio in gasification at lower S/C ratios of SR. This was also mainly

because of the gasification energy. The more contribution from gasification, the less utilization of the other heat sources, and the more energy would be wasted.

There is also a certain trend as to the position of the minimum points in the cases studied, that is, the higher the S/C ratio is in gasification, the lower S/C ratio in SR at which the minimum point is located. This is, again, the result of the contribution ratio among gasification energy, energy from other heat sources, and energy from external source. For the cases after gasification at S/C of 0.2, there was no external energy required; the energy from heat sources was much more than the energy required at heat sinks. So with the S/C ratio increasing in SR, more energy was required at heat sinks, and thus more energy could be utilized from heat sources, and thus less energy was wasted consequently. For the cases after gasification at S/C of 0.5, the energy required at heat sinks could not be satisfied within the system for all the cases in SR, and when an external energy was required, the energy from the heat sources within the system was utilized to the maximum point and the wasted energy was the smallest at that point.

5.3.4 Detailed results and grand composite curve

Table 30 and Table 31 list the detailed heat integration analysis for coal conversion system. See Table 51–64 in Appendix D for heat integration analysis on other conversion conditions. See section 5.3.2 for the definition of numbers for heat sources/sinks.

Table 30 Heat integration for coal conversion through S/C=0.2 in gasification and S/C=1 in SR

S/C=0.2 in gasification; S/C = 1 in SR													
Subunit	Streams and Temperature								Deficit (kJ)	Accumulated (kJ)		Heat Flows (kJ)	
	Hot streams				Cold streams					Input	Output	Input	Output
	1	2	Ga	T °C	3	4	5						
				1220									
1				870	850				-6305	0	6305	0	6305
2				850	830				2228	6305	4077	6305	4077
3				178	163				-15975	4077	20052	4077	20052
4				100	90				10463	20052	9589	20052	9589
5				35	25				-10736	9589	20325	9589	20325
				25					-298	20325	20623	20325	20623

Table 31 Heat integration for coal conversion through S/C=0.5 in gasification and S/C=2 in SR

S/C=0.5 in gasification; S/C = 2 in SR													
Subunit	Streams and Temperature								Deficit (kJ)	Accumulated (kJ)		Heat Flows (kJ)	
	Hot streams				Cold streams					Input	Output	Input	Output
	1	2	T /°C		3	Ga	4	5					
			1220										
1			870	850					-6283	0	6283	759	7043
2			850	830					5148	6283	1135	7043	1895
3			178	163					-11742	1135	12877	1895	13636
4			100	90					13636	12877	-759	13636	0
5			35	25					-12697	-759	11937	0	12697
			25						-347	11937	12284	12697	13044

The following figures, Figure 15 and Figure 16, are the grand composite curve for the heat integration shown in Table 41 and Table 54, with temperature adjusted to those for the heat sources. They show schematically the temperatures at which external energy is required or energy is wasted from the system. The shaded area is where part of the energy required by the heat sinks of the system could be satisfied from the energy of heat sources. For the case of $S/C = 0.2$ in gasification followed by $S/C = 1$ in SR, which is shown in Figure 15, there was no external energy input required and the total energy wasted was 20623 kJ at three temperature levels. Besides the inevitable energy loss at temperature lower than 100°C, there was also energy wasted as a result of energy excess at temperatures higher than 1000°C and around 600°C to 800°C, which was why when the S/C ratio increased in SR, the energy from heat sources could have satisfied the needs.

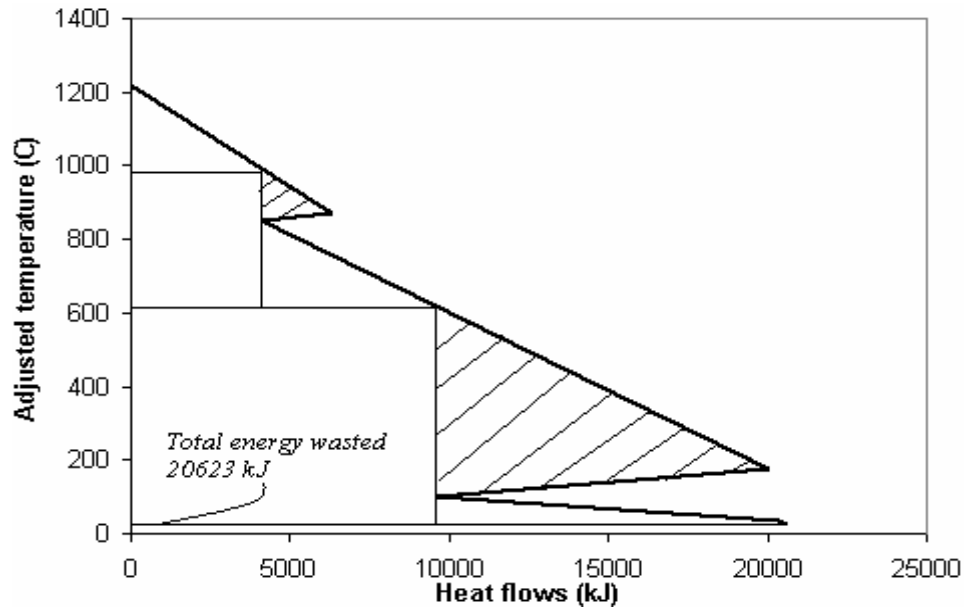


Figure 15 Grand composite curve for heat integration in Table 31 for coal conversion

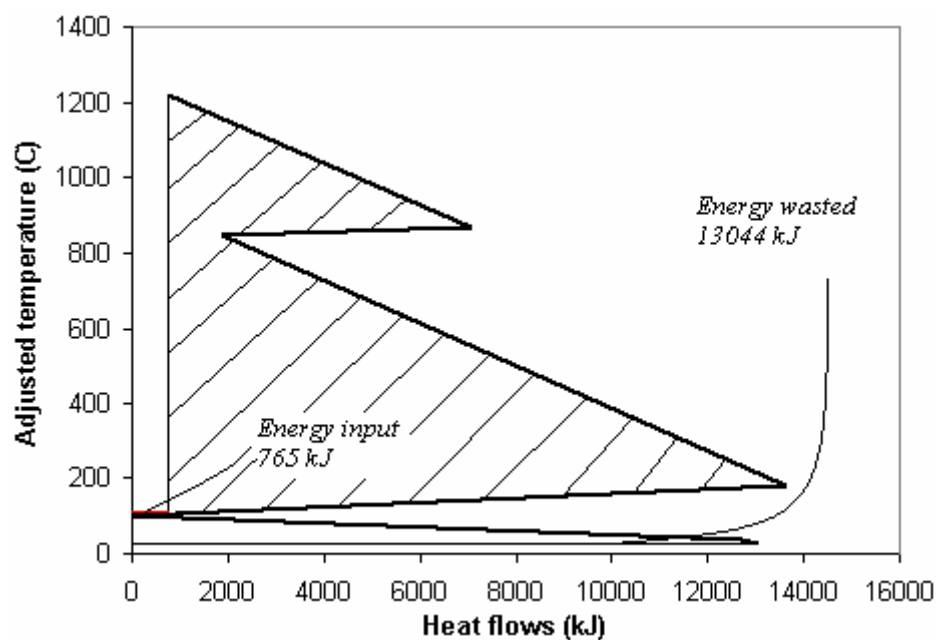


Figure 16 Grand composite curve for heat integration in Table 31 for coal conversion

Similarly, we used stage-wise constant heat capacities data to replace the overall constant heat capacity in Pinch Analysis in the calculation. The specific heat capacities of the streams at different mixture ratios as a result of different amounts of steam input in gasification and in steam reforming were calculated. The results are summarized in Table 32 - 35.

Table 32 Specific heat capacities for heat sources/sinks in coal conversion with through S/C=0.2 in gasification

Coal (kJ/kg/C)			1.32							
S/C = 0.2 in gasification										
	Temperature (°C)		1050	850	680	500	330	140	70	30
Products stream after SR (J/mol/C)	S/C=1	All			34.4	33.4	32.4	31.3		
		No water							30.3	30.0
	S/C=2	All			36.0	34.7	33.6	32.3		
		No water							31.1	30.7
	S/C=3	All			36.4	35.2	34.0	32.7		
		No water							31.5	31.1
	S/C=4	All			36.6	35.3	34.2	32.9		
		No water							31.9	31.3
Products stream after comb. (J/mol/C)	S/C=1	All	43.0	40.9	39.2	37.4	35.7	33.7		
		No water							33.1	32.4
	S/C=2	All	45.0	42.6	40.6	38.4	36.4	34.1		
		No water							33.6	32.8
	S/C=3	All	46.6	43.9	41.7	39.2	37.0	34.4		
		No water							34.0	33.1
	S/C=4	All	48.0	45.1	45.1	40.0	37.5	34.7		
		No water							34.3	33.3
Water (J/mol/C)				34.4	34.1	33.7	33.4	33.4/ 75.6	75.6	

Table 33 Specific heat capacities for heat sources/sinks in coal conversion with through S/C=0.3 in gasification

S/C = 0.3 in gasification										
	Temperature (°C)		1050	850	680	500	330	140	70	30
Products stream after SR (J/mol/C)	S/C=1	All			33.8	32.8	32.0	31.0		
		No water							30.1	29.8
	S/C=2	All			35.4	34.3	33.2	32.0		
		No water							30.8	30.4
	S/C=3	All			36.0	34.8	33.7	32.5		
		No water							31.3	30.8
	S/C=4	All			36.2	35.0	34.0	32.8		
		No water							31.6	31.1
Products stream after comb. (J/mol/C)	S/C=1	All	42.4	40.5	38.8	37.1	35.4	33.6		
		No water							32.9	32.2
	S/C=2	All	44.2	42.0	42.0	38.0	36.1	34.0		
		No water							33.4	33.4
	S/C=3	All	45.7	43.2	41.0	38.8	36.6	34.3		
		No water							33.8	32.9
	S/C=4	All	46.9	44.2	41.9	39.4	37.1	34.5		
		No water							34.0	33.1

Table 34 Specific heat capacities for heat sources/sinks in coal conversion with through S/C=0.4 in gasification

S/C = 0.4 in gasification										
	Temperature (°C)		1050	850	680	500	330	140	70	30
Products stream after SR (J/mol/C)	S/C=1	All			33.2	32.4	31.6	30.8		
		No water							30.0	29.7
	S/C=2	All			34.8	33.8	32.9	31.8		
		No water							30.5	30.2
	S/C=3	All			35.5	34.5	33.4	32.3		
		No water							31.0	30.6
	S/C=4	All			35.8	34.7	33.7	32.6		
		No water							31.3	30.9
Products stream after comb. (J/mol/C)	S/C=1	All	41.9	40.0	38.5	36.8	35.2	33.5		
		No water							32.8	32.1
	S/C=2	All	43.6	41.4	39.6	37.7	35.9	33.8		
		No water							33.3	32.5
	S/C=3	All	44.9	42.5	40.5	38.4	36.4	34.1		
		No water							33.6	32.8
	S/C=4	All	46.0	43.4	41.3	38.9	36.8	34.3		
		No water							33.8	33.0

Table 35 Specific heat capacities for heat sources/sinks in coal conversion with through S/C=0.5 in gasification

S/C = 0.5 in gasification										
	Temperature (°C)		1050	850	680	500	330	140	70	30
Products stream after SR (J/mol/C)	S/C=1	All			32.8	32.0	31.4	30.6		
		No water							29.7	29.5
	S/C=2	All			34.4	33.4	32.6	31.6		
		No water							30.3	30.1
	S/C=3	All			35.1	34.1	33.2	32.1		
		No water							30.8	30.4
	S/C=4	All			35.5	34.4	33.5	32.4		
		No water							31.1	30.7
Products stream after combustion (J/mol/C)	S/C=1	All	41.4	39.6	38.1	36.6	35.1	33.4		
		No water							32.6	31.9
	S/C=2	All	43.0	41.0	39.2	37.4	35.7	33.7		
		No water							33.1	32.4
	S/C=3	All	44.2	42.0	40.0	38.0	36.1	34.0		
		No water							33.4	32.6
	S/C=4	All	45.2	42.8	40.7	38.5	36.5	34.2		
		No water							33.6	32.8

5.4 Summary of Coal Conversion Process

In summary, the amount of mass and energy involved in the coal conversion process, especially the amount of hydrogen produced and total energy requirement, are listed in Table 36.

