FUEL GAS PRODUCTION FROM CO-GASIFICATION OF BLACK LIQUOR MIXED WITH EUCALYPTUS BARK

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การผลิตแก๊สเชื้อเพลิงจากกระบวนการแกซิฟิเคชันร่วมของน้ำยางดำผสมเปลือกยูคาลิปตัส

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กระบวนการแกซิฟิเคชันของน้ำยางดำผสมเปลือกยูคาลิปตัสเป็นวิธีการหนึ่งที่น่าสนใจในการผลิตแก๊สเชื้อเพลิงสำหรับใช้เป็นพลังงาน งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาภาวะที่เหมาะสมในการผลิตในการเกิดปฏิกิริยาที่ให้ปริมาณของแก๊สผลิตภัณฑ์ ร้อยละของการแปรสภาพของคาร์บอนและไฮโดรเจนในวัตถุดิบเป็นแก๊สผลิตภัณฑ์ ค่าความร้อนต่ำ ค่าประสิทธิภาพเชิงความร้อน ปริมาณของแก๊สสังเคราะห์ และอัตราส่วนโดยโมลของ H_2/CO ที่มีค่าสูงที่สุด โดยมีตัวแปรในการศึกษาคือ อุณหภูมิในการทำปฏิกิริยา เท่ากับ 700–900°C อัตราส่วนระหว่างน้ำยางดำต่อเปลือกยูคาลิปตัส เท่ากับ 60:40 และ 40:60 และอัตราส่วนออกซิเจนต่อเชื้อเพลิง เท่ากับ 0.2–0.6 แก๊สผลิตภัณฑ์หลักที่เกิดขึ้นประกอบด้วย CO, H_2 and C_xH_y (ในรูป CH_4) ผลการทดลองของกระบวนการแกซิฟิเคชันของสารผสมโดยใช้เตาปฏิกรณ์แบบนิ่งพบว่า อุณหภูมิในการทำปฏิกิริยาและอัตราส่วนออกซิเจนต่อเชื้อเพลิงมีผลทั้งในเชิงปริมาณและคุณภาพของแก๊สผลิตภัณฑ์ การเพิ่มขึ้นของอุณหภูมิและอัตราส่วนออกซิเจนต่อเชื้อเพลิงส่งผลให้ปริมาณของ CO, H_2 เพิ่มสูงขึ้น และมีปริมาณสูงสุด ที่ 900°C ในขณะที่ปริมาณของแข็งและของเหลวที่เหลือลดลง นอกจากนี้ค่าร้อยละการแปรสภาพของคาร์บอนและไฮโดรเจนเป็นแก๊สผลิตภัณฑ์ ค่าความร้อนต่ำ ค่าประสิทธิภาพเชิงความร้อน และปริมาณของแก๊สสังเคราะห์ จะแปรผันตามอุณหภูมิและอัตราส่วนออกซิเจนต่อเชื้อเพลิงที่เพิ่มขึ้นยกเว้นอัตราส่วนอัตราส่วนโดยโมลของ H_2/CO ค่าประสิทธิภาพเชิงความร้อน และอัตราส่วนโดยโมลของ H_2/CO ที่มีค่าสูงที่สุดที่ได้จากการทดลองนี้ คือ 83.98% และ 1.48 ตามลำดับ ค่าที่สูงที่สุดของปริมาณแก๊สสังเคราะห์และค่าความร้อนต่ำ เท่ากับ 32.43 ลิตร และ 5.66 MJ/m^3 ตามลำดับ ซึ่งได้จากการทดลองที่สภาวะอัตราส่วนของน้ำยางดำต่อเปลือกยูคาลิปตัส เท่ากับ 60:40 อุณหภูมิในการเกิดปฏิกิริยา 900 องศาเซลเซียสและอัตราส่วนออกซิเจนต่อเชื้อเพลิง เท่ากับ 0.6 ถ่านชาร์ที่ได้จากกระบวนการแกซิฟิเคชันมีองค์ประกอบของคาร์บอน โซเดียมและซัลเฟอร์ แสดงให้เห็นว่าถ่านชาร์นี้สามารถนำกลับมาใช้ใหม่เป็นสารตั้งต้นในกระบวนการแกซิฟิเคชันได้ต่อไป นอกจากนี้แล้วโซเดียมและซัลเฟอร์ที่คงเหลือในถ่านชาร์สามารถนำกลับมาใช้เป็นสารเคมีในการผลิตเยื่อกระดาษได้

สาขาวิชา….การจัดการสิ่งแวดล้อม……. ลายมือชื่อนิสิต…………………………..………...
ปีการศึกษา..2553…………………..……... ลายมือชื่อ อ. ที่ปรึกษาวิทยานิพนธ์หลัก…….……….....
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WANVIPA KRIPITTAYAKORN: FUEL GAS PRODUCTION FROM CO-GASIFICATION FROM BLACK LIQUOR MIXED WITH EUCALYPTUS BARK. THESIS ADVISOR: ASST. PROF. VIBOON SRICHAROENCHAIKUL, Ph.D., THESIS CO-ADVISOR: DUANGDUEN ATONG, Ph.D., 106 pp.

Gasification of black liquor mixed with eucalyptus bark residues is an interesting approach to produce gaseous fuels for energy purpose. The objectives of this work were to suggest appropriate gasification parameters that produce the highest gas yield, carbon and hydrogen conversion to product gases, LHV, cold gas efficiency, syngas production and H_2/CO ratio. The operation temperature of 700-900ºC, the ratio of black liquor to eucalyptus bark of 60:40 and 40:60, and equivalence ratio of 0.2-0.6 were applied. Major components in product gases including CO, H_2 and C_xH_y (as CH_4). Results from mixed sample gasification using fixed bed reactor indicated that temperature and ER significantly affecting both quantity and quality of produced gas. The increase in temperature and ER lead to greater production of CO, H_2 with highest gas yield at 900 °C, while solid and liquid yields decreased. In addition, carbon and hydrogen conversion, gas LHV and cold gas efficiency increase with temperature and ER while H_2/CO was lower. The maximum cold gas efficiency and H_2/CO of 83.98% and 1.48 were achieved, respectively. The highest syngas production and LHV equals to 32.43 L and 5.66 MJ/m^3, respectively, obtained from mixed sample 60:40 that gasified at 900°C and ER of 0.6. Char from gasification contained C, Na and S content. It shown that this char can reuse and suggested for use as a feedstock in gasification process for the further work. Furthermore, Na and S in char can be recovered for using as pulping chemical.

Field of Study	: Environmental Management	Student's Signature ....
Academic Year	: 2010	Advisor's Signature ....
		Co-Advisor's Signature ....

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LIST OF ABBREVIATIONS

°C	Degree Celsius
CH_4	Methane
CO_2	Carbon dioxide
CO	Carbon monoxide
ER	Equivalence Ratio
g	Gram
g/min	Gram per minute
H_2	Hydrogen
HHV	Higher Heating Value
LHV	Lower Heating Value
L	Liter
L/min	Liter per minute
L/mole	Liter per mole
MJ/Kg	Megajoule per Kilograme
MJ/m^3	Megajoule per cubic meter
mole/min	Mole per minute
XRF	X-ray fluorescence spectrometer

CHAPTER I

INTRODUCTION

1.1 Introduction

Due to the increasing world population and the improving living standards, the demand for energy resources has continually risen. Recently, agricultural and industrial wastes which are the energy resources from the renewable and alternative sources become more important as future energy (Sricharoenchaikul, 2009; Shimizu el at., 2006). Among the renewable energies, biomass is one of the most important energy sources as the third primary energy sources after coal and oil (Kirubakaran et al., 2007). Biomass waste such as wood wastes and agricultural residues are generally organic. They contain carbon, hydrogen and oxygen along with some moisture. Then, biomass material may be converted into a gaseous fuel (Arthayukti, 1985).

The pulp and paper industry is an important industry in Thailand that providing pulp for domestic and international markets (Jiwjit et al., 2007). It is a major business industry that involves in people life. Everybody utilizes paper everyday and uses for many purposes such as communication, commerce, working and education. From this reason, the pulp and paper industries are continuously increase production rates to response market demands. From this situation, the enormous amounts of wastes are produced. In production process of pulp and paper industry, the activities leading to environmental problems such as the use of water, fuels and chemicals. These activities emit environmental pollutants that give to global warming, smog, toxicity and solid waste produced (Jiwjit et al., 2007). The papermaking of pulp and paper industry generates many types of waste. Biomass waste is an important type of waste that produces from this industry.

This research concerns about the hazardous wastes from the pulp and paper industry in Thailand (Advance Agro Public Co., Ltd.) which are black liquor and eucalyptus bark residues. Black liquor is an aqueous solution of lignin residues, hemicellulose, and the inorganic chemicals which is the remaining substance after the digester process. Black liquor, a major waste from the pulp and paper making industry, containson a dry basis, about 40% of recyclable pulping chemicals (mostly alkaline salts) and 60% of organic compounds with a high fuel value mainly lignin along with some cellulose and hemi-cellulose fibers (Sricharoenchaikul et al., 2003). Mostly, black liquor is managed by using chemical recovery process. From this process, industries can recover chemicals and get energy for use. For eucalyptus wood, it is one of the most important raw materials for the pulp and paper production process. After eucalyptus wood passed debarking process, the eucalyptus bark residues which are the most the fibers will be occurred. Kraft pulping generates the large amount of bark residues which are solid waste. The most common way to get rid of this waste is dumping them to landfill site or combustion in the incinerator. The combustion in the incinerator releases the particulate matter, ash and unburnt materials, which causes the environment pollution. In addition, the valuable materials are lost when managed in landfill site. The costs also increase because a residues to handle, to transport and to dispose away.

From the upper problems, the efficiently waste management is an important method that should be concerned. The thermochemical conversion processes (combustion, pyrolysis and gasification) are the potential conversion methods for produce the valuable fuel-gas products from biomass wastes (Sricharoenchaikul, 2009). Among the thermochemical conversion process, biomass gasification has enchanted and it is the highest interest process (Chopra and Jain, 2007). Because of this process offers several advantages over the combustion and pyrolysis process such as fewer CO_2 emission and gasification products mainly a gas which contain higher gas fraction than pyrolysis (Arthayukti, 1985; Soongprasit, 2006). Therefore, co-gasification of the blend of black liquor with eucalyptus bark residues, which is biomass fuel, is an interest approach for manages wastes and produces fuel gases for use as energy. Co-gasification of the blend of black liquor with eucalyptus bark residues is the potential for using the product gas and the potential for improves pulping operation. Furthermore, this process has environmental benefits such as fewer CO_2 emission, waste water discharge, air emission, solid waste and reduce land use for landfill.

The aim of this research was studied about the feasibility of the co-gasification of the blend of black liquor with eucalyptus bark residues and the production of fuel gas. Black liquor that used in this study is strong black liquor and eucalyptus bark residues were got from debarking process. Both wastes were obtained from local pulp and paper industry. In this experiment, parameters that concerned such as reaction temperature, the ratio of black liquor to eucalyptus bark and equivalent ratio (the ratio of air to fuel). These variables were investigated in order to yield the highest fuel gas products such as H_2, CO and CH_4, the lowest tar and char, and the highest energy efficiency.

1.2 Objectives

1. To study the production of fuel gases from mixed sample between black liquor and eucalyptus bark residues by using fixed bed gasification process.
2. To investigate the effect of temperature, ratio of black liquor to eucalyptus bark residues and equivalence ratio on the quantity and quality of gaseous products.
3. To determine the optimum operating conditions with high energy efficiency and low char and tar.

1.3 Hypotheses

The optimum of equivalence ratio, ratio of black liquor to eucalyptus bark residues and high operating temperature are the influential variables to yield the highest fuel gas products (H_2, CO and CH_4), energy efficiency and the lowest tar and char from the gasification process.

1.4 Scopes of the study

This research deals with the gasification of the blend of black liquor with eucalyptus bark residues which are biomass wastes from the pulp and paper industry in Thailand. Black liquor was obtained from the point which passed the evaporation process and eucalyptus bark residues was obtained from debarking process which is the separation of eucalyptus bark and wood.

- The thermochemical conversion process: The fixed bed gasification process
- The ratio of black liquor to eucalyptus bark residues (on dry basis): 60:40 and 40:60
- The range of operating temperature: 700–900 °C
- The range of equivalence ratio (ER): 0.2–0.6
- The carrier gas and oxidizing gas: nitrogen and oxygen gas
- The mixed sample feeding rate : 5 g/min
- The gaseous products : CO, H_2 and CH_4

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Pulp Production

Pulping is the process which separates wood fibers. There are several different methods of pulp production to make different strengths and grades of paper. The most common classifications are chemical, mechanical, or semi-chemical pulping techniques.

2.1.1 Mechanical Pulping

Mechanical pulping utilizes steam, pressure, and high temperatures instead of chemicals to split the fibers. The fiber quality is extremely reduced because mechanical pulping creates short, weak fibers that still contain the lignin that bonds the fibers together. The lignin limits the amount that the pulp because the lignin binds with the bleaching chemicals. The products of the mechanical pulping process such as newspaper and paperboards.

2.1.2 Semi-Chemical Pulping

Semi-chemical pulping uses weak chemical solutions composed of sodium sulfite (Na_2SO_3) and sodium carbonate (Na_2CO_3) to digest the lignin in the pulp. In addition to the chemical solutions, mechanical refining is used to separate the fibers.