Table 36 Summary of coal conversion

Item	S/C = 0.2 in Gasification				S/C = 0.3 in Gasification				S/C = 0.4 in Gasification				S/C = 0.5 in Gasification			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
S/C in SR																
H ₂ output (mol)	54.8	65.0	70.9	74.9	60.6	71.4	77.4	81.5	66.4	77.8	84.0	88.3	72.2	84.2	90.7	95.0
H ₂ O input (mol)	278.3	299.5	338.0	385.2	298.4	319.4	357.4	404.3	318.0	338.7	376.4	422.8	337.1	357.7	395.1	441.5
H ₂ O output (mol)	251.9	262.9	295.5	338.7	266.2	276.4	308.4	351.2	279.9	289.4	320.8	362.9	293.4	301.9	332.8	374.9
Net Usage of water (mol)	26.4	36.6	42.5	46.5	32.2	43.0	49.0	53.2	38.0	49.4	55.6	59.9	45.8	55.8	62.3	66.6
O ₂ input (mol)	51.8	46.7	43.7	41.7	48.9	43.5	40.5	38.4	46.0	40.3	37.2	35.0	43.1	37.1	33.8	31.7
CO ₂ output (mol)	68.1	68.1	68.1	68.1	68.1	68.1	68.1	68.1	68.1	68.1	68.1	68.1	68.1	68.1	68.1	68.1
Total Energy Input (kJ)	0	0	0	0	0	0	0	763	0	0	778	3372	0	759	3378	5984
Total Energy Waste (kJ)	20623	18411	17211	16395	18730	16382	16922	15032	16848	14338	13794	15516	14984	13044	14290	16009

* The reason that no higher S/C ratio in gasification was considered is, at higher ratio, oxygen is not needed in gasify the coal, where as we assume that oxygen input is positive so that with the combustion reactions, the coal could be essentially gasified completely.

CHAPTER 6

COMPARISON OF HYDROGEN PRODUCTION FROM BIOMASS AND FROM COAL

6.1 Processing Energy

The energy required for mining and processing of coal was calculated through the inputs of different types of fuel to produce 1000 lb of anthracite coal based on the data from NREL site. The fuels needed are: 0.38lb coal, 0.44gal distillate oil, 9.61kwh electricity, 0.064gal gasoline, 3.72scf natural gas, and 0.16gal residual oil (NREL). After multiplying these amounts with the heating values of the corresponding fuels except that the electricity was multiplied by an electricity-coal factor, we obtained the total energy for mining and processing of the 1000lb anthracite coal to be 192651Btu. If all this energy could be provided by the combustion of coal, 20.8lb coal would be needed, which is equivalent to say that 0.0208kg coal is consumed as energy when 1kg coal is produced.

Biomass for pyrolysis is normally waste biomass such as sawdust, barks, wasted wood chips, etc. We assumed that the waste biomass is readily available at wood-manufacturing factories, etc. Therefore, there is no processing energy involved in getting the biomass. It only needs to be shipped to where the pyrolysis system is. Since both of the biomass and coal systems have the transportation issue and energy for this depends on the specific location and distances, we did not consider this aspect in the current study. (Similarly, we did not consider the energy for PSA in the conversion process since both

systems have this and we expect the energy would be close, thus would not change the picture much.)

6.2 Hydrogen Production Efficiencies from Biomass and from Coal

From the calculation in Chapter 4, we obtained the hydrogen production amount and the total energy requirement after heat integration for each combination of the pyrolysis temperature from 450°C to 550°C and S/C ratio from 1 to 4 in steam reforming for biomass conversion. If all the external energy input was provided by the combustion of the woody biomass itself, we could see the hydrogen production efficiency from biomass under different reaction conditions. The heating value of woody biomass is 17000000Btu/ton (NREL), through which we changed the energy requirements to biomass-equivalent base as shown in Table 37.

We can see that although the amount of hydrogen produced always increased with increasing S/C ratio in steam reforming, the hydrogen production efficiency with respect to biomass input has its maximum at the S/C =3 in SR for all the three reaction temperatures in pyrolysis. The highest efficiency among all the cases is biomass conversion with pyrolysis at 550°C followed by steam reforming with S/C =3, that is, 44 mol H₂/ kg biomass.

Table 37 Hydrogen production efficiency from biomass

S/C in SR	S/C = 1	S/C = 2	S/C = 3	S/C=4
Pyrolysis at 450°C				
H ₂ output (mol)	35.2	43.5	47.3	50.0
Total energy input (kJ)	113	1905	3263	4588
Total energy input as biomass (kg)	0.006	0.096	0.165	0.232
Total biomass input (kg)	1.006	1.096	1.165	1.232
Hydrogen production per kg of biomass (mol/kg)	35.0	39.7	40.6	40.4
Pyrolysis at 500°C				
H ₂ output (mol)	37.7	46.7	50.7	53.4
Total energy input (kJ)	0	1912	3373	4796
Total energy input as biomass (kg)	0	0.097	0.171	0.243
Total biomass input (kg)	1.000	1.097	1.171	1.243
Hydrogen production per kg of biomass (mol/kg)	37.7	42.5	43.3	42.9
Pyrolysis at 550°C				
H ₂ output (mol)	38.7	47.5	51.6	54.2
Total energy input (kJ)	0	1902	3402	4870
Total energy input as biomass (kg)	0.000	0.096	0.172	0.247
Total biomass input (kg)	1.000	1.096	1.172	1.247
Hydrogen production per kg of biomass (mol/kg)	38.7	43.3	44.0	43.5

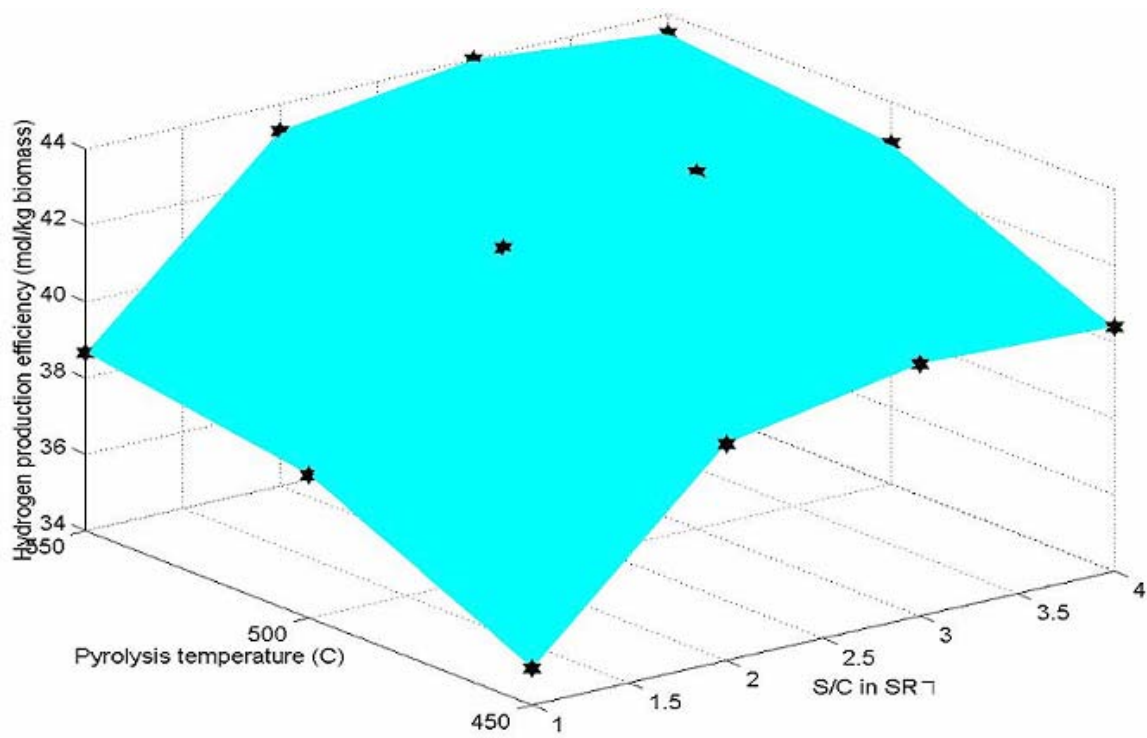


Figure 17 Hydrogen production efficiencies from biomass under different conversion conditions

Note that we have used the average enthalpy, 1.58MJ/kg, for pyrolysis while the range is from 1.18MJ/kg to 1.97MJ/kg. Conducting calculations using the lowest and highest values on the optimal case for biomass conversion, the range for hydrogen production efficiency then lies in 43.3 – 44.8 mol H₂/kg biomass. This is not a wide range since the energy input at pyrolysis was not a significant part of all the energy required. We selected this range as the optimal case of biomass conversion to be compared with the coal conversion. The whole view of hydrogen production efficiency with different pyrolysis temperature and different S/C in SR is illustrated in Figure 17.

From the calculation in Chapter 5, we obtained the hydrogen production amount and the total energy requirement after heat integration for each combination of the S/C ratio from 0.2 to 0.5 and S/C ratio from 1 to 4 in steam reforming for coal conversion. Similarly, we assumed that all the required external energy input in coal conversion cases were provided by coal combustion itself. So the total coal input and hydrogen production efficiency with respect to coal input were calculated in the same manner. The results are listed in Table 38.

We can see that in coal conversion, again, the amount of hydrogen produced always increased with increasing S/C ratio in steam reforming. What is different from the biomass conversion is that the point of maximum hydrogen production with respect to coal input varied with different steam input in gasification. As the S/C ratio in gasification increases, the point of maximum hydrogen production shifts to lower S/C ratios in the steam reforming process. The maximum hydrogen production efficiency points are in bold in Table 52. We selected the highest value of hydrogen production per unit coal input, 80 mol H₂/ kg coal, as the optimal case of coal conversion to be compared with the biomass conversion. This point occurs at S/C = 0.5 in gasification followed by S/C = 2 in steam reforming. The whole view of hydrogen production efficiency with different S/C ratios in gasification and different S/C ratios in SR of coal conversion system is shown in Figure 18.

Table 38 Hydrogen production efficiency from coal

S/C in SR	S/C = 1	S/C = 2	S/C = 3	S/C=4
S/C=0.2 in gasification				
H ₂ output (mol)	54.8	65.0	70.9	74.9
Total conversion energy input (kJ)	0	0	0	0
Total conversion energy input as coal (kg)	0	0	0	0
Total coal input (kg)	1.021	1.021	1.021	1.021
Hydrogen production per kg of coal (mol/kg)	53.7	63.7	69.5	73.4
S/C=0.3 in gasification				
H ₂ output (mol)	60.6	71.4	77.4	81.5
Total conversion energy input (kJ)	0	0	0	763
Total conversion energy input as coal (kg)	0	0	0	0.036
Total coal input (kg)	1.021	1.021	1.021	1.057
Hydrogen production per kg of coal (mol/kg)	59.4	69.9	75.9	77.1
S/C=0.4 in gasification				
H ₂ output (mol)	66.4	77.8	84.0	88.3
Total conversion energy input (kJ)	0	0	778	3372
Total conversion energy input as coal (kg)	0	0	0.036	0.157
Total coal input (kg)	1.021	1.021	1.058	1.181
Hydrogen production per kg of coal (mol/kg)	65.1	76.2	79.4	74.8
S/C=0.5 in gasification				
H ₂ output (mol)	72.2	84.2	90.7	95.0
Total conversion energy input (kJ)	0	759	3378	5984
Total conversion energy input as coal (kg)	0	0.035	0.157	0.278
Total coal input (kg)	1.021	1.057	1.181	1.305
Hydrogen production per kg of coal (mol/kg)	70.7	79.7	76.8	72.8

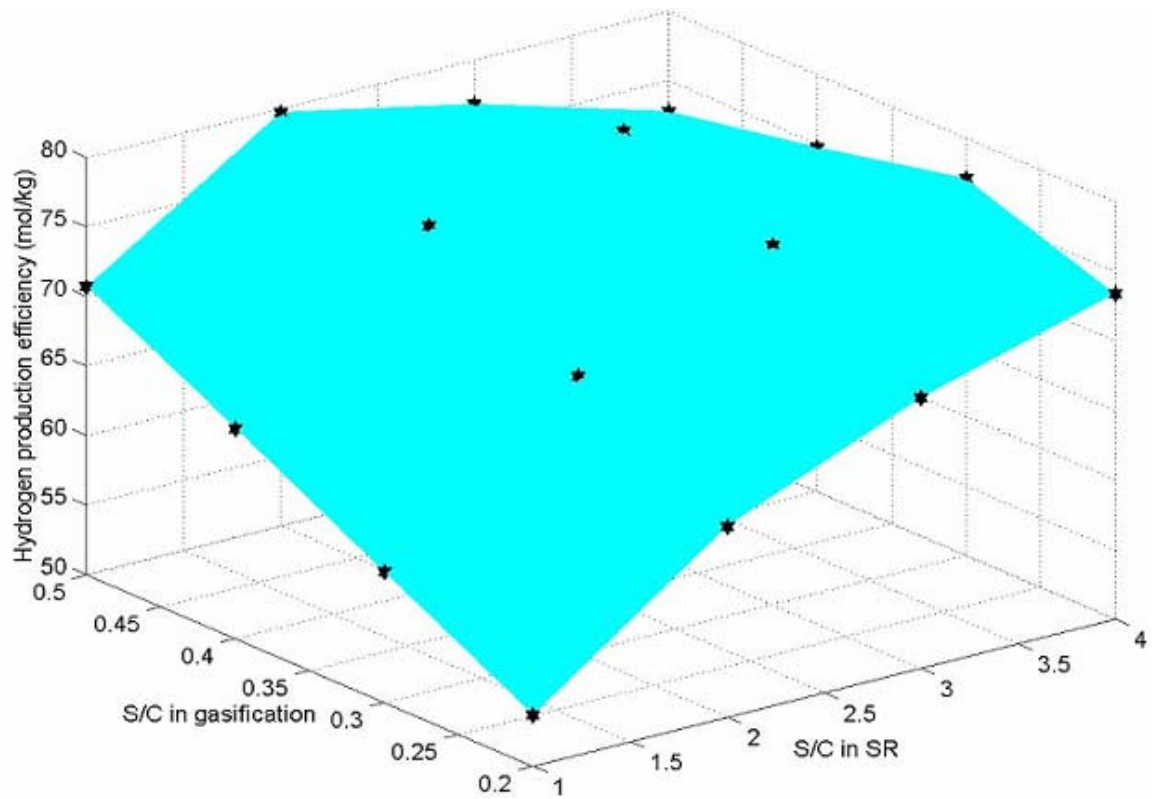


Figure 18 Hydrogen production efficiencies from coal under different conversion conditions

6.3 Comparison of Conversion Processes

Table 39 lists the overall mass balance and energy requirement for the optimal conversion processes from biomass and from biomass with respect to hydrogen production, respectively.