2.1.3 Chemical Pulping

Chemical pulping uses various chemicals to produce long, strong, and stable fibers and to remove the lignin that bonds the fibers together. Chemical pulping, dissolving the lignin in the wood to create a pulp, is the most commonly used pulping process. At present, 75% of pulp production is chemical pulping. It is a favorable method. Commonly, the chemical pulping divides into two main types. The major difference between the two types of chemical pulping is the types of chemicals used to dissolve the lignin.

- *Sulfite pulping* is easier to bleach, yields more bleached pulp, and is easier to refine for papermaking.
- *Sulfate pulping* (most commonly known as kraft pulping). The kraft process uses sodium hydroxide (NaOH) and sodium sulfate (Na_2S) as pulping chemicals. The kraft pulp produces high strength of pulp. The ability of this process can use all species of softwood and hardwood, and the favorable economics due to high chemical recovery efficiency give the kraft process an advantage over other pulping processes.

2.2 The main processes of kraft pulping and chemical recovery

This research only explains the main process of kraft pulping and the chemical recovery that current commonly uses. In the kraft pulping production, the eucalyptus timber is first chipped. Next, it is sent to the digesting (or cooking) process. Sodium hydroxide (NaOH) and sodium sulfate (Na_2S) use as the digesting agents. The schematic diagram of kraft pulp production as presents in Figure 2.1.

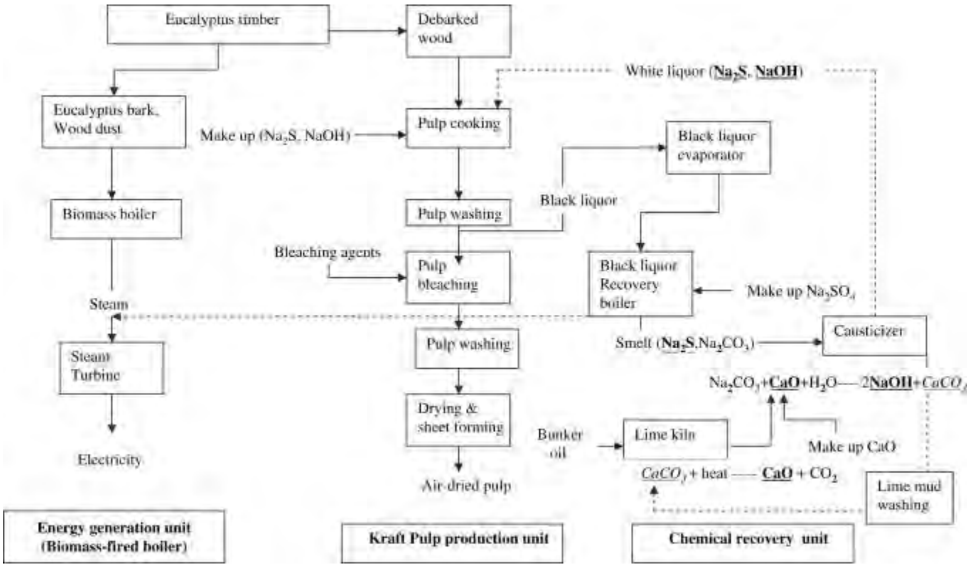


Figure 2.1 Schematic diagram of kraft pulp production (jawjit et al., 2007)

The main processes of kraft pulping and chemical pulping describes as follow;

2.2.1 Digestion process

The first step in pulping wood is to digest the wood chips. A digester cooks the wood chips in white liquor (a mix of sodium hydroxide (NaOH) and sodium sulfide (Na_2S)). The digestion dissolves most of the lignin, hemicelluloses and cellulose. After the digestion, the kraft pulp and weak black liquor are occurred as Figure 2.2.

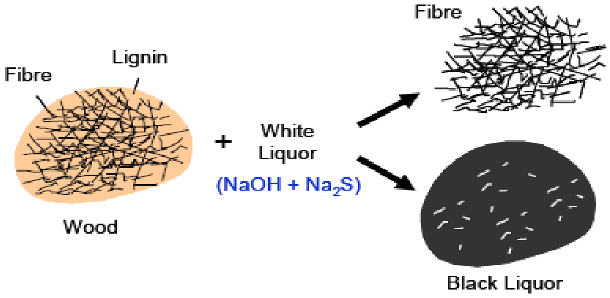


Figure 2.2 Products from the digestion process

2.2.2 Washing process

Washing removes weak black liquor from the pulp which is sent to the chemical recovery process. This also prevents contamination during subsequent processing steps. There are many types of washers. All the washer types use water (fresh or recycled) and are usually placed in series to achieve higher removal efficiency. The black liquor is diluted by the wash waste.

2.2.3 Bleaching process

The purpose of the bleaching process is to enhance the physical and optical qualities of the pulp by removing or decolorizing the lignin. Two approaches are used in the chemical bleaching of pulps. One approach called brightening uses selective chemicals, such as hydrogen peroxide that destroy chromatographic groups but do not attack the lignin. Brightening produces a product with a temporary brightness (such as newspaper) that discolors from exposure to sunlight or oxygen. The other approach (true bleaching) seeks to almost totally remove residual lignin by adding oxidizing chemicals to the pulp in varying combinations of sequences, depending on the end use of the product. This creates a longer lasting (sometimes permanent) whiteness, but it weakens the fibers and reduces sheet strength.

2.2.4 Chemical recovery

The advantage of kraft pulping is economically successful that the used cooking liquor can be recovered and reused in the chemical recovery process from the black liquor. The steps of chemical recovery are 4 steps.

Step1: Evaporation

This process removes excess water from the black liquor and maximizes the fuel value for the recovery furnace. Weak black liquor is evaporated to strong black liquor, the concentrated black liquor.

Step2: Combustion

The concentrated black liquor (strong black liquor) is burned in a recovery boiler. The objective is not only to complete the combustion of the organic matter in black liquor, but also to recover the sodium and sulfur content in a form suitable for regenerating the pulping chemicals. The overall combustion reaction can be represented by:

$$\text{Black liquor} + O_2 \rightarrow \underbrace{Na_2CO_3 + Na_2S}_{\text{(green liquor)}} + \text{flue gas} \qquad (2.1)$$

The formation of Na_2S requires a local absence of oxygen. This reduction step is critical. The only part of the recovery cycle where oxidized sulfur compounds can be converted to sulfide is during combustion. The inorganic compound melt and flow out of the furnace as a mixture of molten salts called smelt.

The recovery boiler is also a stream generator using black liquor as fuel and is a part of the mill's stream and power system. In recent year, the cost of energy has escalated, the recovery boiler has carried and increasing fraction of the stream and power load at the mill. Operating pressure has increased to allow maximum electrical power generation. High pressure stream is passed through a turbine to generate power for the mill. The lower pressure stream is extracted from the turbine used in the pulp and paper mill.

Step 3: Causticizing

The smelt leaving the furnace is dissolved in water to produce a solution called green liquor (Na_2S and Na_2CO_3). The green liquor color comes from impurities, The green liquor is clarified and causticized with lime to produce white liquor which is suitable for pulping. The reaction is

$$Na_2CO_3 + CaO + H_2O \rightarrow 2NaOH + CaCO_3 \qquad (2.2)$$

(The Na_2S passes through unchanged)

The $CaCO_3$ is insoluble in white liquor and is removed as lime mud. The strongly alkaline white liquor, containing mainly NaOH and Na_2S, is sent on to the digester again.

Step 4: Calcining

The lime is washed to remove entrained white liquor, and the weak wash liquor is sent to the dissolving tank where smelt from the furnace is dissolved in water. The washed mud is then calcined in a lime kiln or fluid bed calciner to regenerated lime. The calcining reaction is

$$\underset{\text{(lime mud)}}{CaCO_3} + \text{heat} \rightarrow \underset{\text{(lime)}}{CaO} + CO_2 \qquad (2.3)$$

The resulting lime is used for causticizing, and the calcium cycle is complete. Calcining is a high temperature, heat absorbing (endothermic) reaction. Recent trends have been toward increased thermal efficiencies for kilns and the use of substitute fuels for oil or natural gas.

2.3 Black liquor

Black liquor is a by-product from the chemical kraft pulping process; consist mainly of degraded lignin, dissolved wood components, residual inorganic pulping chemical and water (Frederick et al., 1994; Preto et al., 2008; Carlsson et al., 2010). Black liquor is liquid biomass which is also an important renewable liquid fuel and a source of energy for the pulp and paper industry (Preto et al., 2008). Black liquor generates after digester and washer process which are described in Section 2.2.

2.3.1 Black liquor properties and analysis

The amount of black liquor solids produced per unit amount of pulp production varies considerably depending primarily on yield

- *Composition of black liquor*

The substances in black liquor derive from two sources, wood and white liquor. The dissolved wood substances consist of the following classes:

Ligneous materials	(polyaromatic in character)
Saccharinic (hydroxy)	(degraded carbohydrate)
Low molecular weight organic acids	
Extraction	(fatty acid and resins)

These organic constituents are combined chemically with sodium hydroxide (NaOH) in the form of sodium salts. The inorganic constituents in black liquor are

Sodium hydroxide	(NaOH)
Sodium sulfide	(Na_2S)
Sodium carbonate	(Na_2CO_3)
Sodium sulfate	(Na_2SO_4)
Sodium thiosulfate	($Na_2S_2O_3$)
Sodium chloride	(NaCl)

These substances introduce from the white liquor used for pulping. Small amount of inorganic chemicals can enter with the wood.

- *Composition Data*

The composition of black liquor depends on the alkali charge (and with liquor composition), pulp yield, and the wood species used. Considerable differences exist between liquor from different species, especially between hardwood and softwood liquors. Typical ranges for kraft liquor are as follows;

Alkali lignin	30-45%
Hydroxy acids	25-35%
Extractives	3-5%
Acetic acid	2-5%
Formic acid	3-4%
Methanol	1%
Sulfur	3-5%
Sodium	17-20%

- *Nature of constituents*

Lignin : The alkali lignin in black liquor is degraded from its state in wood. Upon wood pulping with a NaOH + Na_2S solution, the lignin fraction of wood is solubilized. Lignin is the main component of the black liquor which is separated from cellulose (Rodriguez-Mirasol et al, 1995). There are condensed, crosslinked macromolecules containing many aromatic group of related structure such as phenols, catechols, and quonones.

Hydroxy and low M.W. organic acids: Practically all of the carbohydrates dissolved during kraft pulping are degraded to a complicated mixture of nonvolatile hydroxyl acid and simple mono or dicarboxylic acids. Rhese substances are very soluble in water and show no apparent tendency to precipitate from concentrated liquor. They tie up a significant portion of the sodium in the black liquor. Because these substances are well oxygenated, they have relatively low heating values.

Extractives: The extractives in the wood tend to pass through the pulping process unchanged. They can be considered to be made up of three groups, resin acids, fatty acids, and n eutrals. They are present in the black liquor as soaps. Soap begins to precipitate from the black liquor as it is concentrated.

Inorganic compounds: There are many simple inorganic salt present. The inorganic salts come directly from white liquor. The main white liquor components are NaOH and Na_2S.

2.3.2 Black liquor managements

- *Recovery process*: The energy and chemicals in the black liquor are recovered in recovery process. The heat released as a result of black liquor combustion is recovered as high pressure and temperature superheated steam in the recovery boiler. The efficiency in converting the fuel value in kraft black liquor to steam is typically lower than for fossil fuel combustion, because of the heat used to evaporate the water in black liquor, the heat of reaction consumed in producing Na_2S, and the heat carried out with the molten smelt. The kraft recovery process is not easy to operate at high efficiency. Many problems can occur. Recovery boilers also have many problems including fouling of heat transfer tubes and plugging of flue gas, tube corrosion and cracking, floor tube damage, low steam production, water and air emissions. The combustion in recovery process consumes excess oxygen. More of pollution gases occur such as carbon dioxide gas was produced which have low calorific value and this gas is greenhouse gas that effects the environment.
- *Black liquor gasification:* It is essential for the economy of the pulping process that the chemicals can be regenerated and recycled to the process. This means that the recovery process must be an efficient chemical reactor while also being able to convert the energy contained in the black liquor to useful heat and power. But recovery process has many problems both processing and environment impacts. Then, the new trend method that received driving force is gasification. Gasification is an interest process that converts the organic substances in black liquor into combustible fuel gases, mainly carbon monoxide and hydrogen. This development has been the potential for much greater electricity production if the gas produced can be burned in a gas turbine for combined-cycle power generation.

In addition, inorganic was converted into suitable compounds for pulping chemical. The energy efficiency of a pulp mill could significantly increase if the current combustion energy recovery system was replaced by a black liquor gasification system.

2.4 Eucalyptus

Eucalyptus is a diverse genus of flowering tree. There are more than 700 species of eucalyptus, mostly native to Australia (source: http://en.wikipedia.org/wiki/Eucalyptus). Hence, eucalyptus is generally regarded as an Australian tree (Thaiutsa and Taweesuk, 1987). Many of eucalyptus species are known as gum trees because they exude copious sap from any break in the bark (Source: http://en.wikipedia.org/wiki/Eucalyptus).

2.4.1 Wood chemistry (Browning, 1970)

The chemistry of wood is determined by the chemistry of wood components. The substances present are diverse, resulting from the formation and growth of wood as a biological organism. Wood components are

- *Cell wall components :* Almost all the carbohydrate in wood are composed of long polymeric chains of anhydro sugar units that are called “polysaccharides”. They form a partially ordered structure. Lignin is distributed in the structure, but is concentrated particularly in the middle lamella that forms the typical intercellular material.
- *Cellulose:* The main polysaccharide is cellulose, which is the wall material of plant cells. Cellulose is composed of longer chains; chemically it is classed as a glucan. The chain in native cellulose is composed of as many as 10,000 glucose units. Cellulose is insoluble in water, common organic solvents, and aqueous alkaline solutions.
- *Hemicelluloses:* A group of polysaccharides that are collectively called hemicelluloses always accompanies cellulose in plant. The hemicelluloses comprise a diverse group of polysaccharide polymers, but the two most important classes are the galactoglucomannans and the glucoronoarabinoxylans. They have a

slightly branched structure (or linear anhydro sugar backbone with sides units), and have a much lower molecular weight than cellulose. The hemicelluloses are distinguished analytically from cellulose by the greater ease of hydrolysis in hot, dilute, acid solutions, and by solubility in aqueous alkaline solutions.

- *Lignin:* Lignin fills the spaces in the cell wall between cellulose and hemi- cellulose. High lignin wood is a good raw material for pulping to make paper. Lignin must be removed from the pulp before bleached paper. It presents in black liquor that usually burned to produce fuel.

2.4.2 Eucalyptus in Thailand

The eucalyptus wood is the dominant raw material for the pulp and paper production process in Thailand. Exactly, when eucalyptus was introduced to Thailand is not clearly recorded. Although many species of eucalyptus were introduced into Thailand, only a few species and provenances show promising survival and growth. *E. camaldulensis* seems to be the first choice and most popular. It can adapt in saline soils of the north eastern Thailand, and tolerates a variety of climatic conditions. Recently, eucalyptus planting has increased quite substantially both by state and the private sectors. This may be due to these facts. Eucalyptus is relatively easy to establish, provided they are given the right start and the right species are used at the right site. The survival and growth rate of eucalyptus is good.

2.4.3 Eucalyptus bark residues from papermaking and management

Eucalyptus pulps are recommended for papermaking due to specific properties that they impart to paper: bulk, opacity, formation, softness, porosity, smoothness, absorbency, and dimensional stability (Foelkel 2008)

In papermaking, bark removal is required because of the negative effects of bark on pulping process and product quality. Kraft pulping generates the largest amount of bark residues which are solid waste. (United Nation Environment programme, 1982).

Figure 2.3 The eucalyptus bark residues pile in pulp and paper industry

The eucalyptus bark residues are a major solid waste in pulp and paper industry as shown in Figure 2.3. They are hazardous waste because they can ignition by itself. Acceptable disposal methods include incineration for heat generation, compositing and utilization as filler in building block. But the combustion in incinerator releases the particulate matter, ash and residues unburnt material, which causes the environment pollution.

The most of solid waste from the pulping operation is normally disposed of within the industry site as shown in Table 2.1. (United Nation Environment programme, 1982). It is a major waste problem of pulp and paper industry. The good waste management must be concerned. Gasification is a thermoconversion process which chosen replacement of the incineration of bark and biomass waste.

Table 2.1 Most important types of waste generated by the pulp industry (United Nation Environment programme, 1982).

Types of waste	Source	Destination
Bark	Debarking	Incineration (disposal)
Dust and slag	Fuel combustion	Disposal
Residues from chemical recovery system	Recovery system (chemical pulping)	Disposal
Lime mud	Recovery system (kraft pulping)	Disposal

2.5 Biomass

Biomass is a general term to describe all organic carbon-containing material produced by photosynthesis in plants (Boerrigter and Rauch, 2005). Parikka (2004) estimated that the total worldwide energy potential from biomass on a sustainable basis to be 104 EJ/year, of which woody biomass, energy crops and straw constituted 40.1%, 36% and 16.6%, respectively. There are many ways of classifying biomass. Generally, it can be divided into woody biomass and non-woody biomass. This research divided biomass types into eight categories (Rosillo-Calle et al., 2007). Examples of biomass are:

- Agro-industrial plantation wastes: These are forest plantation specifically intended to produce agro-industrial raw materials. Example included tea, coffee, rubber trees, bamboo, oil and coconut palm)
- Crop residues: These include crop and plant residues produced in the field. Examples include straw, leaves and plant stems.

- Processed residues: These include residues from the agro-industrial or processing of crops such as sawdust, bark, bagasse, rice husks, nut shell and sawmill off-cuts.
- Forest plantations: These include both commercial plantations (pulp and paper and furniture) and energy plantation (tree devoted to producing energy such as charcoal and other energy uses)
- Agricultural crops: These include crops that are grown for food, fiber, and energy production.
- Animal wastes: These comprise waste from intensive and extensive animal husbandry. Animal waste may also have a better value as fertilizer. In addition, animal wastes are more frequently used for producing biogas for environmental rather than energy purposes.
- Natural forests/woodlands: These include all biomass in high standing, closed natural forests and woodlands. Thos category will also include forest residues.
- Trees outside forest and woodlands: These include tree grown outside forest or woodlands, consist of bush trees, urban trees, roadside trees and on-farm trees. Tree outside forests have a major role as sources of fruits, firewood, etc.

Biomass includes a wide range of organic materials, which are generally contained cellulose, hemicellulose, lignin, lipids, proteins, simple sugars and starches. Among these compounds, the three main constituents of biomass are cellulose, hemicellulose, and lignin. Biomass also contains inorganic constituents and a fraction of water. Carbon, hydrogen and oxygen are the major compositions of biomass. In addition, there are trace amounts of hydrogen, nitrogen and chlorine (Kirubakaran et al., 2009; Zhang el at., 2010),

Biomass combines solar energy and carbon dioxide into chemical energy in the form of carbohydrates through photosynthesis. Biomass is a renewable resource. The use of biomass as a fuel is a carbon neutral process since the carbon dioxide captured during photosynthesis is released during its combustion (Kumar et al., 2009). In addition, the lower emission of environmentally harmful gases, such as sulfur dioxide (SO_2) and nitrogen oxides (NO_x), during the combustion of biomass is a positive role in reducing global warming and acid rain formation (McKendry, 2002; Zhang el at., 2010).

2.6 Biomass conversion technologies

Biomass is the solar energy stored in chemical form in plant and animal materials. It provides not only food but also energy, building materials, paper, medicines and chemicals. Today, biomass is considered the renewable energy source with the highest potential to contribute to the energy. Two main ways of converting biomass energy are biochemical conversion and thermochemical conversion processes.

2.6.1 Biological conversion technology

This processes such as anaerobic digestion and fermentation which lead to produce a useful gaseous or liquid fuel. Anaerobic digestion occurs in the absence of air like pyrolysis but in this case the decomposition is caused by bacterial action rather than high temperatures. It is a process which takes place in almost any biological material that is decomposing and is favored by warm, wet and of course, airless conditions. In this case the gas product is a mixture mainly of methane and carbon dioxide usually called as biogas.

2.6.2 Thermochemical conversion technologies

Thermochemical conversion technologies include combustion, pyrolysis and gasification. Thermochemical conversion technologies have certain advantages and disadvantages over biochemical conversion technologies. The main advantages are that the feedstock for thermochemical conversion can be any type of biomass including agricultural residues, forestry residues, non-fermentable byproducts from biorefineries, byproducts of industry, byproducts of any bioprocessing facility and even organic municipal wastes. The product gases from thermochemical conversion can be converted to a variety of fuels (H_2, Fischer-Tropsch (FT) diesels, synthetic gasoline) and chemicals (methanol, urea) as substitutes for petroleum-based chemicals. The major disadvantages are the high cost associated with cleaning the product gas from tar and undesirable contaminants like alkali compounds, inefficiency due to the high temperatures required, and the unproven use of products (syngas and bio-oil) as transportation fuels

.

2.6.2.1 *Combustion*

This process is the oxidation of biomass. The combustion of biomass is the most direct and easiest process. The overall efficiency of generating heat from biomass energy is low. Combustion of wood can be divided into four stages with increasing temperature described as follows:

In the initial stage water inside the wood evaporates as temperature increases. In the second stage, the volatile content is freed from the wood. In the third stage, the gases emitted are mixed with air and burn at a high temperature. The proportions of mixing should be enough for combustion to take place and a flame should be present to ignite the combustible gas mixture. In the fourth stage, after gases have been the excreted, remaining wood (mostly carbon in the form of char) burns and ash is left as a residue in the end. The parameters necessary for effective burning are: high enough temperatures, enough air, and long enough residence time for complete combustion. For complete combustion of solid fuels, excess air is needed, and high combustion temperatures generate more NO_x and other emissions, as compared with the products by gasification.

2.6.2.2 *Pyrolysis*

Pyrolysis is the thermal decomposition of organic matter by heat in the absence of air, typically at 300–500 °C, until the volatile matter has been released from the biomass. Pyrolysis generally converts biomass into three products (Basu, 2006) by following:

- Light gases such as H_2, CO, CO_2, H_2O, and CH4
- Char, a solid residue mainly containing carbon
- Tar, a black, viscous and corrosive liquid composed of heavy organic and inorganic molecules.

2.6.2.3 *Gasification*

Gasification is the conversion of carbonaceous materials (coal, petroleum coke, biomass, etc) into a combustible gas called producer gas (Balat et.al, 2009; Soongprasit, 2006). This process is a partial oxidation of fuel at elevated temperature (McKendry, 2002). In a sense, gasification is a form of incomplete combustion. The producer gas is a mixture of carbon monoxide, hydrogen and methane, together with carbon dioxide and nitrogen. Gasification of biomass is generally observed to follow this reaction;

$$\begin{aligned}\text{Biomass} + O_2\,(\text{or } H_2O) \rightarrow\ & CO, CO_2, H_2O, H_2, CH_4 \\ & + \text{other } CH_s + \text{tar} + \text{char} + \text{ash} \qquad (2.4)\end{aligned}$$

In a broad sense, it includes evaporation by heating, although the term is generally reserved for processes involving chemical change. Also coal gasification (Figure 2.3) refers to the over all process of converting coal to a product gas, including the initial pyrolysis and subsequent gas upgrading steps. In this section the term applied more narrowly to the gas phase and gas-solid chemical reactions that occur at elevated temperatures within the gasifier itself (Probstein and Hicks, 1982).

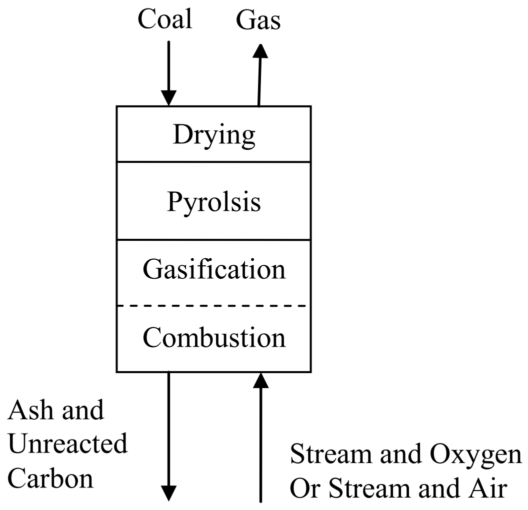


Figure 2.4 Schematic of moving bed gasifier (Probstein and Hicks, 1982)

2.7 Gasification process (Kumar el at., 2009; Boerrigter and Rauch, 2005; Draphco el at., 2008)

Gasification takes place at high temperature in the presence of an oxidizing agent (also called a gasifying agent). Heat is supplied to the gasifier either directly or indirectly which raises the gasification temperature of 600–1,000°C. Oxidizing agents are typically air, steam, nitrogen, carbon dioxide, oxygen or a combination of these. In the presence of an oxidizing agent at high temperature, the large polymeric molecules of biomass decompose into lighter molecules and eventually to permanent gases (CO, H_2, CH_4 and lighter hydrocarbons), ash, char, tar and minor contaminants. Char and tar are the result of incomplete conversion of biomass as shown in Figure 2.5.

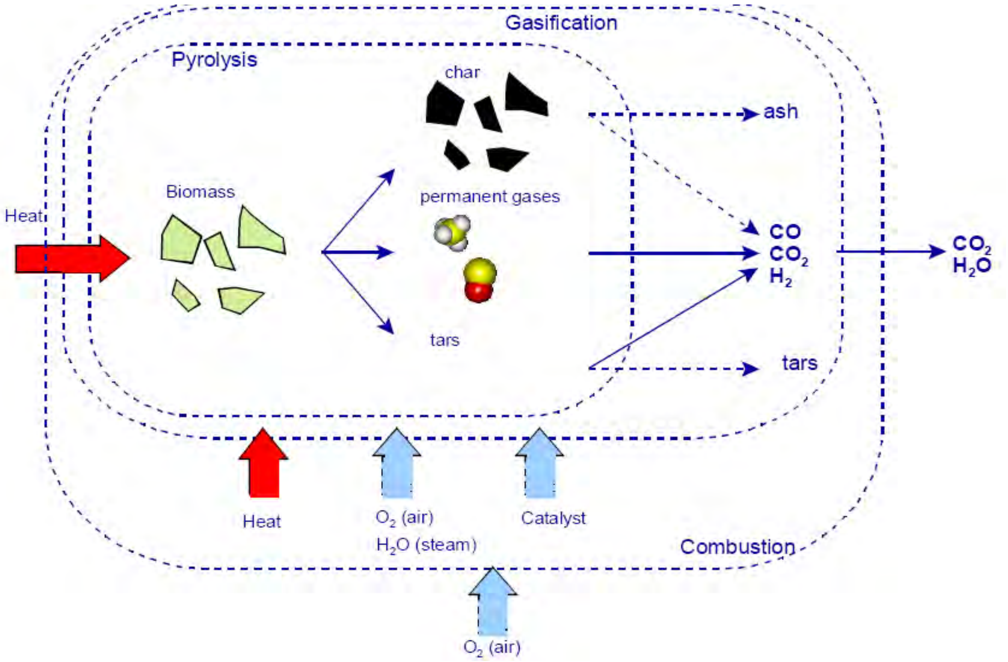


Figure 2.5 Schematic of gasification process (Knoef, 2005)

Gasification is a two-step, endothermic (i.e. heat absorbing) process. In the first reaction, pyrolysis, the volatile components of the fuel are vaporized at temperatures below 600°C. The volatile vapours consist of hydrocarbon gases, hydrogen, carbon monoxide, carbon dioxide, tar, and water vapour. As biomass fuels tend to have more volatile than coal, pyrolysis plays a major play in biomass gasification than in coal gasification. Char (fixed carbon) and ash are the pyrolysis by-products, which are not vaporized. In the second step, the char is gasified through reactions with oxygen, steam, carbon monoxide and hydrogen. The heat needed for the endothermic gasification reactions is generated by combustion of part of the fuel, char, or gases, depending on the reactor technology.