Table 39 Comparison of optimal conversion processes form biomass and from coal

System	Optimal case studied	Conversion equation	Energy wasted
Biomass conversion	Pyrolysis at 550°C and S/C=3 in SR	1) 1kg Dry biomass + 0.3kg Steam + 0.6kg O ₂ → 1.7kg CO ₂ + 0.1kg H ₂ + 0.1 kg Char 2) 0.17kg biomass + 0.34kg O ₂ → 0.19kg H ₂ O + 0.33kg CO ₂ + 3402kJ	7882 kJ (25 – 100°C)
Coal conversion	S/C =0.5 in gasification and S/C=2 in SR	1) 1kg Coal + 1.0kg Steam + 1.2 kg O ₂ → 3.0kg CO ₂ + 0.2kg H ₂ 2) 0.06 kg coal + 0.17kg O ₂ → 0.06kg H ₂ O + 0.17kg CO ₂ + 1226kJ	13044kJ (25 – 100°C)

For the optimal conversion cases of hydrogen production from biomass and coal respectively, the hydrogen production efficiency of coal is about twice that of biomass. However, on the other hand, the oxygen usage in coal conversion is about 1.5 times that of the biomass conversion; the net water usage is about 8.7 times that of the biomass conversion; carbon dioxide from coal conversion is about 1.6 times that from biomass conversion; the energy waste from coal conversion is about 1.7 times that from the biomass conversion. Besides, in biomass conversion, there was 110g char produced, which could be used to make slow release fertilizer. However, the hydrogen production per unit mass of coal is about 2 times of that per unit mass of biomass.

6.4 Sunlight to Hydrogen

For both the biomass and coal conversion systems, it is the solar energy carried by the current biomass or the coal (ancient biomass) that has been used as the original energy source. So it is interesting to calculate how much solar energy is involved in the two conversion systems.

Jeffrey Dukes (Dukes, 2003) stated in his study that 15.6% of the carbon in plant matter was preserved in peat, and that 69% of the carbon in peat was preserved when it was converted to anthracite coal. So to make 1kg C as in anthracite coal, 9.293kg C as in plant matter was required. We assumed a high carbon ratio in ancient coal-forming biomass, 65%, and a similar net primary productivity of the biomass as today's biomass forming forests. Using the same data of sunlight amount that reaches the surface of the earth, $4.3 \text{ kWh m}^{-2} \text{ day}^{-1}$ on average annually (DOE, Sunlight) for both systems, the hydrogen production efficiency of the coal conversion system in terms of solar energy was then calculated to be $1.35 \times 10^{-3} \text{ mol H}_2 / \text{MJ sunlight}$.

The net primary productivity of pine was predicted to be $11.2 \text{ t ha}^{-1} \text{ yr}^{-1}$ (McNulty, et. al., 1996) on average. With the same amount of sunshine, the hydrogen production efficiency of the biomass conversion system in terms of solar energy was calculated to be $8.72 \times 10^{-3} \text{ mol H}_2 / \text{MJ solar energy}$. This is 6.46 times the efficiency of hydrogen production from coal regarding sunlight usage. The range for hydrogen production based on sunlight input was calculated to be $8.56 \times 10^{-3} \sim 8.86 \times 10^{-3} \text{ mol H}_2 / \text{MJ solar energy}$

corresponding to the range of pyrolysis energy, which was 6.32 to 6.54 times the efficiency of hydrogen production from coal in regards to sunlight usage.

Figure 19 shows the overall processes from ancient sunlight and current sunlight to hydrogen, respectively. Obviously, much of the energy is lost during the process of coal formation; only less than one tenth of the energy stored in ancient biomass is preserved.

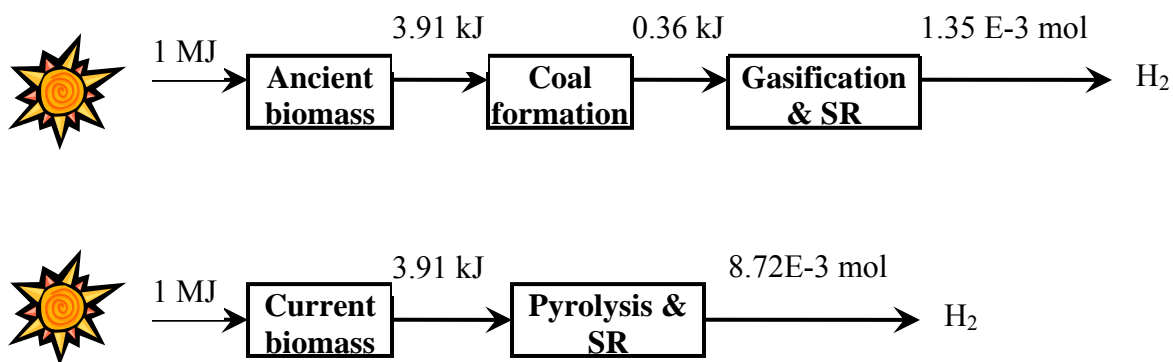


Figure 19 Sunlight to hydrogen through current biomass and coal

CHAPTER 7

CONCLUSIONS

In this study, we examined two complete conversion processes to produce hydrogen from current biomass, pine, and ancient biomass, coal, using pyrolysis and gasification, respectively, both followed by steam reforming. The results showed that the coal conversion system had higher hydrogen production per unit mass of coal compared to that of biomass conversion per unit mass of biomass, if only the current conversion processes were looked at. However, if the ultimate energy source, sunlight were considered, about 6.46-fold more sunlight would be required for the coal to hydrogen than that for biomass to hydrogen. The efficiency of immediate usage of the sunlight in biomass rather than waiting for it to percolate through forming peat and coal easily outweighs the advantage of coal for hydrogen production. Furthermore, coal represents the sequestration of carbon, to which the pyrolysis of current biomass can add through its char product. The long term value of carbon sequestration is yet to be quantified, but qualitatively, this favors the option of leaving the coal in the ground and converting current sunlight to hydrogen.

Form literature review, we know that 26.0 million tonnes of dry bark and 74.5 million tonnes of dry wood residues were generated at primary lumber processing mills in the United States in 1991 (McKeever, 1995), which, using the lower heating value of hydrogen, could provide a total amount of $1\text{E}12$ MJ energy per year. From IEA's statistics, the total primary energy supply in the United States in the year 2000 was

2299.67 million tons oil-equivalent (IEA), which is equal to $9\text{E}13$ MJ/yr. So the hydrogen energy from wasted forestry biomass from lumber processing mills of the U.S. is only about 1% of the overall U.S. energy requirement, not a significant fraction. However, other waste biomass, such as municipal wastes, agricultural wastes, and industrial wastes, and forestry wastes from other processing factories, can also be used as sources for hydrogen potential, although the process performance and efficiencies will need to be studied. Besides, decisions on forestry management have significant impact on the amount of waste biomass that could be produced, which could be integrated into energy development strategy and be beneficial for hydrogen production from biomass.

To get a global view, let's look at the biomass production and energy requirement of the world. We know that the average global net biomass carbon production was estimated to be 77.49 Gt annually (Whittaker, et. al., 1975). Hypothetically, if all of this biomass is used to produce hydrogen, altogether $1.4\text{E}13$ kg H_2 /yr could be produced based on the highest hydrogen production efficiency from biomass that we studied. Using the lower heating value of hydrogen, the total energy from this much hydrogen is $1.5\text{E}15$ MJ/yr. On the other hand, the total worldwide primary in the year 2000 was 10109.59 million tons oil-equivalent (IEA), which is equal to $4\text{E}14$ MJ/yr. So the total hydrogen energy from global biomass sources is 3.8 times the energy required globally, which indicates the biomass as an energy source with great potential. Although it is unreasonable to have all of the nature's biomass production and use it for hydrogen, but this demonstrates that a reasonable solution could provide a significant portion of world energy through biomass.

CHAPTER 8

FUTURE WORK

Our future work will be the following extensions from current work:

1. To refine elements of this analysis. The PSA energy requirements have not been factored in the analysis, nor the energy requirements of the fertilizers that promote the growth of the current biomass. These elements should be included for a more complete analysis.
2. To study other reaction technologies for converting current biomass and ancient biomass to hydrogen and to evaluate their conversion efficiencies. In particular the current route of natural gas to hydrogen will be examined.
3. To couple the production of hydrogen to the production of a fertilizer, based on the char and ammonia, to understand the overall energy requirements of this system.
4. To include the whole chain of the system of biomass from growth to harvest.
5. To study other ways to make hydrogen from current sunlight, such as photovoltaics.
6. To work more on the bio-oil composition estimation method to provide sound estimation theory or method.

APPENDIX A: PROGRAMMING CODES

A.1 MATLAB code for bio-oil composition estimation

A.1.1 Major code

.....

```
% define the starting point for the calculation
```

```
X = ones(1,89);  
W0 = X'/100;
```

```
% components' formula
```

```
For = [ ...  
1 2 2; 1 2 1; 1 2 0.666666667; 1 2 1.5; 1 2 0.5; ...  
1 2 0.4; 1 1.6 0.6; 1 2 0.333333333; 1 0.857142857 0.285714286; 1 2 0.285714; ...  
1 4 1; 1 3 0.5; 1 3 1; 1 2 0.333333333; 1 2 0.25; ...  
1 1.6 0.4; 1 1.33 0.33; 1 1.714286 0.14286; 1 1.71 0.142857143; 1 1.5 0.125; ...  
1 1.75 0.125; 1 2 1; 1 2 0.5; 1 1.333333333 0.333333333; 1 1.6 0.2; ...  
1 2 0.2; 1 1 1; 1 1 0.166666667; 1 1.142857 0.142857; 1 1.142857 0.142857; ...  
1 1.142857 0.142857143; 1 1.25 0.125; 1 1.25 0.125; 1 1.25 0.125; 1 1.25 0.125; ...  
1 1.25 0.125; 1 1.33333 0.11111; 1 1 0.333333; 1 1 0.33333; 1 1 0.333333; ...  
1 1.142857 0.428571; 1 1 0.5; 1 2 1; 1 1.5 0.5; 1 1.6 0.4; ...  
1 1.2 0.4; 1 1.666666667 0.833333333; 1 2 1; 1 2 1; 1 2 1; ...  
1 2 1; 1 1.6666667 0.8333; 1 1.66667 0.83333; 1 1.142857 0.2857; 1 1.25 0.25; ...  
1 1.3333333 0.222222; 1 1.2 0.2; 1 1.2 0.2; 1 1.4 0.2; 1 1.111111 0.3333333; ...  
1 1.2 0.3; 1 1.25 0.375; 1 1.33333 0.3333333; 1 1.4 0.3; 1 1.454545 0.2727; ...  
1 1.111111 0.44444; 1 1.272727273 0.272727273; 1 1.2 0.4; 1 1 0.25; 1 1.2 0.2; ...  
1 1 0.5; 1 0.8 0.4; 1 1.2 0.4; 1 1.2 0.4; 1 0.8 0.6; ...  
1 1 0.333333; 1 1 0.5; 1 2 1; 1 2 0.66667; 1 2.3333333 0.333333333; ...  
1 1.6 0.6; 1 1.333333 0.333333; 1 1.3333333 0.3333333; 1 1.6 0.6; 1 1 0.5; ...  
1 1.3333333 0.2222222; 1 1 0.375; 1 1.714285714 0; 1 1.2857 0.428571429];
```

```
% components' molecular weights
```

```
elem = [12 1 16]; % elem: 1*3  
Mwcomp = For * elem'; % Mwcomp: 89*1
```

```
% bio-oil composition formula & molecular weight
```

```
Bio = [1 1.43 0.332]; % Bio: 1*3 without water (from reference)
```

```

Mwbio = Bio * elem';          % Mwbio: 1*1

For1 = For(:,1);              % For1: 89*1
For2 = For(:,2);              % For2: 89*1
For3 = For(:,3);              % For3: 89*1

Aeq1 = For1./Mwcomp/100;      % A1: 89*1
Aeq2 = For2./Mwcomp/100;      % A2: 89*1
Aeq3 = For3./Mwcomp/100;      % A3: 89*1

beq = Bio'/Mwbio;             % beq: 3*1
Aeq = [Aeq1 Aeq2 Aeq3]';      % Aeq: 3*89

Lb = [0.375 0.625 0.125 0.125 0.125 0.125 0.125 0.125 0.25 0.375 ...
      0.5 0.75 0.875 3.5 0.375 0.25 0.125 0.25 0.375 0.125 ...
      0.25 0.125 0.125 0.75 0.125 0.625 1.125 0.125 0.125 0.125 ...
      0.125 0.125 0.125 0.25 0.125 0.125 0.375 0.125 0.125 0.125 ...
      0.75 0.75 0.125 0.125 0.25 0.125 0.5 0.5 0.875 0.125 ...
      0.125 0.75 3.875 0.125 0.125 0.125 0.125 0.125 0.125 1 ...
      1 0.875 0.125 0.25 0.125 0.125 0.125 0.125 0.125 0.125 ...
      0.125 0.125 0.125 0.125 0.5 0.125 0.375 1.125 0.875 0.125 ...
      0.125 0.125 0.125 0.125 0.25 0.125 0.125 0.875 31.25]'; % nonwater base

Lbrelax = Lb .* 0.5;          % Lbrelax: 89*1

Ub = [12.13333333 16 2.4 1.2 0.666666667 1.066666667 0.533333333 0.4 0.4 0.4 ...
      3.2 1.866666667 2.66667 3.733333 1.2 0.533333 2.533333 0.4 0.4 0.666667 ...
      0.533333 4.4 11.333333 1.2 0.666667 0.66667 6.13333 5.0666667 0.8 0.53333 ...
      0.666667 0.666667 0.4 0.5333333 0.533333 1.733333 0.4 0.93333 0.4 2.533333 ...
      0.8 0.8 1.2 1.2 0.266667 1.6 1.8666667 1.733333 3.866667 1.866667 ...
      0.133333 4.26667 4.1333 1.46667 2.533333 0.8 3.06667 9.6 0.53333 1.066667 ...
      1.066666667 6.4 0.4 0.266666667 2 2 0.4 0.4 0.4 0.26667 ...
      1.46667 1.46667 0.13333 6.93333 0.53333 0.8 2.9333 17.3333 9.86667 0.26667 ...
      1.066667 0.6666667 2.53333 1.06667 0.53333 0.533333 1.4666667 0.933333 40]';

Ubrelax = Ub .* 1.1;          % Ubrelax: 89*1

[W, fval] = fmincon(@sumofvar, W0, [], [], Aeq, beq, Lbrelax, Ubrelax);

% look for the bio-oil composition that can produce minimal amount of hydrogen

[WL, fvalL] = fmincon(@sumofcoeffH2lb, W0, [], [], Aeq, beq, Lbrelax, Ubrelax);

% look for the bio-oil composition that would produce the maximum amount of hydrogen

[WU, fvalU] = fmincon(@sumofcoeffH2ub, W0, [], [], Aeq, beq, Lbrelax, Ubrelax);

% calculate the sum of variance to the target composition of the Lb and Ub composition