The overall reaction in an air and/or steam gasifier can be described by Equation 2.5

$$CHxOy\text{ (biomass)} + O_2\text{ (21\% of air)} + H_2O\text{ (steam)} \rightarrow CH_4 + CO + CO_2 + H_2 + H_2O\text{(unreacted steam)} + C\text{ (char)} + \text{tar} \quad (2.5)$$

Equations 2.6–2.12 are common reactions involved during gasification. Among these, Equations 2.8–2.11 occur when steam is available during gasification.

Exothermic reactions

$$C + \tfrac{1}{2} O_2 = CO\text{ (partial oxidation reaction)} \quad (2.6)$$

$$C + O_2 = CO_2\text{ (complete oxidation reaction)} \quad (2.7)$$

$$C + 2H_2 = CH_4\text{ (hydrogasification reaction)} \quad (2.8)$$

$$CO + H_2O = CO_2 + H_2\text{ (water gas shift reaction)} \quad (2.9)$$

$$CH_4 + H_2O = CO + 3H_2\text{ (steam reforming reaction)} \quad (2.10)$$

Endothermic reactions

$$C + H_2O = CO + H_2\text{ (water gas reaction)} \quad (2.11)$$

$$C + CO_2 = 2CO\text{ (Boudourd reaction)} \quad (2.12)$$

2.7.1 Effects of gasification operating conditions on the product properties (Kumar el at., 2009)

To obtain the desired product gas composition, the least amount of impurities, and to increase the net energy conversion efficiency, the gasification operating conditions need to be optimized. The following section describes the effects of the main operating conditions on the quantity and composition of the product gas and its impurities.

- Biomass flow rate, type and properties

Overfeeding of biomass can lead to plugging and reduced conversion efficiencies whereas starve-feeding results in less gas yield. Hence, an optimum biomass flow rate is desired for the gasification system to maximize energy efficiency. Optimum biomass flow rate is depend on the design of the gasifier and the properties of the biomass. Co-firing of biomass with coal also is being studied. Kumabe (2007) observed that by varying the ratio of coal to biomass for the gasification, the extent of the water gas shift reaction was maximal at the ratio of 0.5 which they attributed to the synergy between the coal and biomass. With increase in biomass ratio, they observed increases in gas and CO_2 yields, decreases in char, tar and H_2 but CO, and hydrocarbons (HCs) were unchanged. Gasification of coal with biomass reduces problems associated with high ash and sulfur contents of the coal

- Air flow rate (equivalence ratio, ER)

Equivalence ratio (ER) is measurement of the air (or oxygen) flowrate. ER is the ratio of airflow to the airflow required for stoichiometric combustion of the biomass, which indicates extent of partial combustion. Higher airflow rate results in higher temperature which leads to higher biomass conversion and a higher quality of fuel. But, an excess degree of combustion, on the other hand, results in decreased energy content of the gas produced because a part of biomass energy is spent during combustion. Higher airflow also shortens the residence time which may decrease the extent of biomass conversion.

- Temperature

Gasification temperature is one of the most important factors affecting the product gas composition and properties. Higher temperature results in increased gas yield because of higher conversion efficiency. Since, the reactions (Equations 2.6–2.11) occur simultaneously, the contents and ratios of H_2, CO, CO_2 and CH_4 in the product gas are affected by temperature and partial pressures of reactants. Complete gasification is achieved at temperature above 500 °C (Kirubakaran et al., 2007). At temperatures above 750–800 °C, the endothermic nature of the H_2 production reactions (steam reforming and water-gas reactions) results in an increase in H_2 content and a decrease in CH_4 content with an increase in temperature. At temperatures above 850–900 °C, both steam reforming and the Boudouard reactions (Equations 2.10–2.12) dominate, resulting in increases in CO content. High temperature also favours destruction and reforming of tar leading to a decrease in tar content and an increase in gas yield.

2.7.2 Product gas characteristics (Probstein and Hicks, 1982)

- Hydrogen and carbon monoxide production increases with decreasing oxygen, pressure, and with increasing temperature. Hydrogen increases and carbon monoxide decreases with increasing stream rate. Additional stream must then be added in a shift converter in which the hydrogen to carbon monoxide ratio is increased by oxidizing some of carbon monoxide following Equation 2.9.

$$CO + H_2O = CO_2 + H_2 \text{ (water gas shift reaction)} \qquad (2.9)$$

- Methane production is favored by low temperature and high pressure. Variations of feed conditions do not significantly affect its formation

- Carbon dioxide production increases with increasing oxygen and pressure. However, at high temperature carbon dioxide formation suppressed in favor of carbon monoxide.

2.7.3 Utilizations of product gas (Kumar el at., 2009 ; Draphco el at., 2008)

The main application at presence of product gas from gasification is found in direct or indirect combustion to generate power with co-production of heat. The syngas components are H_2 and CO. The utilizations of product gas are;

2.7.3.1 *Power generation*

The main advantages of producing heat and electricity using gasification over direct combustion are (a) fuel-gas based technologies such as gas engines or gas turbines can achieve higher efficiencies than combustion efficiency, (b) the overall efficiency of gasification is higher because gaseous fuels, having improved combustion characteristics, burn more efficiently than solid fuel, and (c) production of gas provides an opportunity to remove contaminants that ultimately produce NO_x and SO_x emissions

- *Co-firing*

The application of product gas is co-firing in existing coal power plants by injecting the product gas in the combustion zone of the coal boiler. Co-firing percentages up to 10% (on energy basis) are feasible without the need for substantial modifications of the coal boiler. Critical issue in co-firing is the impact of the biomass ash on the quality of the boiler fly and bottom ash. The application of the fly and bottom ash in construction and cement production often sets the specifications for the amount and type of biomass that can be co-fired.

- *Combined heat and power (CHP)*

In combined heat and power (CHP) plants the product gas is fired on a gas engine. Modified gas engines can run without problems on most product gases even those from air-blown gasification that have calorific values of approximate 5-6 MJ/m^3. The main technical challenge in the implementation of integrated biomass gasification CHP plants has been, and still is, the removal of “tar” from the product gas. Tar aerosols and deposits lead to more frequent maintenance and repair of especially gas cleaning equipment. This leads to a decrease of revenues or to higher investments. In 1998, Berglin and Berntsson studied CHP in the pulp industry using black liquor gasification.

- *Integrated gasification combined cycle (IGCC)*

In practice, the scale of integrated biomass gasification CHP plants will be limited by the local heat demand. For electricity production on larger scales, integrated gasification combined cycles (IGCC) are preferred in which the gas is fired on a gas turbine.

- *Fuel cells*

The product gas application in fuel cells for the production of electricity is still early development. In theory, the electrical efficiencies of fuel cells have higher than simple combustion systems and gas engines. The fuel cell can be connected to a gasifier, is a simpler system, to have a high electric efficiency and a high overall efficiency in a CHP (combined heat and power) system. A fuel cell burns H_2 and produces electricity directly through electrochemical reactions. Depending on the type of fuel cell, also CO, CH_4 and other fuels can be converted.

2.7.3.2 *Synthetic Natural Gas (SNG)*

SNG is a gas with similar properties as natural gas but produced by methanation of H_2 and CO in gasification product gas. Whereas high-temperature gasification processes yield biosyngases with high concentrations of carbon monoxide and little methane, interest in Synthetic Natural Gas (SNG) production is concentrated on gasification processes that yield product gases with high methane contents. Methanation is the catalytic reaction of carbon monoxide and/or carbon dioxide with hydrogen, forming methane and water;

$$CO + 3H_2 = CH_4 + H_2O \tag{2.13}$$

The methanation reactions of both carbon monoxide and carbon dioxide are highly exothermic. Such high heat releases strongly affect the process design of the methanation plant since it is necessary to prevent excessively high temperatures in order to avoid catalyst deactivation and carbon deposition.

2.7.3.3 *Catalytic synthesis of methanol and higher alcohols*

CO, H_2, CO_2 and H_2O are used to produce methanol using methanol synthesis reactions in the temperature range of 220 to 300 °C and pressures of 50 to 100 bars using Cu/ZnO catalysts (Equations 2.9 and 2.14). Methanol is used as a heat fuel or as a blend with gasoline. It is, however, widely used as a component of methyl tertiary-butyl ether (MTBE), which is a high octane oxygenate that is added to gasolines. Methanol is used for making various fuels and chemicals. Currently, it is used primarily for making formaldehyde, dimethylether and acetic acid. Methanol also is used for converting fats and oil to biodiesel.

$$CO + H_2O \; = \; CO_2 + H_2 \qquad (2.9)$$

$$CO_2 + 3H_2 \; = \; CH_3OH + H_2O \qquad (2.14)$$

Furthermore, syngas can be converted to higher alcohols using catalysts.

2.7.3.4 *Fischer-Tropsch Synthesis (FTS) diesel and gasoline*

The Fischer Tropsch (FT) process is a method to produce alkanes from syngas as represented by Equation 2.15.The process takes place at 20 to 40 bars and 180–250 °C. The FT product needs to be hydrocracked with H_2 to reduce the double bonds of unsaturated hydrocarbons producing hydrocarbons in the diesel fuel range. Larger (higher than C5) hydrocarbons are desired for use as liquid fuels. FT products are free of sulfur. The yield of FT diesel is estimated to be 120 L/mt biomass with a prediction of ultimately reaching 210 L/mt. The research challenge for the FT synthesis process is to narrow the range of resulting hydrocarbons. The chain lengths of FT products vary from 1 to 50 producing hydrocarbons ranging from methane, gasoline range, diesel range, naphtha, kerosene, to heavy waxes.

$$CO + H_2 \; = \; C_xH_y + H_2O \qquad (2.15)$$

Around 2.1:1 H_2/CO ratio is desired for FT synthesis depending on selectivity. As syngas from biomass gasification has less H_2/CO ratio, shift reactions are required to increase the H_2 content suitable for the FT process.

2.7.3.5 *Fermentation of syngas to ethanol*

Fermentation of synthesis gas (Equations 2.16 and 2.17) is a process to produce ethanol as a transportation fuel. The fermentation takes place at lower temperature as compared to catalytic conversion of the synthesis gas to liquid fuels; the wet gas cleaning can be used for removal of impurities from the product gas. Moreover, ethanol (blended with gasoline) has been used successfully as a transportation fuel. As compared to the biochemical conversion with hydrolysis and fermentation processes, gasification and fermentation have potential to use a much wide variety of feedstock producing ethanol.

$$6CO + 3H_2O \rightarrow C_2H_5OH + 4CO_2 \qquad (2.16)$$

$$6H_2 + 2CO_2 \rightarrow C_2H_5OH + 3H_2O \qquad (2.17)$$

2.8 Types of gasifier

Several types of gasifiers have been developed. These gasifiers have different hydrodynamics (especially the way in which the solid fuel and the gasification agent are contacted), gasification agents (air, oxygen and/or stream) and operating conditions such as temperature and pressure (Balat et al., 2009). Gasifiers are categorized based on types of bed and flow. The most important types are fixed bed (updraft or downdraft fixed beds) gasifiers, fludized-bed gasifiers and entrained flow gasifiers.

2.8.1 Fixed bed gasifiers

The particles that fed into gasifier remain fixed in their positions, the equipment is called a fixed-bed gasifier. Fixed bed gasifiers are usually fed from the top of the reactor. The different fixed bed gasifier types are often characterized by the direction of gasflow through the reactor or the direction of solid flow. Fixed bed gasifier can be classified into three types: updraft gasifiers, downdraft gasifiers and cross draft gasifiers (Figure 2.7).

2.8.1.1 *Updraft (countercurrent) gasifiers*

The updraft gasifier is the older and simplest form fixed bed gasification. In the updraft gasifiers, the fuel (biomass) is introduced from the top and moves downwards while carrier and gasifying agents (N_2, air, oxygen, steam etc.) are introduced at the bottom of the gasifier so the product gas moves upwards. In this case, the combustion takes place at the bottom of the bed which is the hottest part of the gasifier and product gas exits from the top at lower temperature (around 500 °C). Because of the lower exit temperature, the product gas contains large amounts of tar. The dust content in producer gas is low because low gas velocities.

In their downward movement, the biomass particles undergo the following main processes: drying, devolatilization (pyrolysis), gasification, and combustion. These processes that occurring in the updraft gasifier is described as Figure 2.6 starting from the top of the fuel bed.

- *Drying of fuel*

During this event, the temperature of the fuel is increased and the moisture is evaporated by heat exchange between the fuel and the hot gas stream that is coming from the combustion zone.