```



```
Alpha2 = [8 6 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 ...
          0 8 0 0 0 0 10 0 0 0 0 0 0 0 0 0 0 0 0 0 ...
          0 0 0 0 0 0 4 0 0 0 0 10 0 0 0 0 0 0 0 0 ...
          0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 2 5 0 ...
          0 0 0 0 0 0 0 0 1]';          % Alpha2: 89*1
```

```
Wt1 = [4.83, 5.48, 0, 0, 0, 0, 0, 0, 0, 0, 0, ...
       0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, ...
       0, 3.92, 0, 0, 0, 0, 0, 2.48, 0, 0, 0, ...
       0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, ...
       0, 0, 0, 0, 0, 0, 8.22, 0, 0, 0, 0, ...
       0, 2.48, 0, 0, 0, 0, 0, 0, 0, 0, 0, ...
       0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, ...
       0, 0, 0, 0, 0, 0, 0, 13.32, 6.27, 0, ...
       0, 0, 0, 0, 0, 0, 0, 0, 0, 32.51]';
```

```
fval4L = sum(Alpha2.^2 .* (WL - Wt1).^2);
```

```
fval4U = sum(Alpha2.^2 .* (WU - Wt1).^2);
```

```
% calculate the H2 production ability of W
```

```
CoeffN = [0 1 1.333333333 0.5 1.5 1.6 1.2 1.666666667 1.142857143 1.714285714 ...
          2 2 1.5 1.666666667 1.75 1.4 1.333333333 1.714285714 1.714285714 1.625 ...
          1.75 1 1.5 1.333333333 1.6 1.8 0.5 1.333333333 1.428571429 1.428571429 ...
          1.428571429 1.5 1.5 1.5 1.5 1.5 1.55556 1.166667 1.16667 1.16667 ...
          1.142857143 1 1 1.25 1.4 1.2 1 1 1 1 ...
          1 1 1 1.285714286 1.375 1.444444444 1.4 1.4 1.5 1.222222222 ...
          1.3 1.25 1.333333333 1.4 1.454545455 1.111111111 1.363636364 1.2 1.25 1.4 ...
          1 1 1.2 1.2 0.8 1.166666667 1 1 1.333333333 1.833333333 ...
          1.2 1.33333 1.33333 1.2 1 1.44444 1.125 1.857142857 1.214285714]';
```

```
fvalH2 = sum(CoeffN .* W);
```

```
.....
```

A.1.2 Related code for self-defined functions

```
.....
```

```
% define the objective function to find composition most similar to the target one
```

```
function f = sumofvar(W)
```

```
% define the target composition by wt%
```

```
Wt = [4.83, 5.48, 0, 0, 0, 0, 0, 0, 0, 0, 0, ...
```

```

0, 0, 0, 0, 0, 0, 0, 0, 0, 0, ...
0, 3.92, 0, 0, 0, 0, 2.48, 0, 0, 0, ...
0, 0, 0, 0, 0, 0, 0, 0, 0, 0, ...
0, 0, 0, 0, 0, 0, 8.22, 0, 0, 0, ...
0, 2.48, 0, 0, 0, 0, 0, 0, 0, 0, ...
0, 0, 0, 0, 0, 0, 0, 0, 0, 0, ...
0, 0, 0, 0, 0, 0, 0, 13.32, 6.27, 0, ...
0, 0, 0, 0, 0, 0, 0, 0, 32.51]';    % Wt: 89*1 normalized to nonwater base

% weight

Alpha2 = [8 6 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 ...
0 8 0 0 0 0 10 0 0 0 0 0 0 0 0 0 0 0 ...
0 0 0 0 0 0 4 0 0 0 0 10 0 0 0 0 0 0 ...
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 2 5 0 ...
0 0 0 0 0 0 0 0 1]';    % Alpha2: 89*1

% compute function value at W

f = sum(Alpha2.^2 .* (W - Wt).^2);

.....

.....

% define the objective to find the composition for lb of hydrogen production

function g = sumofcoeffH2lb(WL)

% coefficient matrix (y/2+x-z)

CoeffN = [0 1 1.333333333 0.5 1.5 1.6 1.2 1.666666667 1.142857143 1.714285714 ...
2 2 1.5 1.666666667 1.75 1.4 1.333333333 1.714285714 1.714285714 1.625 ...
1.75 1 1.5 1.33333 1.6 1.8 0.5 1.333333333 1.428571429 1.428571429 ...
1.428571429 1.5 1.5 1.5 1.5 1.5 1.5555556 1.1666667 1.1666667 1.1666667 ...
1.142857143 1 1 1.25 1.4 1.2 1 1 1 1 ...
1 1 1 1.285714 1.375 1.444444444 1.4 1.4 1.5 1.222222222 ...
1.3 1.25 1.333333 1.4 1.454545455 1.111111 1.363636364 1.2 1.25 1.4 ...
1 1 1.2 1.2 0.8 1.166666667 1 1 1.333333333 1.833333333 ...
1.2 1.333333333 1.333333 1.2 1 1.44444 1.125 1.857142857 1.214285714]';

% compute the function value at WL

g = sum(CoeffN .* WL);

.....

.....

```

```

% define the objective to find the composition for ub of hydrogen production

function h = sumofcoeffH2ub(WU)

% coefficient matrix (y/2+x-z)

CoeffN = [0 1 1.333333333 0.5 1.5 1.6 1.2 1.666666667 1.142857143 1.714285714 ...
          2 2 1.5 1.666666667 1.75 1.4 1.333333333 1.714285714 1.714285714 1.625 ...
          1.75 1 1.5 1.333333333 1.6 1.8 0.5 1.333333333 1.428571429 1.428571429 ...
          1.428571429 1.5 1.5 1.5 1.5 1.5 1.5555556 1.166666667 1.166666667 1.1666667 ...
          1.142857143 1 1 1.25 1.4 1.2 1 1 1 1 ...
          1 1 1 1.285714286 1.375 1.444444444 1.4 1.4 1.5 1.222222222 ...
          1.3 1.25 1.333333333 1.4 1.454545455 1.111111111 1.363636364 1.2 1.25 1.4 ...
          1 1 1.2 1.2 0.8 1.166666667 1 1 1.333333333 1.833333333 ...
          1.2 1.3333333 1.333333 1.2 1 1.444444 1.125 1.857142857 1.214285714]';

% compute the function value at WU

h = - sum(CoeffN .* WU);

.....

```

A.2 MATLAB code for gasification calculation

```

.....

function [ ] = equ(t)

global Cori
global Hori
global Oori
global K1
global K2
global K3
global St
global P

coal = 1;

Cori = coal * 0.8166 * 1000 / 12; % mol
Hori = coal * 0.0568 * 1000 / 1; % mol
Oori = coal * 0.0983 * 1000 / 16; % mol

for l = 1:6, % steam-to-carbon ratio

Steamln(l) = Cori * l / 10; % mol
St = Steamln(l);

```

for J = 1:4, % temperature

T(J) = 850 + 50 * (J - 1) + 273; % K
Pbar = 50; % bar
P = Pbar * 100/101.325; % atm

dH0 = [172 131 -75]; % kJ/mol % dH: 1*3
% dS = [-14.2 139.4 -74.9]; % J/mol/K % dS: 1*3

CpO2 = 25.48 + 1.520/100 * T(J) - 0.7155/100000 * T(J)^2 + 1.312/(10^9) * T(J)^3;
CpCO = 28.16 + 0.1675/100 * T(J) + 0.5372/100000 * T(J)^2 - 2.222/(10^9) * T(J)^3;
CpCO2 = 22.26 + 5.986/100 * T(J) - 3.501/100000 * T(J)^2 + 7.469/(10^9) * T(J)^3;
CpCH4 = 19.89 + 5.024/100 * T(J) + 1.269/100000 * T(J)^2 - 11.01/(10^9) * T(J)^3;
CpH2 = 29.11 - 0.1916/100 * T(J) + 0.4003/100000 * T(J)^2 - 0.8704/(10^9) * T(J)^3;
CpH2O = 32.24 + 0.1923/100 * T(J) + 1.055/100000 * T(J)^2 - 3.595/(10^9) * T(J)^3;

syms Tint;

R = 8.314; % J/mol/K

HO2 = double(int(25.48 + 1.520/100 * Tint - 0.7155/100000 * Tint^2 + 1.312/10^9 *
Tint^3, Tint, 298, T(J))); % J/mol
HCO = double(int(28.16 + 0.1675/100 * Tint + 0.5372/100000 * Tint^2 - 2.222/10^9 *
Tint^3, Tint, 298, T(J)));
HCO2 = double(int(22.26 + 5.986/100 * Tint - 3.501/100000 * Tint^2 + 7.469/10^9 *
Tint^3, Tint, 298, T(J)));
HCH4 = double(int(19.89 + 5.024/100 * Tint + 1.269/100000 * Tint^2 - 11.01/10^9 *
Tint^3, Tint, 298, T(J)));
Hh2 = double(int(29.11 - 0.1916/100 * Tint + 0.4003/100000 * Tint^2 - 0.8704/10^9 *
Tint^3, Tint, 298, T(J)));
Hh2o = double(int(32.24 + 0.1923/100 * Tint + 1.055/100000 * Tint^2 - 3.595/10^9 *
Tint^3, Tint, 298, T(J)));

H1 = dH0(1) + 2 * HCO/1000 - HCO2/1000; % kJ/mol
H2 = dH0(2) + HCO/1000 + Hh2/1000 - Hh2o/1000;
H3 = dH0(3) + HCH4/1000 - 2 * Hh2/1000;

syms Tin;

K1 = exp(double(int(H1*1000/R /Tin^2, Tin, 298, T(J)))) * 2.0919 * 10^(-21);
K2 = exp(double(int(H2*1000/R /Tin^2, Tin, 298, T(J)))) * 2.0832 * 10^(-16);
K3 = exp(double(int(H3*1000/R /Tin^2, Tin, 298, T(J)))) * 1.71 * 10^9;

% dG = dH - T(J) * dS / 1000; % kJ/mol % dG: 1*3

% K1 = exp(-dG(1) * 1000/R / T(J));
% K2 = exp(-dG(2) * 1000/R / T(J));
% K3 = exp(-dG(3) * 1000/R / T(J));

x0 = [42.07; 1.22; 24.76; 12.84; 0.076; 2.22; 80.96; 3.56; 34.95; 24.76; 4.79; 1];

```

options=optimset('MaxFunEvals', 50000, 'MaxIter', 50000, 'TolFun', 1e-4); %
[x, fval] = fsolve(@equations, x0)

H2Pro(I, J) = x(1) + 4*x(3) + x(4)

Ener(I, J) = x(8) * 172 + x(9) * 131 + x(10) * (-75) + x(11) * (-394) + x(12) * (-242)

OxyIn(I, J) = x(6)

end

end

% seven equations

function h = equations(x)

global Cori
global Hori
global Oori
global K1
global K2
global K3
global St
global P

h = [Cori - x(1) - x(2) - x(3); ...
     Hori + 2*St - 2 * x(5) - 4 * x(3) - 2 * x(4); ...
     Oori + St + 2 * x(6) - x(5) - x(1) - 2 * x(2); ...
     x(7) - x(1) - x(2) - x(3) - x(4) - x(5); ...
     K1 - (x(1) / x(7) * P)^2 / (x(2) / x(7) * P); ...
     K2 - x(4) / x(7) * P * x(1) / x(7) * P / (x(5) / x(7) * P); ...
     K3 - x(3) / x(7) * P / (x(4) / x(7) * P)^2; ...
     x(11) - x(8) - x(2); ...
     2 * x(8) + x(9) - x(1); ...
     x(10) - x(3); ...
     x(6) - x(11) - 1/2 * x(12) + 1/2 * Oori; ...
     x(9) - 2 * x(10) - x(12) - x(4) + 1/2 * Hori];

```

.....

A.3 gPROMS code for steam reforming calculation

A.3.1 SR of bio-oil (S/C=1)

.....

PARAMETER

K1, K2	as	real
SteamIn	as	real
COirr	as	real
H2irr	as	real
SteamRxn	as	real
P	as	real
WaterinGas	as	real

VARIABLE

CO	AS	AMOUNT
CO2, CH4	AS	AMOUNT
H2, H2O	AS	AMOUNT
Total	as	amount

EQUATION

1. $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$
 # 2. $\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}$

COirr = CO + CO2 + CH4;
 SteamIn - SteamRxn + WaterinGas + CH4 - CO2 = H2O;
 H2irr + CO2 - 3 * CH4 = H2;
 Total = CO + CO2 + CH4 + H2 + H2O;
 $K1 = \text{H}_2 * \text{CO}_2 / (\text{CO} * \text{H}_2\text{O});$
 $1/K2 = (\text{CH}_4/\text{Total} * P) * (\text{H}_2\text{O}/\text{Total} * P) / (\text{H}_2/\text{Total} * P)^3 / (\text{CO}/\text{Total} * P);$

.....

UNIT

S101 as steam_reform_bio

SET

S101.K1 := 0.532441904;
 S101.K2 := 40.29337;
 S101.P := 1.78;
 S101.SteamIn := 30.347126; # mol S/C = 1
 S101.SteamRxn := 23.35297;
 S101.COirr := 36.88534645;
 S101.H2irr := 49.92605101;
 S101.WaterinGas := 6.766;

SCHEDULE

CONTINUE FOR 10

.....

A.3.2 SR of coal-gas (S/C=0.2 in Gasification; S/C=1 in SR)

.....

PARAMETER

K1, K2	AS	REAL
SteamIn	as	real
COori	as	real
CO2ori	as	real
CH4ori	as	real
H2ori	as	real
H2Oori	as	real
P	as	real

VARIABLE

CO	AS	AMOUNT
CO2, CH4	AS	AMOUNT
H2, H2O	AS	AMOUNT
Total	as	amount

EQUATION

1. $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$
 # 2. $\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}$

$\text{COori} + \text{CO2ori} + \text{CH4ori} = \text{CO} + \text{CO}_2 + \text{CH}_4$;
 $\text{SteamIn} + \text{H2Oori} + 2 * \text{CH4ori} + \text{H2ori} = \text{H}_2\text{O} + \text{H}_2 + 2 * \text{CH}_4$;
 $\text{COori} + 2 * \text{CO2ori} + \text{H2Oori} + \text{SteamIn} = \text{CO} + 2 * \text{CO}_2 + \text{H}_2\text{O}$;
 $\text{Total} = \text{CO} + \text{CO}_2 + \text{CH}_4 + \text{H}_2 + \text{H}_2\text{O}$;
 $\text{K1} = \text{H}_2 * \text{CO}_2 / (\text{CO} * \text{H}_2\text{O})$;
 $1/\text{K2} = (\text{CH}_4/\text{Total} * \text{P}) * (\text{H}_2\text{O}/\text{Total} * \text{P}) / (\text{H}_2/\text{Total} * \text{P})^3 / (\text{CO}/\text{Total} * \text{P})$;

.....

UNIT

S101 as SR_coalgas

SET

S101.K1 := 0.532441904;
 S101.K2 := 40.29337;
 S101.P := 1.78;

```

S101.COori      := 50.3274;
S101.CO2ori     := 1.8135;
S101.CH4ori     := 15.9091;
S101.H2ori      := 10.1181;
S101.H2Oori     := 0.073709;
S101.SteamIn    := 67.9763;

```

SCHEDULE

CONTINUE FOR 10

.....

A.4 gPROMS code for combustion with air (S/C=1 in SR)

.....

PARAMETER

```

EquilCO        as      real
EquilCO2       as      real
EquilCH4       as      real
EquilH2        as      real
SteamIn        as      real  # Steam added in the reforming step

```

VARIABLE

```

O2, N2, Air    as      amount
CO2            as      amount
H2O            as      amount
Qcomb          as      energy
SteamAdd       as      amount
Hh2o, HCO2, HN2 as     energy
Hh2oadded      as      energy
TsteamIn       as      amount
HsteamL        as      energy
HsteamE        as      energy
HsteamV        as      energy
H4water        as      energy

```

EQUATION

Combustion

```

# 1. 2H2 + O2 --> 2H2O
# 2. 2CO + O2 --> 2CO2

```


3. CH₄ + 2O₂ --> CO₂ + 2H₂O

O₂ = EquilH₂ * 0.3 /2 + EquilCO /2 + EquilCH₄ *2;

N₂ = 4 * O₂;

Air = O₂ + N₂;

H₂O = EquilH₂ * 0.3 + EquilCH₄ * 2;

CO₂ = EquilCO + EquilCH₄ + EquilCO₂;

Qcomb = -241.826 * EquilH₂ * 0.3 -282.995 * EquilCO -802.324 * EquilCH₄;

Energy Adsorbed by the combustion products from 25C to 1220C

Hh_{2o} = H₂O * INTEGRAL(Tint:= 298:1493; 32.24 + 0.1923/100 * Tint + 1.055/100000 * Tint² - 3.595/10⁹ * Tint³)/1000;

HCO₂ = CO₂ * INTEGRAL(Tint:= 298:1493; 22.26 + 5.986/100 * Tint - 3.501/100000 * Tint² + 7.469/10⁹ * Tint³)/1000;

HN₂ = N₂ * INTEGRAL(Tint:= 298:1493; 28.90 - 0.1571/100 * Tint + 0.8081/100000 * Tint² - 2.873/(10⁹) * Tint³)/1000;

Energy adsorbed by the added steam from 163C to 1220C

Hh_{2oadded} = SteamAdd * INTEGRAL(Tint:= 436:1493; 32.24 + 0.1923/100 * Tint + 1.055/100000 * Tint² - 3.595/10⁹ * Tint³)/1000;

- Qcomb = Hh_{2o} + HCO₂ + Hh_{2oadded} + HN₂;

Steam Boiling, Evaporation & Superheating from 25C to 163C

TsteamIn = SteamIn + SteamAdd;

HsteamL = TsteamIn * 75.56 * (163 - 25)/1000;

HsteamE = TsteamIn * 37.23; # kJ

HsteamV = SteamIn * INTEGRAL(Tint:= 436:1123; 32.24 + 0.1923/100 * Tint + 1.055/100000 * Tint² - 3.595/10⁹ * Tint³)/1000;

H_{4water} = HsteamL + HsteamE + HsteamV;

.....

UNIT

C101 as combustAir

SET

C101.EquilCO := 30.48931645; # mol

C101.EquilCO₂ := 4.10863;

C101.EquilCH₄ := 2.2874;

C101.EquilH₂ := 47.17248101;

C101.SteamIn := 30.347126;

SCHEDULE

CONTINUE FOR 10

.....

A.5 gPROMS code for gasification calculation (S/C=0.2 in gasification)

.....

PARAMETER

Cori	AS	REAL
Hori	as	real
Oori	as	real
R	as	real
P	as	real
SteamIn	as	real
T	as	real
H10, H20, H30	as	real

VARIABLE

COout	as	amount
CO2out	as	amount
CH4out	as	amount
H2out	as	amount
H2Oout	as	amount
O2in	as	amount
Total	as	amount
K1, K2, K3	as	equil
CpO2, CpCO	as	heatcap
CpCO2, CpCH4	as	heatcap
CpH2, CpH2O	as	heatcap
H1, H2, H3	as	ene
HO2, HCO, HCO2	as	ene
HCH4, Hh2, Hh2o	as	ene
Inter1, Inter2, Inter3	as	aug
Hydro	as	amount
C1,C2,C3,C4	as	amount
H25	as	amount
Ener	as	ene

EQUATION

Equilibriums

$CpO_2 = 25.48 + 1.520/100 * T - 0.7155/100000 * T^2 + 1.312/(10^9) * T^3$; # J/mol/K
 $CpCO = 28.16 + 0.1675/100 * T + 0.5372/100000 * T^2 - 2.222/(10^9) * T^3$;
 $CpCO_2 = 22.26 + 5.986/100 * T - 3.501/100000 * T^2 + 7.469/(10^9) * T^3$;
 $CpCH_4 = 19.89 + 5.024/100 * T + 1.269/100000 * T^2 - 11.01/(10^9) * T^3$;
 $CpH_2 = 29.11 - 0.1916/100 * T + 0.4003/100000 * T^2 - 0.8704/(10^9) * T^3$;
 $CpH_2O = 32.24 + 0.1923/100 * T + 1.055/100000 * T^2 - 3.595/(10^9) * T^3$;

$HO_2 = \text{INTEGRAL}(Tint:= 298:T; 25.48 + 1.520/100 * Tint - 0.7155/100000 * Tint^2 + 1.312/10^9 * Tint^3)$; # J/mol
 $HCO = \text{INTEGRAL}(Tint:= 298:T; 28.16 + 0.1675/100 * Tint + 0.5372/100000 * Tint^2 - 2.222/10^9 * Tint^3)$;
 $HCO_2 = \text{INTEGRAL}(Tint:= 298:T; 22.26 + 5.986/100 * Tint - 3.501/100000 * Tint^2 + 7.469/10^9 * Tint^3)$;
 $HCH_4 = \text{INTEGRAL}(Tint:=298:T; 19.89 + 5.024/100 * Tint + 1.269/100000 * Tint^2 - 11.01/10^9 * Tint^3)$;
 $Hh_2 = \text{INTEGRAL}(Tint:= 298:T; 29.11 - 0.1916/100 * Tint + 0.4003/100000 * Tint^2 - 0.8704/10^9 * Tint^3)$;
 $Hh_{2o} = \text{INTEGRAL}(Tint:= 298:T; 32.24 + 0.1923/100 * Tint + 1.055/100000 * Tint^2 - 3.595/10^9 * Tint^3)$;

$H_1 = H_{10} + 2 * HCO/1000 - HCO_2/1000$; # kJ/mol
 $H_2 = H_{20} + HCO/1000 + Hh_2/1000 - Hh_{2o}/1000$;
 $H_3 = H_{30} + HCH_4/1000 - 2 * Hh_2/1000$;

$Inter_1 = \text{INTEGRAL}(Tin := 298:T; H_1*1000/R /Tin^2)$;
 $Inter_2 = \text{INTEGRAL}(Tin := 298:T; H_2*1000/R /Tin^2)$;
 $Inter_3 = \text{INTEGRAL}(Tin := 298:T; H_3*1000/R /Tin^2)$;

$K_1 = \text{EXP}(Inter_1) * 2.0919 * 10^{(-21)}$;
 $K_2 = \text{EXP}(Inter_2) * 2.0832 * 10^{(-16)}$;
 $K_3 = \text{EXP}(Inter_3) * 1.71 * 10^9$;

$K_1 = (CO_{out} / Total * P)^2 / (CO_{2out} / Total * P)$;
 $K_2 = (H_{2out} / Total * P) * CO_{out} / H_{2Oout}$;
 $K_3 = CH_{4out} / (H_{2out}^2 / Total * P)$;

Mass balances

$Cori = CO_{out} + CO_{2out} + CH_{4out}$;
 $Hori + 2 * SteamIn = 2 * H_{2Oout} + 4 * CH_{4out} + 2 * H_{2out}$;
 $Oori + SteamIn + 2 * O_{2in} = H_{2Oout} + CO_{out} + 2 * CO_{2out}$;

Auxiliary equation

$Total = CO_{out} + CO_{2out} + CH_{4out} + H_{2out} + H_{2Oout}$;

Hydrogen production potential

$Hydro = CO_{out} + 4 * CH_{4out} + H_{2out}$;

Energy requirements

```

C4 - C1 = CO2out;           # CO2 balance
2* C1 + C2 = COout;        # CO balance
C3 = CH4out;                # CH4 balance
O2In - C4 - 1/2*H25 + 1/2 * Oori = 0; # O2 balance
C2 - 2 * C3 - H25 = H2out - 1/2 * Hori; # H2 balance

```

```

Ener = C1 * 172 + C2 * 131 + C3 * (-75) + C4 * (-394) + H25 * (-242);

```

```

.....