- *Devolatilization (Pyrolysis zone)*

The temperature of the fuel is increased further and the volatile products are released from fuel thereby leaving char. For all biomass, volatiles represent a significant portion of the fuel and in gasifiers; devolatilization provides part of the produced gases. The release of volatiles is driven by increase of temperature. As the fuel slowly descend, the hot gases produced in the gasification and combustion zones exchange energy with the colder solid. Three main fractions are produced during pyrolysis of biomass:

1. Light gases: H_2, CO, CO_2, H_2O, and CH_4.
2. Tar: composed of relatively heavy organic and inorganic molecules that escape the solid as gases and liquid in the form of vapor.

3. Char: the remaining solid residue.

- *Gasification (reduction)*

After drying and pyrolysis, the char enters the gasification zone where carbon reacts with steam, carbon dioxide, and hydrogen. Endothermic reactions in this section produce carbon monoxide and hydrogen (Equations 2.11 and 2.12). The slightly exothermic reaction of hydrogen with carbon produces methane (Equation 2.8). The carbon monoxide produced also reacts with water to produce hydrogen and carbon dioxide in the water gas shift reaction (Equation 2.9). Differentiation between the gasification zone and combustion zone is based on the presence or absence of oxygen. The reactions that take place in this region of the gasifier can be represented by;

$C + 2H_2 = CH_4$ (hydrogasification reaction) (2.8)

$CO + H_2O = CO_2 + H_2$ (water gas shift reaction) (2.9)

$C + H_2O = CO + H_2$ (water gas reaction) (2.11)

$C + CO_2 = 2CO$ (Boudourd reaction) (2.12)

Equations 2.11 and 2.12 are main reduction reaction and are endothermic have the capability of reducing gas temperature. Mostly, the temperature in gasification zone is 800-1,000°C. Lower the gasification zone temperature (about 700-800 °C) produced calorific value of producer gas (Rajvanshi, 1986).

- *Combustion*

The remaining char is burned, using oxygen from air in the feed gas and leaving an ash residue according to

$C + \frac{1}{2} O_2 = CO$ (partial oxidation reaction) (2.6)

$C + O_2 = CO_2$ (complete oxidation reaction) (2.7)

$2CO + O_2 = 2CO_2$ (2.18)

From the point of view of energy generation and consumption, if taken as irreversible, the combination of exothermic Equations 2.6 and 2.18 involves an energy input of carbon and is mainly responsible for the energy requirements of the process. This energy is used to promote and sustain the gasification and pyrolysis reactions, which are mostly endothermic.

The major advantages of fixed bed gasifiers are its simplicity, high charcoal urn-out and internal heat exchange leading to relatively low gas exit temperatures and high gasification efficiencies. Because of the internal heat exchange the fuel is dried in the top of gasifier and therefore fuels with high moisture content (up to 60%) can be used. Furthermore, this type of gasifier can even process relatively small sized fuel particles and accepts some size variation in the fuel feedstock. Major drawbacks are the high amounts of tar and pyrolysis products, because the pyrolysis gas is not combusted. This is of minor importance if the gas is used for direct heat applications, in which the tars are simply to burnt. In case the gas is used for power generation, extensive gas cleaning is required (Knoef, 2005).

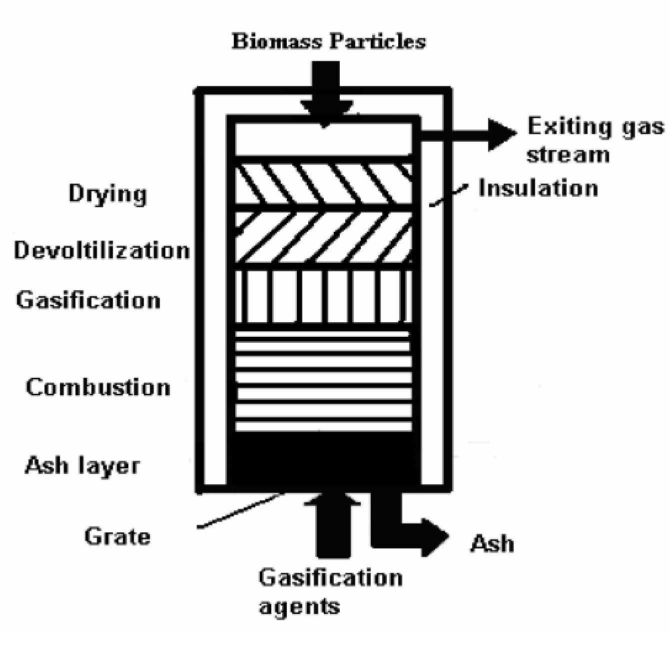


Figure 2.6 Process zone of updraft fixed bed gasifier

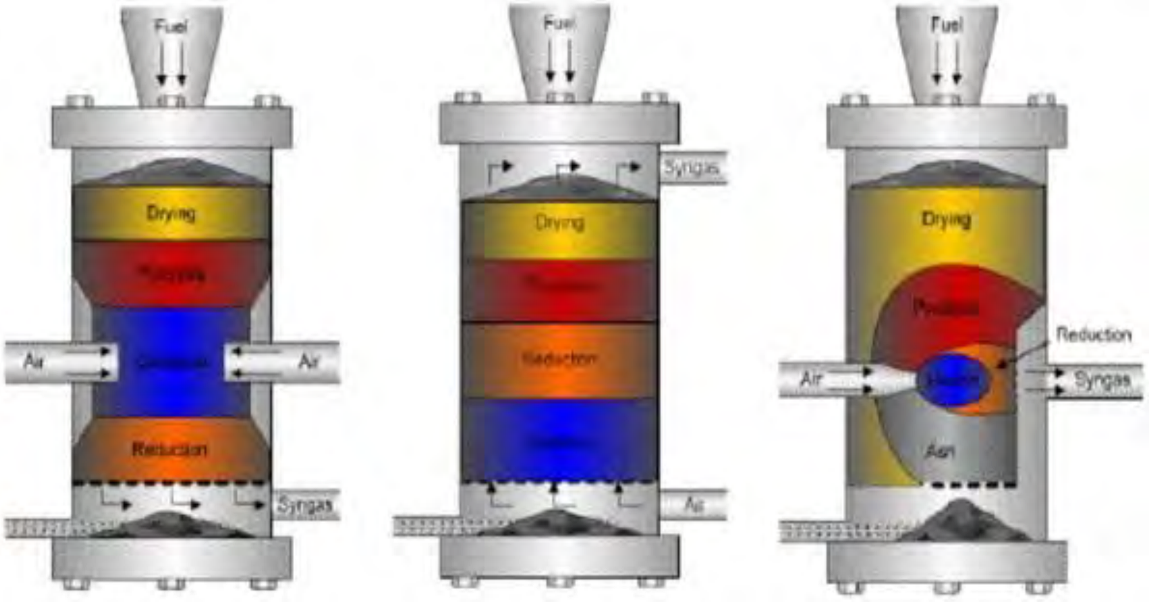
2.8.1.2 *Downdraft gasifiers*

In downdraft gasifiers, biomass is fed at the top and the air intake is also at the top or form the side. The product gas exits at the bottom of the reactor with higher temperature. So, the fuel moves in the same direction. In this case, most of tars are consumed because the gas flows through a high temperature region. However, heat needs to be recovered from high temperature product gas to increase the energy efficiency.

The main advantage of dawndraft gasifier is the production of gas with low tar content, which is nearly suitable for engine applications. Downdraft gasifiers produce the lowest level of tar and are therefore the best option for engine applications.

2.8.1.3 *Crossdraft gasifier*

In a crossdraft gasifier, biomass is added at the top of the reactor and moves downwards. Air is introduced from one side of the reactor and the gas products are released from the other side of the reactor on the same horizontal level. The combustion zone is located in the area of air injection, and the drying and pyrolysis zones are above the vessel.



Downdraft gasifier Updraft gasifier Crossdraft gasifier

Figure 2.7 Three types of fixed bed gasifiers (Olofsson et al., 2005)

2.8.2 Fluidized bed gasifier

The fluidized bed gasifier, the feed gas is introduced at the bottom, which is fluidized using air, nitrogen and/or steam and the product gas then moves upward. There are more particulates in the product gas from this gasifier. Fluidization of the bed enhances the heat transfer to the biomass particle leading to increases in reaction rates and conversion efficiencies. Fluidized beds also are able to tolerate a wide variation in fuel types and their characteristics. A fluidized bed can be either a bubbling fluidized bed or a circulating fluidized bed. Fluidized bed systems can also have high volumetric capacity and the temperature can be easily controlled. Table 2.2 compared advantages and disadvantage of various types of fixed bed gasifier and fluidized bed gasifier.

Table 2.2 Advantages and Disadvantages of various types of fixed bed gasifier and fluidized bed gasifier

Gasifier Type	Advantages	Disadvantages
Updraft fixed bed	- simple, inexpensive process - small pressure drop - high carbon efficiency - little tendency towards slag formation - less sensitive to variations in size and quality of fuel - low dust levels in gas	- great sensitivity to moisture - large tar production - relatively long time required for start up of IC engine - poor reaction capability with heavy gas load - small feed size
Downdraft fixed bed	- flexible adaptation of gas production to load - low sensitivity to charcoal dust and tar content of fuel	- design tends to be tall - very sensitive to feedstock size and quality, not feasible for very small particle size of fuel
Crossdraft fixed bed	- short design height - very fast response time to load - flexible gas production	- very high sensitivity to slag formation - high pressure drop
Fluidized bed	- flexible feed rate and composition - able to pressurize - high CH_4 in product gas - high volumetric capacity - easy temperature control	- high product gas temperature - high tar and fines contents on gas - Possibility of high C content in fly ash

(Adapt from: Rajvanshi, 1986; Chopra and Jain, 2007; Zhang el at., 2010).

2.9 Biomass gasification

Biomass gasification differs from coal gasification. Biomass is a carbon-neutral and sustainable energy source unlike coal. Because biomass is more reactive and has higher volatiles content than coal, biomass gasification occurs at a lower temperature. Lower temperature reduces the extent of heat loss, emissions and material problems associated with high temperatures. Biomass also has low sulfur content, which results in lower SO_x emission. But the high alkali contents in biomass, like sodium and potassium, cause slagging and fouling problems in gasification equipment (Kumar el at., 2009).

2.9.1 The main steps of biomass gasification

The main steps involved in the gasification process can be categorized as upstream processing, gasification and downstream processing as shown in Figure 2.8

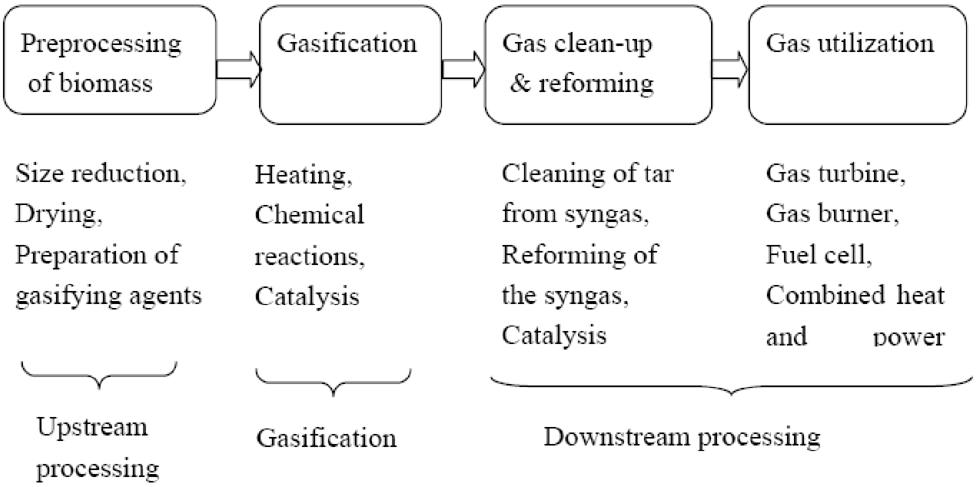


Figure 2.8 Processes in biomass gasification (Kumar et al., 2009)

2.9.1.1 *Upstream Processing*

Upstream processing includes processing of the preparation of biomass to make it suitable for gasification operations.

- *Size reduction*

Smaller particles have larger surface areas per unit mass and larger pore sizes which facilitate faster rates of heat transfer and gasification. Lv (2004) observed that the smaller particles resulted in more CH_4, CO, C_2H_4 and less

CO_2 which tend to higher gas yields, gas energy content (LHV) and carbon conversion efficiency. The increased heat transfer in smaller size particles was affected to the higher gas yields and energy efficiencies.

- *Drying*

Biomass that collected may contain high moisture. Drying is a process which makes a suitable range of water content for the gasification processes. However, in case of gasification, waste heat can be used to decrease the moisture content of the biomass which will increase the overall efficiency of the process. In the case of generating combined heat and power, biomass moisture should be as low as possible to increase the overall efficiency and decrease the net cost of electricity. However, for low moisture raw biomass (less than 10%) drying stage may not be needed.

2.9.1.2 *Gasification* (explained in Section 2.7)

2.9.1.3 *Downstream Processing*

- *Gas clean-up:* This is syngas cleaning such as particulate removal, tar removal.

- *Gas utilization:* The product gas from biomass gasification needs to be processed further for effective utilization.

Biomass material may be converted into a gaseous fuel that can be burned or ignited in an internal combustion engine. This gaseous fuel is commonly called producer gas. The producer gas contain carbon monoxide (CO), hydrogen (H_2), some carbon dioxide (CO_2), some methane (CH_4) and traces of oxygen and higher hydrocarbons (Arthayukti, 1985).