```

UNIT

T101 as gasification

SET

```

T101.Cori := 68.05;  # mol
T101.Hori := 56.8;
T101.Oori := 6.14;
T101.R    := 8.314;  # J/mol/K
T101.H10  := 172;    # kJ/mol
T101.H20  := 131;
T101.H30  := -75;
T101.P    := 49.35;  # atm
T101.T    := 1123;
T101.SteamIn := 13.61; # mol

```

SCHEDULE

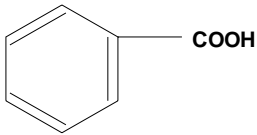
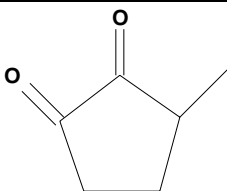
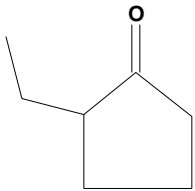
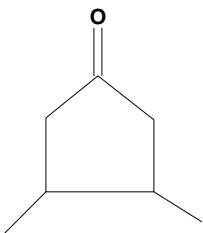
CONTINUE FOR 10

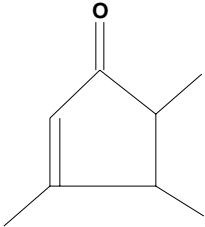
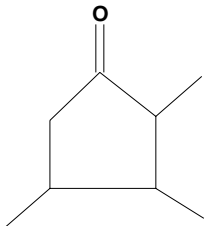
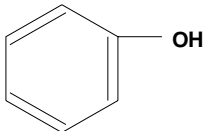
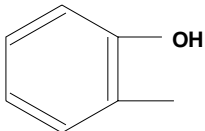
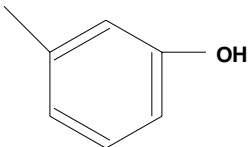
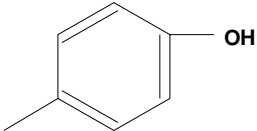
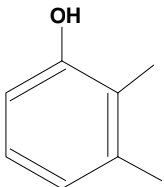
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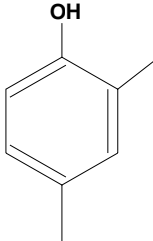
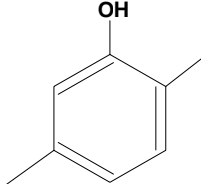
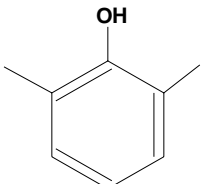
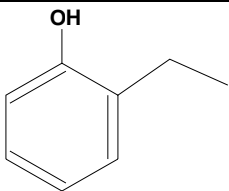
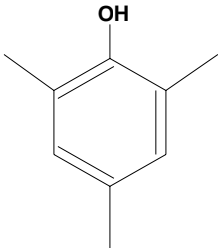
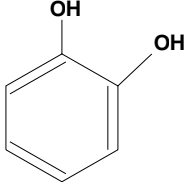
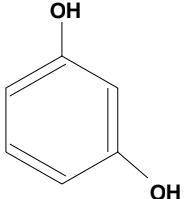
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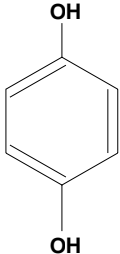
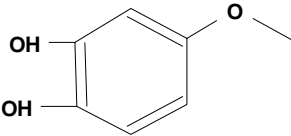
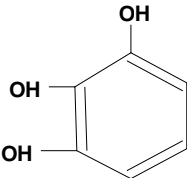
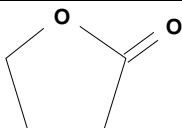
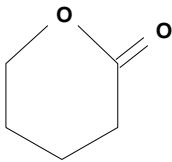
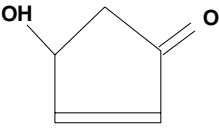
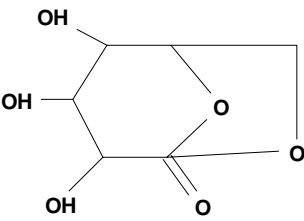
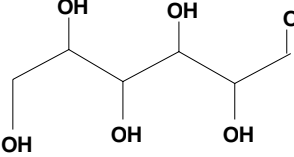
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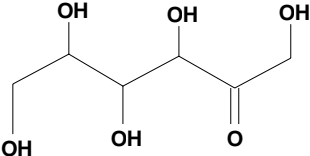
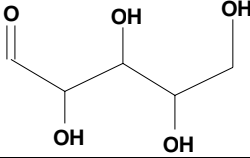
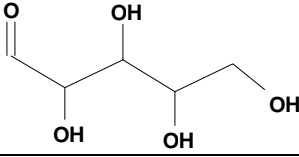
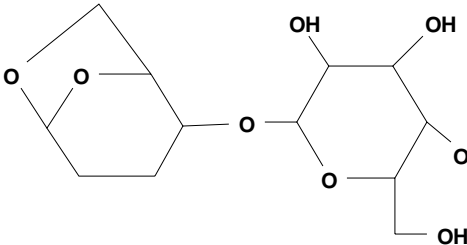
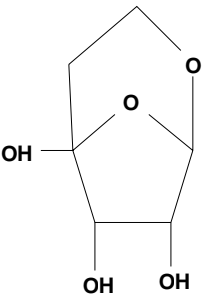
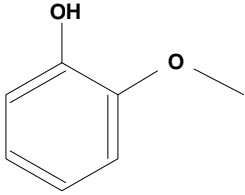
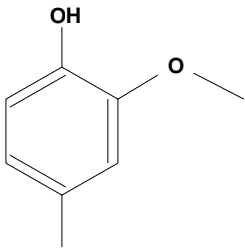
**APPENDIX B: ATOMIC STRUCTURES AND FORMULAS FOR
COMPONENTS IN BIO-OIL ORGANICS**

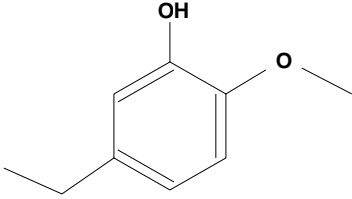
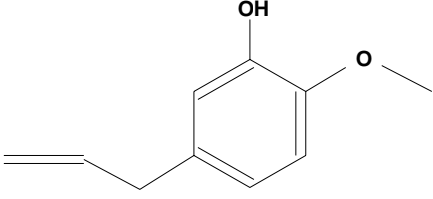
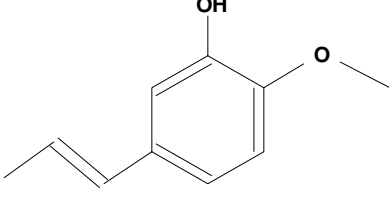
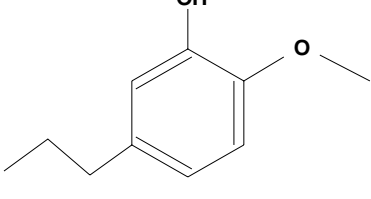
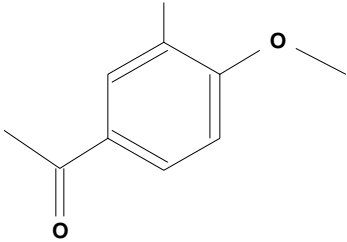
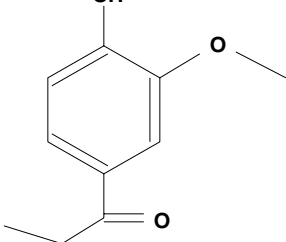
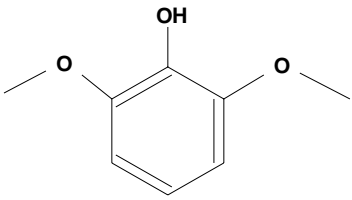
1	Formic acid	H-COOH	CH ₂ O ₂
2	Acetic acid	CH ₃ -COOH	C ₂ H ₄ O ₂
3	Propanoic acid	CH ₃ -CH ₂ -COOH	C ₃ H ₆ O ₂
4	Hydroxyacetic acid	OH-CH ₂ -COOH	C ₂ H ₄ O ₃
5	Butanoic acid	CH ₃ -(CH ₂) ₂ -COOH	C ₄ H ₈ O ₂
6	Pentanoic acid	CH ₃ -(CH ₂) ₃ -COOH	C ₅ H ₁₀ O ₂
7	4-Oxypentanoic acid	CH ₃ -CO-(CH ₂) ₂ -COOH	C ₅ H ₈ O ₃
8	Hexanoic acid	CH ₃ -(CH ₂) ₄ -COOH	C ₆ H ₁₂ O ₂
9	Benzoic acid		C ₇ H ₆ O ₂
10	Heptanoic acid	CH ₃ -(CH ₂) ₅ -COOH	C ₇ H ₁₄ O ₂
11	Methanol	CH ₃ -OH	CH ₄ O
12	Ethanol	CH ₃ -CH ₂ -OH	C ₂ H ₆ O
13	Ethylene Glycol	OH-CH ₂ -CH ₂ -OH	C ₂ H ₆ O ₂
14	Acetone	CH ₃ -CO-CH ₃	C ₃ H ₆ O
15	2-Butanone	CH ₃ -CO-CH ₂ -CH ₃	C ₄ H ₈ O
16	2,3-Pentenedione	CH ₃ -CO-CO-CH ₂ -CH ₃	C ₅ H ₈ O ₂
17	3Me2cyclopenten2ol1one		C ₆ H ₈ O ₂
18	2-Et-cyclopentanone		C ₇ H ₁₂ O
19	Dimethylcyclopentanone		C ₇ H ₁₂ O

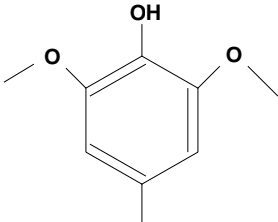
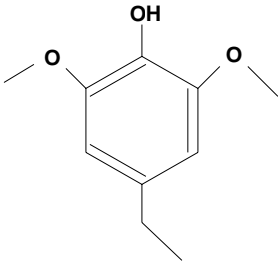
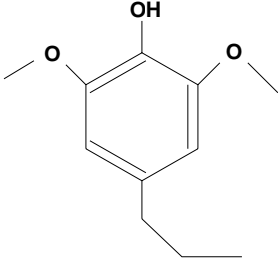
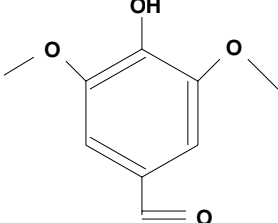
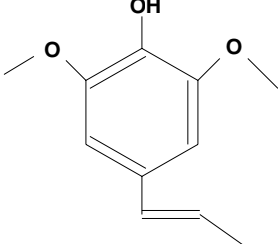
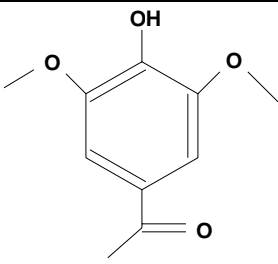
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21	Trimethylcyclopentanone		$C_8H_{14}O$
22	Formaldehyde	H-CHO	CH_2O
23	Acetaldehyde	CH_3-CHO	C_2H_4O
24	2-Propenal	$CH_2=CH-CHO$	C_3H_4O
25	2-Methyl-2-butenal	$CH_3-CH=C(CH_3)-CHO$	C_5H_8O
26	Pentanal	$CH_3-(CH_2)_3-CHO$	$C_5H_{10}O$
27	Ethanedial	CHO-CHO	$C_2H_2O_2$
28	Phenol		C_6H_6O
29	2-Methyl Phenol		C_7H_8O
30	3-Methyl Phenol		C_7H_8O
31	4-Methyl Phenol		C_7H_8O
32	2,3 Dimethyl Phenol		$C_8H_{10}O$

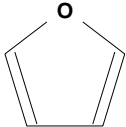
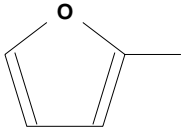
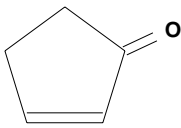
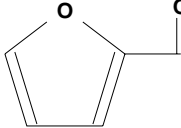
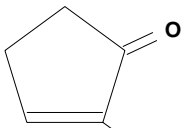
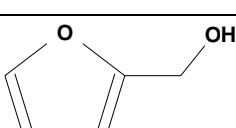
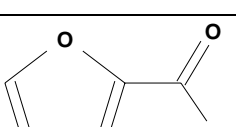
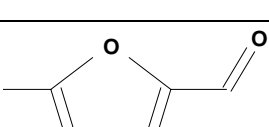
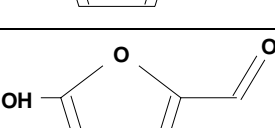
33	2,4 Dimethyl Phenol		$C_8H_{10}O$
34	2,5 Dimethyl Phenol		$C_8H_{10}O$
35	2,6 Dimethyl Phenol		$C_8H_{10}O$
36	2-Ethylphenol		$C_8H_{10}O$
37	2,4,6 TriMe Phenol		$C_9H_{12}O$
38	1,2 DiOH Benzene		$C_6H_6O_2$
39	1,3 DiOH Benzene		$C_6H_6O_2$

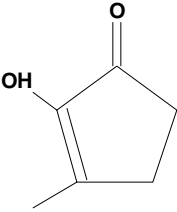
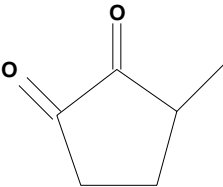
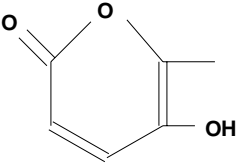
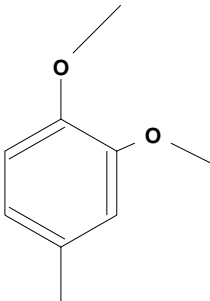
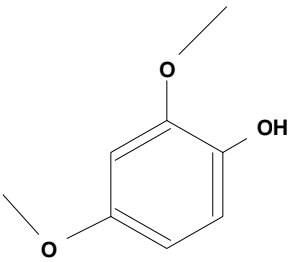
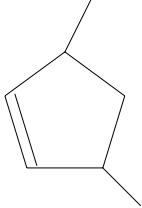
40	1,4 DiOH Benzene		$C_6H_6O_2$
41	4-Methoxy Catechol		$C_7H_8O_3$
42	1,2,3 Tri-OH-Benzene		$C_6H_6O_3$
43	Methyl Formate	$CH_3-O-CHO$	$C_2H_4O_2$
44	Butyrolactone		$C_4H_6O_2$
45	Valerolactone		$C_5H_8O_2$
46	Angelicalactone		$C_5H_6O_2$
47	Levogluconan		$C_6H_{10}O_5$
48	Glucose		$C_6H_{12}O_6$

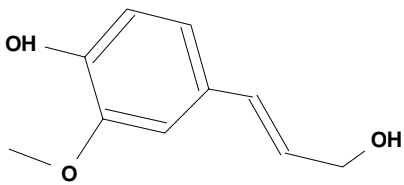
49	Fructose		$C_6H_{12}O_6$
50	D-Xylose		$C_5H_{10}O_5$
51	D-Arabinose		$C_5H_{10}O_5$
52	Cellobiosan		$C_{12}H_{20}O_{10}$
53	1,6 Anhydroglucofuranose		$C_6H_{10}O_5$
54	2-Methoxy Phenol		$C_7H_8O_2$
55	4-Methyl Guaiacol		$C_8H_{10}O_2$

56	Ethyl Guaiacol		$C_9H_{12}O_2$
57	Eugenol		$C_{10}H_{12}O_2$
58	Isoeugenol		$C_{10}H_{12}O_2$
59	4-Propylguaiacol		$C_{10}H_{14}O_2$
60	Acetoguaiacol		$C_9H_{10}O_3$
61	Propioguaiacol		$C_{10}H_{12}O_3$
62	2,6-DiOMe Phenol		$C_8H_{10}O_3$

63	Methyl Syringol		$C_9H_{12}O_3$
64	4-Ethyl Syringol		$C_{10}H_{14}O_3$
65	Propyl Syringol		$C_{11}H_{16}O_3$
66	Syringaldehyde		$C_9H_{10}O_4$
67	4-Propenyl Syringol		$C_{11}H_{14}O_3$
68	4-OH-3,5-DiOMe Phenyl Ethanone		$C_{10}H_{12}O_4$

69	Furan		C_4H_4O
70	2-Methyl Furan		C_5H_6O
71	2-Furanone		$C_4H_4O_2$
72	Furfural		$C_5H_4O_2$
73	3-Methyl-2(3h) Furanone		$C_5H_6O_2$
74	Furfural alcohol		$C_5H_6O_2$
75	Furoic Acid		$C_5H_4O_3$
76	5-Methyrfurfural		$C_6H_6O_2$
77	5-OH-Methyl-2-Furfural		$C_6H_6O_3$
78	Hydroxyacetaldehyde	$OH-CH_2-CHO$	$C_2H_4O_2$
79	Acetol	$CH_3-CO-CH_2-OH$	$C_3H_6O_2$
80	Acetal	$(C_2H_5O)CH-CH_3$	$C_6H_{14}O_2$
81	Acetyloxy-2-propanone	$CH_3-CO-O-CH_2-CO-CH_3$	$C_5H_8O_3$

82	2-OH-3-Me-2-cyclopentene-1-one		$C_6H_8O_2$
83	Methyl Cyclopentenolone		$C_6H_8O_2$
84	1-Acetyloxy-2-Propanone	$CH_3-CO-O-CH_2-CO-CH_3$	$C_5H_8O_3$
85	2-Methyl-3-hydroxy-2-pyrone		$C_6H_6O_3$
86	2-Methoxy-4-methylanisole		$C_9H_{12}O_2$
87	4-OH-3-methoxybenzaldehyde		$C_8H_8O_3$
88	Dimethylcyclopentene		C_7H_{12}

89	Pyrolytic Lignin		$C_7H_9O_3$
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APPENDIX C: ENERGY OF FORMATION OF STRUCTURAL GROUPS IN ORGANIC MOLECULES ((Perry's, 1997)

	Δ_H	Δ_G		Δ_H	Δ_G
Nonring Increments			Oxygen Increments (Cont.)		
—CH ₃	-76.45	-43.96	—CHO (aldehyde)	-162.03	-143.48
—CH ₂ —	-20.64	8.42	—COOH (acid)	-426.72	-387.87
—CH—	29.89	58.36	—COO— (ester)	-337.92	-301.95
—C—	82.23	116.02	≡O (except for above)	-247.61	-250.83
≡CH ₂	-9.63	3.77	Nitrogen Increments		
≡CH	37.97	48.53	—NH ₂	-22.02	14.07
≡C—	83.99	92.36	—NH (nonring)	53.47	89.39
≡C≡	142.14	136.70	—NH (ring)	31.65	75.61
≡CH	79.30	77.71	—N— (nonring)	123.34	163.16
≡C—	115.51	109.82	—N≡ (nonring)	23.61	—
Ring Increments			—N≡ (ring)	55.52	79.93
—CH ₂ —	-26.80	-3.68	≡NH	93.70	119.66
—CH—	8.67	40.99	—CN	88.43	89.22
—C—	79.72	87.88	—NO ₂	-66.57	-16.83
≡CH (aromatic or cyclic olefin)	2.09	11.30	Sulfur Increments		
≡C— (aromatic or cyclic olefin)	46.43	54.05	—SH	-17.33	-22.99
Oxygen Increments			—S— (nonring)	41.87	33.12
—OH (alcohol)	-208.04	-189.20	—S— (ring)	39.10	27.76
—OH (phenol)	-221.65	-197.37	Halogen Increments		
—O— (nonring)	-132.22	-105.00	—F	-251.92	-247.19
—O— (ring)	-138.16	-98.22	—Cl	-71.55	-64.31
—C=O (nonring)	-133.22	-120.50	—Br	-29.48	-38.06
—C=O (ring)	-164.50	-126.27	—I	21.06	5.74

APPENDIX D: DETAILED HEAT INTEGRATION RESULTS

Table 40 Heat integration for biomass conversion through pyrolysis at 450 °C and S/C = 1 in SR

450C S/C=1															
Sub-unit	Streams and Temperature										Deficit (kJ)	Accumulated (kJ)		Adjusted (kJ)	
	Heat sources				Heat sinks							Input	Output	Input	Output
	1	2	3	T /°C	4	5	6	7	8						
				1220											
1				870	850						-3842	0	3842	113	3955
2				850	830						2678	3842	1163	3955	1276
3				470	450						-3851	1163	5014	1276	5128
4				450	435						1382	5014	3633	5128	3746
5				178	163						-2381	3633	6013	3746	6126
6				100	90						6126	6013	-113	6126	0
7				35	25						-6561	-113	6448	0	6561
				25							-182	6448	6630	6561	6743

Table 41 Heat integration for biomass conversion through pyrolysis at 450 °C and S/C = 3 in SR

450C S/C=3															
Sub-unit	Streams and Temperature										Deficit (kJ)	Accumulated (kJ)		Adjusted (kJ)	
	Heat sources			Heat sinks								Input	Output	Input	Output
	1	2	3	T /°C		4	5	6	7	8					
				1220											
1				870	850						-3053	0	3053	3263	6317
2				850	830						2793	3053	261	6317	3524
3				470	450						-3161	261	3421	3524	6685
4				450	435						1408	3421	2013	6685	5277
5				178	163						-1853	2013	3867	5277	7130
6				100	90						7130	3867	-3263	7130	0
7				35	25						-6975	-3263	3711	0	6975
				25							-189	3711	3901	6975	7164

Table 42 Heat integration for biomass conversion through pyrolysis at 450 °C and S/C = 4 in SR

450C S/C=4															
Sub-unit	Streams and Temperature										Deficit (kJ)	Accumulated (kJ)		Adjusted (kJ)	
	Heat sources				Heat sinks										
	1	2	3	T /°C		4	5	6	7	8		Input	Output	Input	Output
				1220											
1				870	850						-2865	0	2865	4588	7453
2				850	830						2734	2865	131	7453	4719
3				470	450						-3004	131	3135	4719	7723
4				450	435						1411	3135	1724	7723	6312
5				178	163						-1729	1724	3453	6312	8041
6				100	90						8041	3453	-4588	8041	0
7				35	25						-7776	-4588	3189	0	7776
				25							-204	3189	3393	7776	7981

Table 43 Heat integration for biomass conversion through pyrolysis at 500 °C and S/C = 1 in SR

500C S/C=1															
Sub-unit	Streams and Temperature										Deficit (kJ)	Accumulated (kJ)		Adjusted (kJ)	
	Heat sources				Heat sinks										
	1	2	3	T /°C	4	5	6	7	8	Input		Output	Input	Output	
				1220											
1				870	850					-4118	0	4118	0	4118	
2				850	830					2870	4118	1248	4118	1248	
3				520	500					-3583	1248	4831	1248	4831	
4				500	485					1364	4831	3467	4831	3467	
5				178	163					-3070	3467	6537	3467	6537	
6				100	90					6527	6537	10	6537	10	
7				35	25					-7045	10	7055	10	7055	
				25						-195	7055	7250	7055	7250	

Table 44 Heat integration for biomass conversion through pyrolysis at 500 °C and S/C = 2 in SR

500C S/C=2															
Sub-unit	Streams and Temperature									Deficit (kJ)	Accumulated (kJ)		Adjusted (kJ)		
	Heat sources			Heat sinks											
	1	2	3	T /°C		4	5	6	7		8	Input	Output	Input	Output
				1220											
1				870	850						-3569	0	3569	1912	5482
2				850	830						3048	3569	521	5482	2434
3				520	500						-3158	521	3680	2434	5592
4				500	485						1385	3680	2295	5592	4208
5				178	163						-2635	2295	4930	4208	6842
6				100	90						6842	4930	-1912	6842	0
7				35	25						-6919	-1912	5006	0	6919
				25							-192	5006	5198	6919	7111

Table 45 Heat integration for biomass conversion through pyrolysis at 500 °C and S/C = 3 in SR

500C S/C=3															
Sub-unit	Streams and Temperature										Deficit (kJ)	Accumulated (kJ)		Adjusted (kJ)	
	Heat sources				Heat sinks							Input	Output	Input	Output
	1	2	3	T /°C	4	5	6	7	8						
				1220											
1				870	850						-3273	0	3273	3373	6646
2				850	830						2990	3273	283	6646	3656
3				520	500						-2941	283	3224	3656	6596
4				500	485						1392	3224	1832	6596	5204
5				178	163						-2402	1832	4233	5204	7606
6				100	90						7606	4233	-3373	7606	0
7				35	25						-7492	-3373	4120	0	7492
				25							-203	4120	4322	7492	7695

Table 46 Heat integration for biomass conversion through pyrolysis at 500 °C and S/C = 4 in SR

500C S/C=4															
Sub-unit	Streams and Temperature										Deficit (kJ)	Accumulated (kJ)		Adjusted (kJ)	
	Heat sources					Heat sinks						Input	Output	Input	Output
1	2	3	T /°C		4	5	6	7	8						
				1220											
1				870	850					-3071	0	3071	4796	7867	
2				850	830					2927	3071	144	7867	4940	
3				520	500					-2795	144	2939	4940	7735	
4				500	485					1395	2939	1544	7735	6339	
5				178	163					-2243	1544	3787	6339	8583	
6				100	90					8583	3787	-4796	8583	0	
7				35	25					-8352	-4796	3557	0	8352	
				25						-219	3557	3775	8352	8571	