2.10 Literature reviews

Backman et al. (1993) studied basic studies on black liquor pyrolysis and char gasification. They found that complete gasification of organic of black liquor is thermodynamically possible with air ratio exceeding 0.3 and temperature above 700 °C. The gasification temperature affected the sodium vaporization. They said the rate of sodium vaporization was lose greater at higher temperature. At atmospheric pressure, a higher fraction of carbon in black liquor is converted to gases at higher pyrolysis temperature. The fraction of sodium volatilized during pyrolysis was not strongly temperature-dependent below 800 °C but increased rapidly with temperature above 900 °C.

Frederick et al. (1994) determined the yield of volatiles and the carbon content of black liquor char by pyrolyzing single liquor droplet in N_2/CO at 600–1200°C. They found that the amount of volatiles formed increased and the carbon content of char decreased with increasing reaction time. The amount of volatiles increased and the amount of carbon content of char decreased with reaction temperature in a pyrolysis environment. The volatiles yield increased from 33% to 75% over the temperature, while carbon content of char residues decreased from 65% to 12% over the same temperature range.

Demirbas et al. (2001) studied pyrolysis and stream gasification process of black liquor. Results indicated then the yields of liquid and gaseous products from the black liquor pyrolysis and the yields in the gaseous products from the black liquor steam gasification increase with increasing temperature.

Na et al. (2003) studied characteristics of oxygen-blown gasification for combustible waste in a fixed-bed gasifier. The experiment gasified combustible waste pellets mixed with plastic and cellulosic materials in an updraft fixed bed gasifier using O_2 as the gasifying medium. They found that the formation of char decreased and CO_2 was increased with the amount of O_2 was increased. The O_2/ waste ratio was above 0.45 causes the concentration of CO, H_2 and CH_4 decreased. O_2 gasification was reported to produce a medium heating value (MHV) gas (10-18 MJ/Nm3), which is suitable for limited pipeline distribution and as synthesis gas for conversion to methane and methanol.

Lacas et al., (2005) investigated the high temperature air/steam gasification process for gasification of bark, charcoal, woodchips and wood pellets in a conventional batch type countercurrent updraft gasifier. They found that the increase of steam fraction led to increase in fraction of H_2 (10.4 to 29.9 %) and decrease in CO (29.4 to 18.4 %) in the producer gas.

Yang et al. (2006) studied performance and analysis of fixed-bed biomass gasifier using high-temperature air. The experimental is used high temperature air gasification of wood pellets in a batch type updraft fixed bed gasifier. The gasifier was a vertical cylindrical reactor and the feedstock bed was supported by a bed of ceramic. The results shown that a higher gasification rate, a higher molar fraction of fuel gases and a higher LHV are obtained when the temperature is increased (650 to 830 °C). The higher temperature led to increase in concentration of CO (20.1 to 26.8%) and H_2 (6.6 to 12.7 %) in producer gas. When the oxygen concentration in the feed gas is increased, the gasification rate, the concentration of fuel gas species are also increased and the LHV of the fuel gas is higher because of less nitrogen is introduced to the gasifier and the product gas by consequence is less diluted.

Kumabe et al. (2007) examined co-gasification of woody biomass and coal with air and steam using a downdraft type fixed bed gasifier at 900°C. They found that the conversion to syngas increased with increase in biomass in the feedstock. On the other hand, the conversionto char and tar decreased with increase in biomass. The increase in biomass fraction resulted in a decrease in H_2 composition and increase in CO_2 composition. This experiment provided a cold gas efficiency ranging from 65% to 85%. Similar results were obtained by Lapuerta et al. (2008) on the thermal efficiency of an air blown circulating flow gasifier who reported that cold gas efficiency increased from 15% to 40% with the addition biomass to coal. The reason for higher thermal efficiency from the use of biomass was attributed to different C–C bonds in the materials. The coal structure (char) consists of mainly C=C bonds resulting from its significant heavy polycyclic aromatic hydrocarbons (PAH's) content which requires high activation energy to crack such bonds. However, the cellulose and lignin content of the biomass consists mainly of weaker bonds, such as, R–O–R (phenols, aldehydes, ketones, etc.), which can easily be broken.

Jarusmas (2008) studied thermochemical conversion of mixed solid sample from *Jatropha curcus* and glycerol wastes which carried out using a small scale reactor with feeding rate 5 g/min. The proportion between *Jatropha curcus* and glycerol wastes (100:0–70:30), reaction temperature (700–900°C) and ER (0–0.6) were investigated. Results shown that the increase in reaction temperature affected the increase in quantity of gas product, the conversion to CO, H_2, and CH_4, while the quantity of solid and liquid decreased. The conversion of CO, H_2, and CH_4 decreased when ER increased from 0.3 to 0.6. At 900°C and ER of 0 of mixed sample ratio 70:30 given the maximum heating value (17.24%). The maximum of mole ratio of H_2/CO obtained is 0.59.

Chuchai (2008) investigated product from gasification of palm shell waste mixed with crude glycerol. The experiment parameters are reaction temperature of 700–900°C, ER of 0-0.6,ratio of palm shell waste to crude glycerol of 100:0 and 70:30, total flow rate of 15 L/min, and feeding rate of 5 g/min. The results shown that the maximum of mole ratio of H_2/CO and heating value were obtained from the reaction temperature of 900°C and ER of 0. The LHV that gained from this study are 4.32 – 17.62 MJ/m^3.

Preto et al. (2008) studied stream gasification of carbon residue in bed solids of a low-temperature (600–800 °C) black liquor gasifier by using a thermogravimetric system at 3 bar. The effects of particles size and adding H_2 and CO to the gasification agent were investigated. They found that complete gasification of carbon residue was achieved in about 10 min as the reaction temperature increased to 800 °C. Increasing temperature appeared to be the most effective way to enhance the carbon conversion. The particle size did not significant effect on the rate of gasification. The adding H_2

and CO effected to inhibit the beginning of gasification process because the reverse reactions of carbon gasification by stream ($C + H_2O \leftrightarrow H_2 + CO$).

Fermoso et al. (2009) studied co-gasification of coal with biomass and petroleum coke in the steam-oxygen gasification. The results indicated the H_2 and CO increased with increasing temperature. CH_4 production remained constant and is not affected by the variation in reaction temperature. When gasifying agent increased, CO_2 increased but H_2 and CO decreased. They found that temperature and oxygen concentration were the most influential variables during the gasification process.

CHAPTER III

METHODOLOGY

3.1 Materials

3.1.1 Strong Black Liquor

Strong Black Liquor was supplied from Advance Agro Public Co., Ltd., Prachinburi province, Thailand. It was obtained from the point which passed the evaporation process. In this study, strong black liquor that mixed with eucalyptus bark was used in liquid form (as received). The strong black liquor was collected 1 time and used in all of experiments.

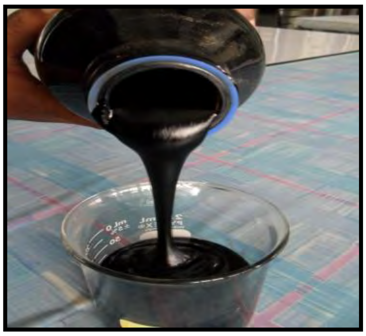
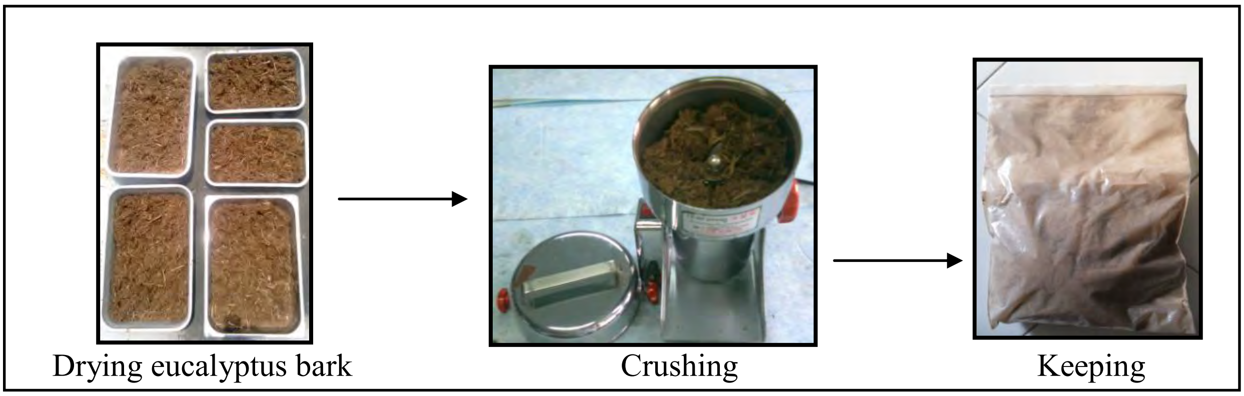


Figure 3.1 Strong black liquor

3.1.2 Eucalyptus Bark

Eucalyptus Bark was supplied from Advance Agro Public Co., Ltd., Prachinburi province, Thailand. It was obtained from debarking process. The preparation of eucalyptus bark, it was dried eucalyptus bark in the air 1-2 days to removed excess water. When it dried, it was crushed until eucalyptus bark changed to dust. Then, the dried eucalyptus dust was collected and kept in zip lock bag to prevented it from the moisture.



Drying eucalyptus bark Crushing Keeping

Figure 3.2 The eucalyptus bark preparation

3.1.3 Alumina ball

Alumina ball uses as bed support. Its diameter is 1 mm. In this experiment, puts 85 g of Alumina ball bed into the reactor. The height of Alumina ball bed about 10 cm..

Figure 3.3 Alumina ball bed

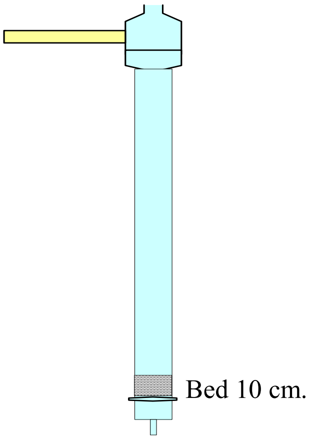


Figure 3.4 Bed level in the reactor

3.2 Equipments

3.2.1 High Speed Crusher Machine from Ngow Hoat Yoo.

It uses to crush dried eucalyptus bark and the mixed sample into the small partical sizes.

Figure 3.5 High Speed Crusher Machine

3.2.2 Sieve mesh 2.0 mm.

When the sample (black liquor and dried eucalyptus bark) has already mixed together, it was sieved 2 mm.

Figure 3.6 Sieve mesh 2.0 mm.

3.2.3 Digital Scale, OHAUS, Pioneer^{TM}

All of materials (black liquor, dried eucalyptus bark and mixed sample) and by-products (char and liquid) from gasification process are weighed by digital scale.

Figure 3.7 Digital Scale

3.2.4 Nitrogen gas (N_2 99.99%) from Thai Industry Gas (TIG)

It acts as the carrier gas in this experiment.

3.2.5 Pure O_2 from Bangkok Industrial Gas (BIG)

It is the oxidizing gas in this experiment.

Figure 3.8 Pure O_2 (right) and nitrogen gas (left)

3.2.6 Temperature control system

This system controls temperature of the experimental condition

Figure 3.9 Temperature control system

3.2.7 Tubular Stainless Steel Reactor from SUAN LUANG ENGNEERING LTD., PART. Upper O.D. 46 mm., I.D. 39.5 mm.. Lower O.D. 24.5 mm., I.D. 18.5 mm.. Height 1100 mm..

Figure 3.10 Tubular Stainless Steel Reactor

3.2.8 Vertical Tubular Furnace with height 1005 mm. and width 450 mm. from SUAN LUANG ENGNEERING LTD., PART. It acts as the temperature control of reactor. It changes electric power into heat power.

Figure 3.11 Vertical tubular furnace

3.2.9 Feeder

The feeder is on the top of reactor. The mixed sample was fed through feeder under gravity to gasifier by a semi-continuous-feeding system.

Figure 3.12 Feeder Set

3.2.10 Flowmeter for N_2 and pure O_2, dwyer

Flowmeters control the flow rate of nitrogen gas and pure O_2 which used in this experiment.

Figure 3.13 Flowmeter for N_2 (right) and pure O_2 (left)

3.2.11 Purification unit

It consists of cyclone, condensers and washer. They act as the cleaner set to clean and catch unwanted products such as dust, char, tar and liquid from the producer gas before pass through gas analyzer.

Figure 3.14 Cyclone, Condensers and Washer (from right to left)

3.2.12 $H_2/CO/CO_2/CH_4$ ANALYZER, MRU AIR, SWG 200^{-1}.

It is an on-line gas analyzer. It can detect CO_2, CO, H_2 and CH_4 all run time. The NDIR used for detect CO_2, CO and hydrocarbon. Gas chromatography technique used for detects H_2 by using TCD as detector.

Figure 3.15 $H_2/CO/CO_2/CH_4$ ANALYZER

3.2.13 Totalizer

The total of gas production was through the totalizer to investigate the volume of producer gas that produce from gasification process.