Table 47 Heat integration for biomass conversion through pyrolysis at 550 °C and S/C = 1 in SR

550C S/C=1															
Sub-unit	Streams and Temperature										Deficit (kJ)	Accumulated (kJ)		Adjusted (kJ)	
	Heat sources				Heat sinks										
	1	2	3	T /°C		4	5	6	7	8		Input	Output	Input	Output
				1220											
1				870	850						-4180	0	4180	0	4180
2				850	830						2895	4180	1286	4180	1286
3				570	550						-3087	1286	4373	1286	4373
4				550	535						1360	4373	3013	4373	3013
5				178	163						-3617	3013	6630	3013	6630
6				100	90						6603	6630	28	6630	28
7				35	25						-7162	28	7190	28	7190
				25							-198	7190	7387	7190	7387

Table 48 Heat integration for biomass conversion through pyrolysis at 550 °C and S/C = 2 in SR

550C S/C=2															
Sub-unit	Streams and Temperature										Deficit (kJ)	Accumulated (kJ)		Adjusted (kJ)	
	Heat sources				Heat sinks							Input	Output	Input	Output
	1	2	3	T /°C		4	5	6	7	8					
				1220											
1				870	850						-3631	0	3631	1902	5532
2				850	830						3048	3631	583	5532	2485
3				570	550						-2728	583	3311	2485	5213
4				550	535						1380	3311	1931	5213	3833
5				178	163						-3113	1931	5045	3833	6946
6				100	90						6946	5045	-1902	6946	0
7				35	25						-7071	-1902	5169	0	7071
				25							-196	5169	5365	7071	7266

Table 49 Heat integration for biomass conversion through pyrolysis at 550 °C and S/C = 3 in SR

550C S/C=3															
Sub-unit	Streams and Temperature										Deficit (kJ)	Accumulated (kJ)		Adjusted (kJ)	
	Heat sources					Heat sinks						Input	Output	Input	Output
	1	2	3	T /°C		4	5	6	7	8					
				1220											
1				870	850						-3331	0	3331	3402	6733
2				850	830						2985	3331	346	6733	3748
3				570	550						-2541	346	2887	3748	6289
4				550	535						1387	2887	1500	6289	4902
5				178	163						-2841	1500	4341	4902	7743
6				100	90						7743	4341	-3402	7743	0
7				35	25						-7675	-3402	4273	0	7675
				25							-207	4273	4480	7675	7882

Table 50 Heat integration for biomass conversion through pyrolysis at 550 °C and S/C = 4 in SR

550C S/C=4															
Sub-unit	Streams and Temperature										Deficit (kJ)	Accumulated (kJ)		Adjusted (kJ)	
	Heat sources					Heat sinks						Input	Output	Input	Output
	1	2	3	T /°C		4	5	6	7	8					
				1220											
1				870	850						-3126	0	3126	4870	7996
2				850	830						2920	3126	206	7996	5076
3				570	550						-2415	206	2621	5076	7491
4				550	535						1390	2621	1231	7491	6101
5				178	163						-2655	1231	3886	6101	8756
6				100	90						8756	3886	-4870	8756	0
7				35	25						-8571	-4870	3701	0	8571
				25							-224	3701	3924	8571	8794

Table 51 Heat integration for coal conversion through S/C=0.2 in gasification and S/C=2 in SR

S/C=0.2 in gasification; S/C = 2 in SR													
Sub-unit	Streams and Temperature								Deficit (kJ)	Accumulated (kJ)		Heat Flows (kJ)	
	Heat sources				Heat sinks					Input	Output	Input	Output
	1	2	Ga	T /°C		3	4	5					
				1220									
1				870	850				-5556	0	5556	0	5556
2				850	830				2045	5556	3511	5556	3511
3				178	163				-14811	3511	18322	3511	18322
4				100	90				11342	18322	6980	18322	6980
5				35	25				-11126	6980	18106	6980	18106
				25					-305	18106	18411	18106	18411

Table 52 Heat integration for coal conversion through S/C=0.2 in gasification and S/C=3 in SR

S/C=0.2 in gasification; S/C = 3 in SR													
Sub-unit	Streams and Temperature								Deficit (kJ)	Accumulated (kJ)		Heat Flows (kJ)	
	Heat sources				Heat sinks					Input	Output	Input	Output
	1	2	Ga	T /°C	3	4	5						
				1220									
1				870	850				-5100	0	5100	0	5100
2				850	830				1849	5100	3251	5100	3251
3				178	163				-14114	3251	17365	3251	17365
4				100	90				12903	17365	4462	17365	4462
5				35	25				-12420	4462	16881	4462	16881
				25					-330	16881	17211	16881	17211

Table 53 Heat integration for coal conversion through S/C=0.2 in gasification and S/C=4 in SR

S/C=0.2 in gasification; S/C = 4 in SR													
Sub-unit	Streams and Temperature								Deficit (kJ)	Accumulated (kJ)		Heat Flows (kJ)	
	Heat sources				Heat sinks					Input	Output	Input	Output
	1	2	Ga	T /°C	3	4	5						
				1220									
1				870	850				-4783	0	4783	0	4783
2				850	830				1729	4783	3054	4783	3054
3				178	163				-13634	3054	16688	3054	16688
4				100	90				14811	16688	1877	16688	1877
5				35	25				-14156	1877	16033	1877	16033
				25					-362	16033	16395	16033	16395

Table 54 Heat integration for coal conversion through S/C=0.3 in gasification and S/C=1 in SR

S/C=0.3 in gasification; S/C = 1 in SR													
Sub-unit	Streams and Temperature								Deficit (kJ)	Accumulated (kJ)		Heat Flows (kJ)	
	Heat sources				Heat sinks					Input	Output	Input	Output
	1	2	Ga	T /°C		3	4	5					
				1220									
1				870	850				-6570	0	6570	0	6570
2				850	830				2803	6570	3767	6570	3767
3				178	163				-14588	3767	18355	3767	18355
4				100	90				11251	18355	7103	18355	7103
5				35	25				-11314	7103	18417	7103	18417
				25					-313	18417	18730	18417	18730

Table 55 Heat integration for coal conversion through S/C=0.3 in gasification and S/C=2 in SR

S/C=0.3 in gasification; S/C = 2 in SR													
Sub-unit	Streams and Temperature								Deficit (kJ)	Accumulated (kJ)		Heat Flows (kJ)	
	Heat sources				Heat sinks					Input	Output	Input	Output
	1	2	Ga	T /°C	3	4	5						
				1220									
1				870	850				-5804	0	5804	0	5804
2				850	830				2680	5804	3124	5804	3124
3				178	163				-13392	3124	16516	3124	16516
4				100	90				12125	16516	4391	16516	4391
5				35	25				-11671	4391	16062	4391	16062
				25					-320	16062	16382	16062	16382

Table 56 Heat integration for coal conversion through S/C=0.3 in gasification and S/C=3 in SR

S/C=0.3 in gasification; S/C = 3 in SR													
Sub-unit	Streams and Temperature								Deficit (kJ)	Accumulated (kJ)		Heat Flows (kJ)	
	Heat sources				Heat sinks					Input	Output	Input	Output
	1	2	Ga	T /°C		3	4	5					
				1220									
1				870	850				-5338	0	5338	0	5338
2				850	830				2520	5338	2818	5338	2818
3				178	163				-12678	2818	15496	2818	15496
4				100	90				13669	15496	1827	15496	1827
5				35	25				-12938	1827	14765	1827	14765
				25					-343	14765	15109	14765	15109

Table 57 Heat integration for coal conversion through S/C=0.3 in gasification and S/C=4 in SR

S/C=0.3 in gasification; S/C = 4 in SR													
Sub-unit	Streams and Temperature								Deficit (kJ)	Accumulated (kJ)		Heat Flows (kJ)	
	Heat sources				Heat sinks					Input	Output	Input	Output
1	2	Ga	T /°C	3	4	5							
				1220									
1				870	850				-5016	0	5016	763	5778
2				850	830				2402	5016	2613	5778	3376
3				178	163				-12189	2613	14802	3376	15565
4				100	90				15565	14802	-763	15565	0
5				35	25				-14657	-763	13894	0	14657
				25					-376	13894	14270	14657	15032

Table 58 Heat integration for coal conversion through S/C=0.4 in gasification and S/C=1 in SR

S/C=0.4 in gasification; S/C = 1 in SR													
Sub-unit	Streams and Temperature								Deficit (kJ)	Accumulated (kJ)		Heat Flows (kJ)	
	Heat sources				Heat sinks					Input	Output	Input	Output
	1	2	Ga	T/°C	3	4	5						
				1220									
1				870	850				-6832	0	6832	0	6832
2				850	830				3363	6832	3468	6832	3468
3				178	163				-13198	3468	16666	3468	16666
4				100	90				12019	16666	4647	16666	4647
5				35	25				-11873	4647	16520	4647	16520
				25					-328	16520	16848	16520	16848

Table 59 Heat integration for coal conversion through S/C=0.4 in gasification and S/C=2 in SR

S/C=0.4 in gasification; S/C = 2 in SR													
Sub-unit	Streams and Temperature								Deficit (kJ)	Accumulated (kJ)		Heat Flows (kJ)	
	Heat sources				Heat sinks					Input	Output	Input	Output
1	2	Ga	T /°C		3	4	5						
				1220									
1				870	850				-6046	0	6046	0	6046
2				850	830				3312	6046	2734	6046	2734
3				178	163				-11965	2734	14700	2734	14700
4				100	90				12889	14700	1811	14700	1811
5				35	25				-12193	1811	14004	1811	14004
				25					-334	14004	14338	14004	14338

Table 60 Heat integration for coal conversion through S/C=0.4 in gasification and S/C=3 in SR

S/C=0.4 in gasification; S/C = 3 in SR													
Sub-unit	Streams and Temperature								Deficit (kJ)	Accumulated (kJ)		Heat Flows (kJ)	
	Heat sources				Heat sinks					Input	Output	Input	Output
	1	2	Ga	T /°C		3	4	5					
				1220									
1				870	850				-5571	0	5571	778	6349
2				850	830				3166	5571	2406	6349	3184
3				178	163				-11236	2406	13642	3184	14420
4				100	90				14420	13642	-778	14420	0
5				35	25				-13437	-778	12660	0	13437
				25					-357	12660	13016	13437	13794

Table 61 Heat integration for coal conversion through S/C=0.4 in gasification and S/C=4 in SR

S/C=0.4 in gasification; S/C = 4 in SR													
Sub-unit	Streams and Temperature								Deficit (kJ)	Accumulated (kJ)		Heat Flows (kJ)	
	Heat sources				Heat sinks					Input	Output	Input	Output
	1	2	Ga	T /°C	3	4	5						
				1220									
1				870	850				-5239	0	5239	3372	8611
2				850	830				3048	5239	2191	8611	5563
3				178	163				-10732	2191	12922	5563	16294
4				100	90				16294	12922	-3372	16294	0
5				35	25				-15127	-3372	11756	0	15127
				25					-388	11756	12144	15127	15516

Table 62 Heat integration for coal conversion through S/C=0.5 in gasification and S/C=1 in SR

S/C=0.5 in gasification; S/C = 1 in SR													
Sub-unit	Streams and Temperature								Deficit (kJ)	Accumulated (kJ)		Heat Flows (kJ)	
	Heat sources			Heat sinks									
	1	2	T /°C		3	Ga	4	5		Input	Output	Input	Output
			1220										
1			870	850					-7091	0	7091	0	7091
2			850	830					5115	7091	1977	7091	1977
3			178	163					-13018	1977	14995	1977	14995
4			100	90					12771	14995	2223	14995	2223
5			35	25					-12418	2223	14642	2223	14642
			25						-342	14642	14984	14642	14984

Table 63 Heat integration for coal conversion through S/C=0.5 in gasification and S/C=3 in SR

S/C=0.5 in gasification; S/C = 3 in SR													
Sub-unit	Streams and Temperature								Deficit (kJ)	Accumulated (kJ)		Heat Flows (kJ)	
	Heat sources			Heat sinks									
	1	2	T /°C		3	Ga	4	5		Input	Output	Input	Output
			1220										
1			870	850					-5800	0	5800	3378	9178
2			850	830					5019	5800	781	9178	4160
3			178	163					-10997	781	11779	4160	15157
4			100	90					15157	11779	-3378	15157	0
5			35	25					-13920	-3378	10541	0	13920
			25						-370	10541	10911	13920	14290

Table 64 Heat integration for coal conversion through S/C=0.5 in gasification and S/C=4 in SR

S/C=0.5 in gasification; S/C = 4 in SR													
Sub-unit	Streams and Temperature								Deficit (kJ)	Accumulated (kJ)		Heat Flows (kJ)	
	Heat sources				Heat sinks								
	1	2	T /°C		3	Ga	4	5		Input	Output	Input	Output
			1220										
1			870	850					-5466	0	5466	5984	11450
2			850	830					4908	5466	558	11450	6542
3			178	163					-10490	558	11048	6542	17031
4			100	90					17031	11048	-5984	17031	0
5			35	25					-15607	-5984	9623	0	15607
			25						-402	9623	10025	15607	16009

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