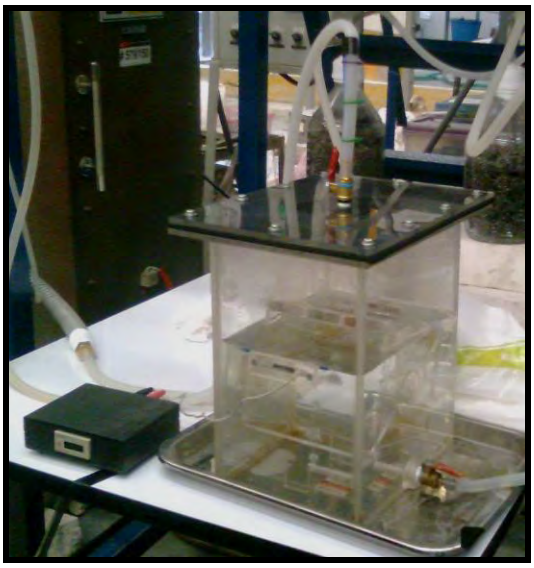


Figure 3.16 Totalizer

3.3 Experimental procedures

3.3.1 Determine the optimum ratio of mixed sample

In this experiment, the sample was called mixed sample. The mixed sample was prepared from the mixture of black liquor and dried eucalyptus dust in various ratios. Determine the suitable mixed sample ratios of black liquor : dried eucalyptus dust (weight on dry basis) from 100:0 to 50:50. Each mixed sample was sieved to particle size less than 2 mm

3.3.2 Analyze the chemical properties, thermal properties and carolific value of raw materials and mixed sample

3.3.2.1 Proximate analysis was studied by Thermogravicmetric analyzer (TGA) to determine quantity of moisture, volatiles, fixed carbon, and ash.

3.3.2.2 Ultimate analysis was studied by CHNS analysis technic (Leco TruSpec® CHNS (micro)Analyzer) to determine element composition of material which are carbon, hydrogen, nitrogen, sulfur.

3.3.2.3 Carolific value was studied by Automatic Bomb Calorimeter (Leco model AC-350) to determined high heating value of materials.

3.3.3 Thermal conversion studies

- *The procedures*

The experiments were performed in the fixed bed gasification system with N_2 as the carrier gas and O_2 as the gasifying agent. The diagram of fixed bed gasification system as displayed in Figure 3.17

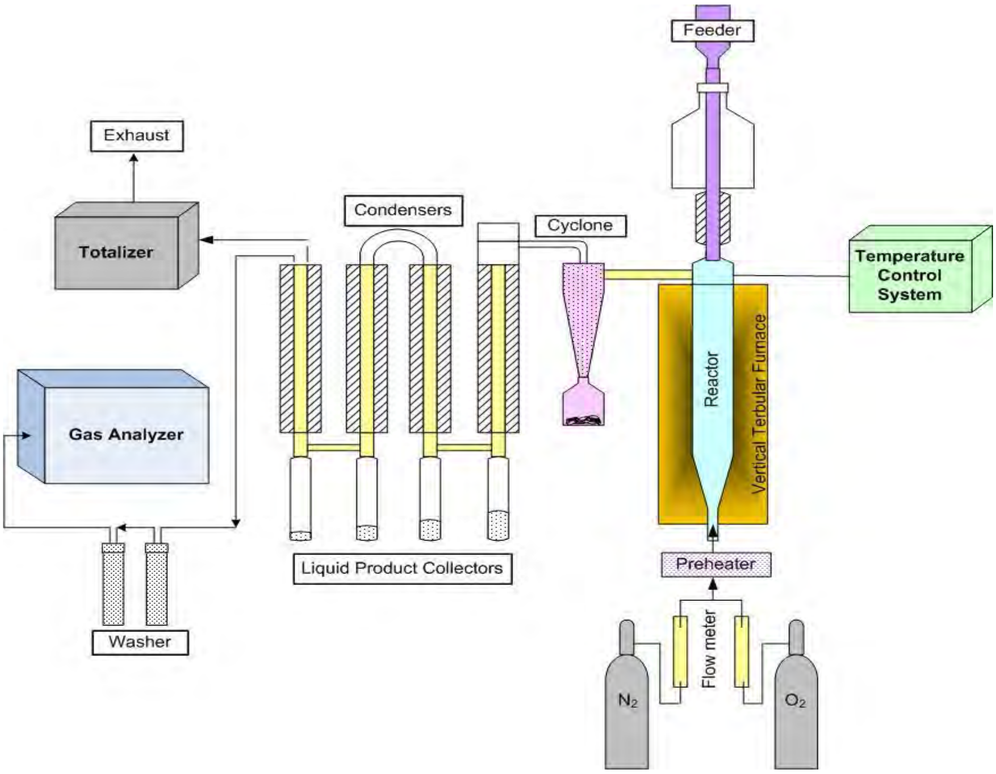


Figure 3.17 Diagram of fixed bed gasification system

The reactor made from stainless steel. Its reaction zone height 700 mm. and its inner diameter was 18.5 mm. The reactor was heated by vertical tubular furnace, it change electric power into heat power. The 85 g of Alumina bed was put into the reactor. The height of Alumina bed about 10 cm.. The temperature of system was controlled by the temperature control system. The temperature that chosen in this study are 700, 800 and 900°C. At the top of reactor, the mixed sample was fed through the feeder under gravity to gasifier by semi-continuous-feeding system.

Initially, the fixed bed gasification system was heated. Air in the reactor was purged with N_2 in the bottom of reactor. Then the temperature was raised gradually, until it reached the selected operating temperature. When temperature reached, O_2 was imported to the system in the suitable flow rate depend on equivalent ratio. When the system conditions were steady, the mixed sample was fed through the feeder into the gasifier. The mixed sample feed rate is 5 g/min. After that the producer gases were produced. All of the experiment conditions schematic was shown in Figure 3.18.

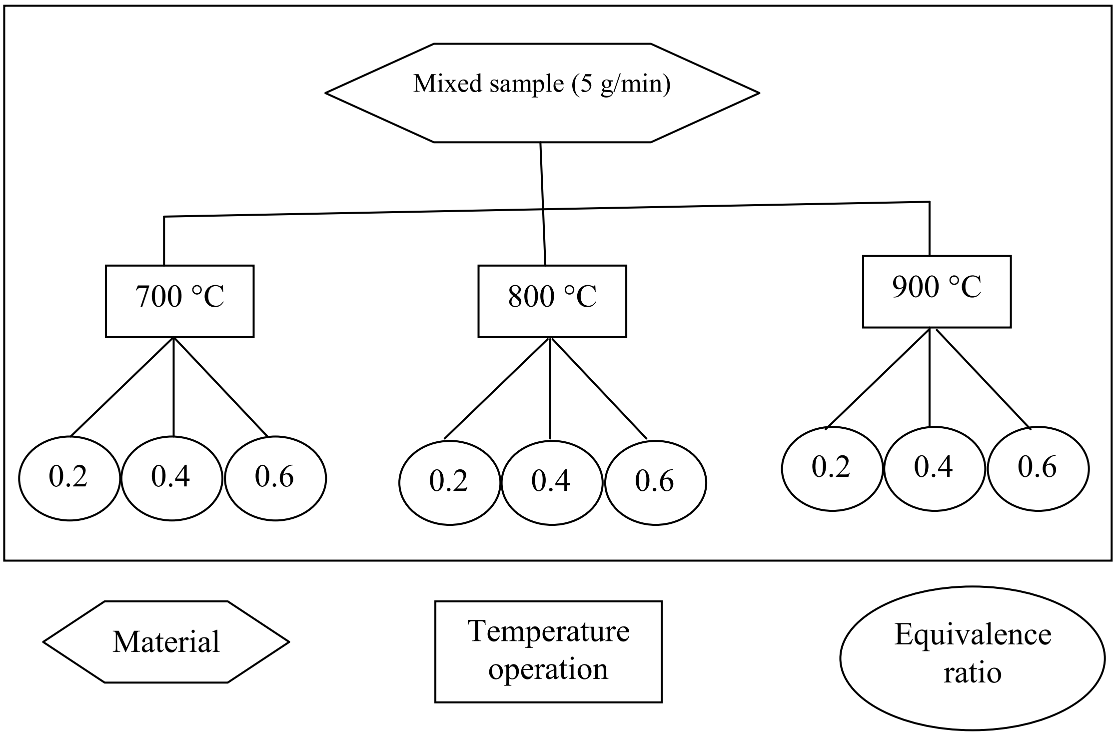


Figure 3.18 The experiment conditions

- *Gas analysis*

The producer gas flow exited and then passed through a cyclone, condensers and washer, respectively which were used as purification system for gas cleaning. After cooling and purifying, the producer gas was separated into 2 parts: First part of producer gas was passed through the totalizer to determine the producer gas flow rate and then it was released out. While a later part of producer gas was analyzed by using an on-line gas analyzer system. CO, H_2 and CH_4 were determined. The gas analyzer reported each type producer gas result in form percent of gas all of run-time. The run time of this experiment is 20 minutes. The percent of each gas was determined every 1 minute.

- *By-product determination*

Before every run-time, cyclone and four liquid collectors were weighed. When experiment was finished, cyclone and four liquid collectors were weighed again to determine the quantity of by-product (both solid and liquid products). In addition, char (solid product) in reactor were collected and weighed. From this, the result that obtained is the weight of solid and liquid products from the gasification.

3.3.4 The results evaluation

The objectives of this study are found the optimum of reaction temperature, equivalence ratio and mixed sample ratio that operated and used in the experiment to investigate the appropriate conditions for produce the maximum of gas yield, lowest of char (solid) and liquid. Then, the evaluation of result was concerned about gas that produced. The evaluation of gas results consist of;

- *Products quantity*

The gas, solid and liquid yields were directly calculated from measured weight of each fraction. The weight of each products can be calculate by equation 3.1. Percent weight of gas, solid and liquid can be calculated by equation 3.2.

$$\text{Weight of gas (g)} = \text{Total mixed sample feeding (g) - solid (g) – liquid (g)} \qquad (3.1)$$

$$\text{\%wt. of gas (or solid and liquid)} = \frac{\text{wt. of gas (or solid and liquid)}}{\text{wt. of total mixed sample feeding}} \times 100 \qquad (3.2)$$

- *Volume, %carbon conversion, %hydrogen conversion of producer gas and H_2/CO*

The data between the total flow rate result which measured by the totalizer and percent average of each gas which analyzed by gas analyzer were calculated. The result from the calculation is volume of each producer gas (CO, H_2 and CH_4) that produced in the experiment. After that, carbon and hydrogen conversion of producer gas and ratio by mole of H_2 to CO will be calculated. The example of the calculations were shown in Appendix A.

- *Lower heating value of product gases*

From volume of producer gas, lower heating value was calculated for investigate the energy efficiency. The example of LHV of product gases was shown in Appendix A.

- *Energy efficiency (cold gas efficiency)*

In this work, cold gas efficiency was calculated by

$$\text{cold gas efficiency} = \frac{\sum LHV_i \times V_i}{LHV_{feed} \times M} \qquad (3.3)$$

where LHV_i is lower heating value of product gas I (MJ/m^3), V_i is volume of product gas i (m^3), LHV_{feed} is lower heating value (MJ/kg) of material feed, and M is mass of material feed (kg). The example of cold gas efficiency was shown in Appendix A.

- *Analysis of char*

Char residues after gasification were examined Ultimate analysis by using CHNS analysis technic (Leco TruSpec® CHNS (micro)Analyzer) to determine element composition of material which are carbon, hydrogen, nitrogen, sulfur. In addition, types and quantity of element in char were investigated by using X-ray fluorescence spectrometer (XRF), Philips PW-2404 as presented in Figure 3.19. The preparation of char sample for analyzing with XRF was shown in Figure 3.20. The all of experiments evaluation was presented in Figure 3.21

Figure 3.19 X-ray fluorescence spectrometer (XRF)

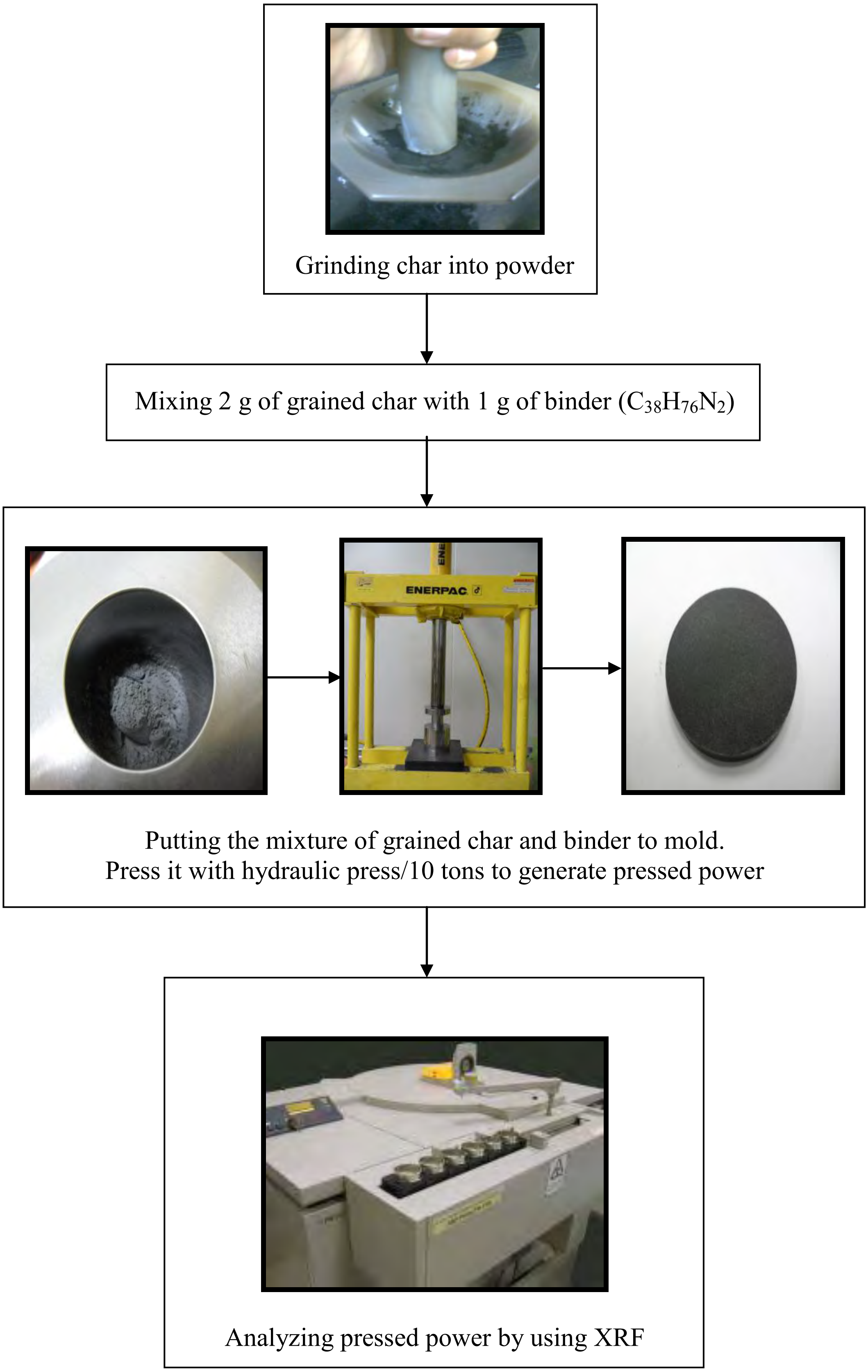


Figure 3.20 The preparation of char sample for analyzing with XRF

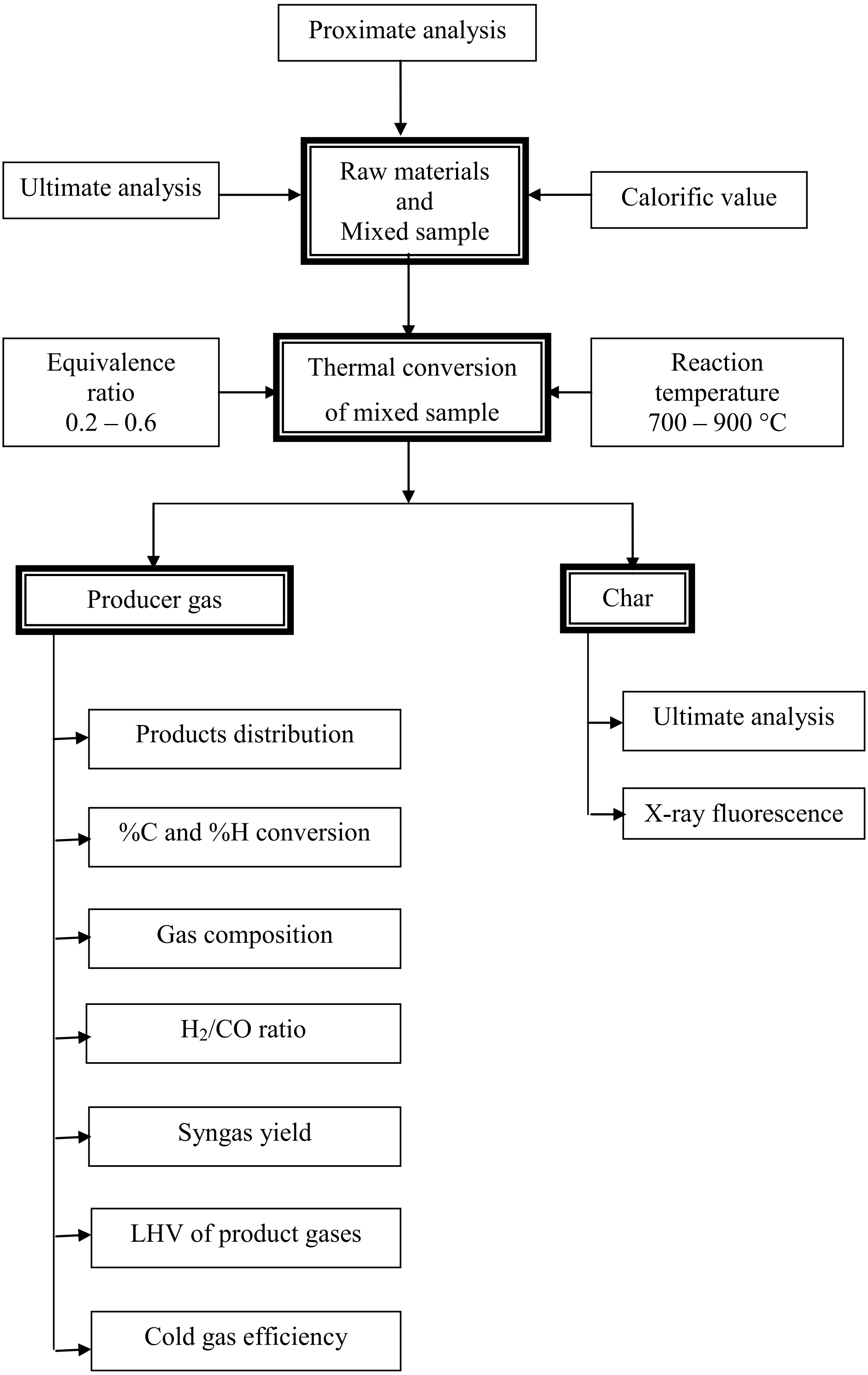


Figure 3.21 The all of experiments evaluation

CHAPTER IV

RESULTS AND DISCUSSION

The feasibility of the co-gasification of the blend of black liquor with eucalyptus bark residues was carried out in this research. Discussion of the results obtained from this work is presented in three sections. The first section deals mainly on the raw materials and mixed sample characterization. The second section deals on thermal conversion of mixed sample at various conditions while the later section focuses on the char residue characterization. The detailed results along with discussion are presented in this entire chapter.

4.1 Raw materials and mixed sample analysis

The proximate analysis was studied by Thermogravicmetric analyzer (TGA) to determine quantity of moisture, volatiles, fixed carbon, and ash. The ultimate analysis was studied by CHNS analysis technic (Leco TruSpec® CHNS (micro)Analyzer) to determine element composition of material which are carbon, hydrogen, nitrogen, sulfur. The higher heating value of samples was studied by Automatic Bomb Calorimeter (Leco model AC-350). The results of this study are shown in Table 4.1.

Table 4.1 Analysis of materials used in this study

Materials	Proximate analysis (wt.%)				Ultimate analysis (wt.%)				HHV[b]
	Moisture	Volatile	FC[a]	ash	C	H	N	S	(MJ/Kg)
Black liquor	28.0	29.5	8.5	34.0	27.2	3.26	0	0.77	14
Eucalyptus bark	3.51	60.97	16.08	7.97	35.0	3.78	0.59	0.36	14.7
Mixed sample (60:40)	-	-	-	-	28.1	3.42	1.38	1.04	14.21
Mixed sample (40:60)	-	-	-	-	35.1	3.97	3.19	1.30	14.35

[z] fixed carbon , [b] higher heating value

The results indicated that raw materials contained high content of volatile and carbon which is suitable for produce gaseous fuel because the ability of material conversion to gas is high. The quantity of oxygen (by difference) was not decisive because there may be other element not analyzed by this method. In addition, low ash content of materials indicated that it should be a good candidate for production of fuel via thermochemical process. From the environmental point of view, mixed sample contained low nitrogen and sulfur contents. Hence, utilization of this mixed sample would help a reduction in NO_x and SO_x emission thus lessen environment pollution.

4.2 Products distribution

The production of mixed sample gasification in this work can be classified into three phases: char (solid), liquid and gas. The product distribution of both mixed sample at varied reaction ER of 0.2–0.6 and reaction temperature of 700-900°C was presented in Figure 4.1. As expected, in case of both mixed samples, the raise in reaction temperature (from 700 to 900°C) and ER (from 0.2 to 0.6) conducted an increase in gas yield and a decrease in solid and liquid yields. These findings similar with results reported by Sricharoenchaikul (2009) and Tavasoli et al. (2009).The decrease in solid and liquid yields with reaction temperature and ER was mainly attributed to an increase in conversion of the organic material to gaseous products. The increase in gas yield with reaction temperature could be a result of (1) more unconverted volatile liberated at higher reaction temperature (2) the raised reaction temperature supported the production of gas through the endothermic char gasification reaction and, (3) the increased in gas yield resulting from cracking of heaver hydrocarbon and tar. In this study, the highest gas yield of both mixed sample obtained at the highest reaction temperature of 900 °C.

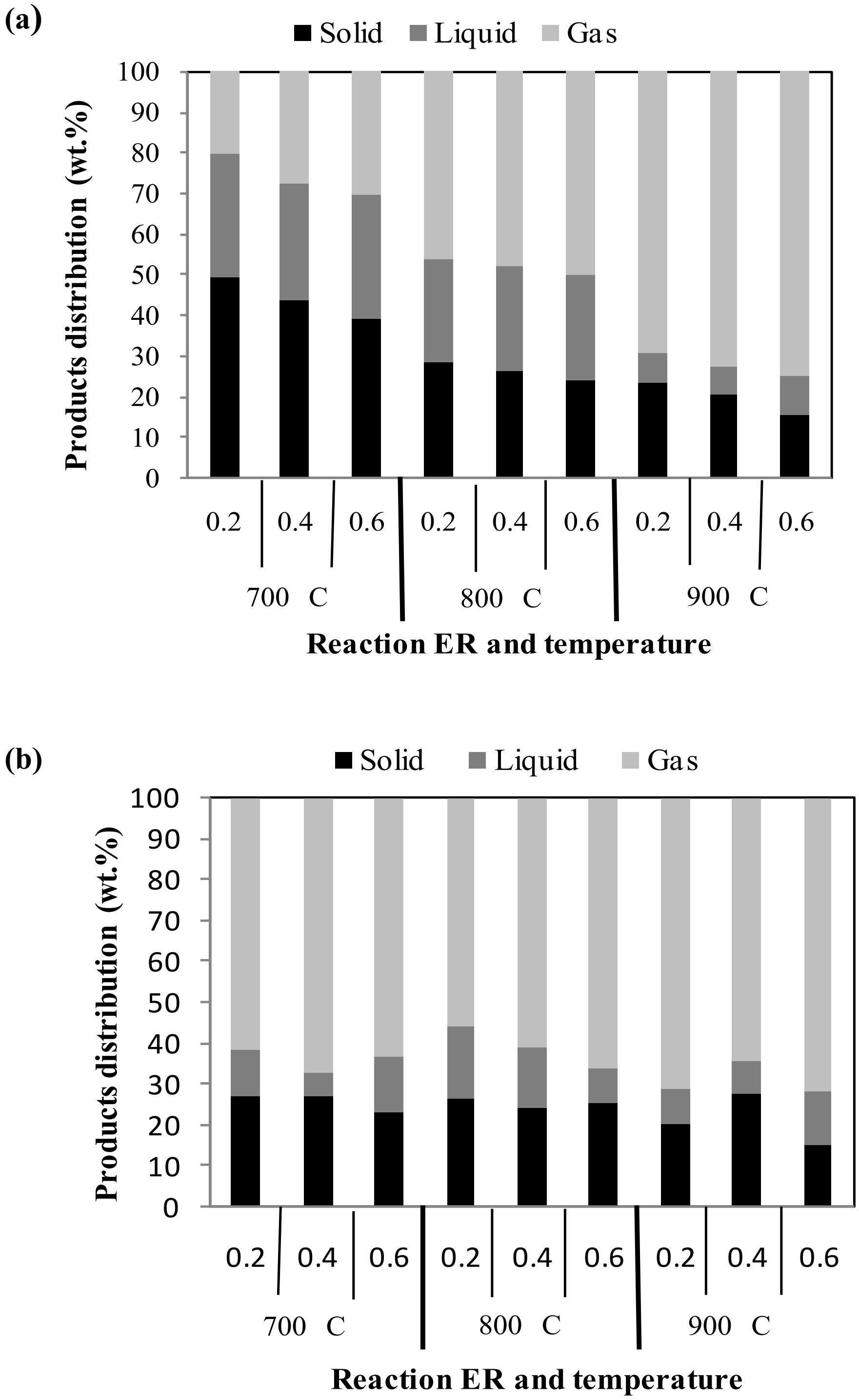


Figure 4.1 Effect of reaction temperature and ER on products distribution from gasification of mixed sample (a) ratio 60:40, (b) ratio 40:60

4.3 Effect of reaction temperature

4.3.1 Effect of reaction temperature on gas composition

Reaction temperature is one of the most important operating parameters affecting the performance of the overall biomass gasification (Carlsson et al., 2010; Fermoso et al., 2009; Zhou et al., 2009; Yan et al.,2010), due to the balance between endothermic and exothermic reactions involved (Fermoso et al., 2009; Zhou et al., 2009). Experiments were performed at different operating temperature but constant ER and mixed sample feed rate.

Figure 4.2 and 4.3 presented effect of reaction temperature on gas composition from gasification of mixed sample ratio 60:40 and ratio 40:60 at various ER. The results of both mixed sample are similar. The result indicated that carbon oxidation reactions, Equations (4.1) and (4.2), which are exothermic reaction, were more significant at low temperature.

Complete oxidation: $C + O_2 = CO_2$ +393.8 kJ/mol (4.1)

Partial oxidation: $C + ½O_2 = CO$ +123.1 kJ/mol (4.2)

Water gas: $C + H_2O = CO + H_2$ - 118.5 kJ/mol (4.3)

Boudouard: $C + CO_2 = 2CO$ -159.9 kJ/mol (4.4)

Methanation: $C + 2H_2 = CH_4$ +87.5 kJ/mol (4.5)

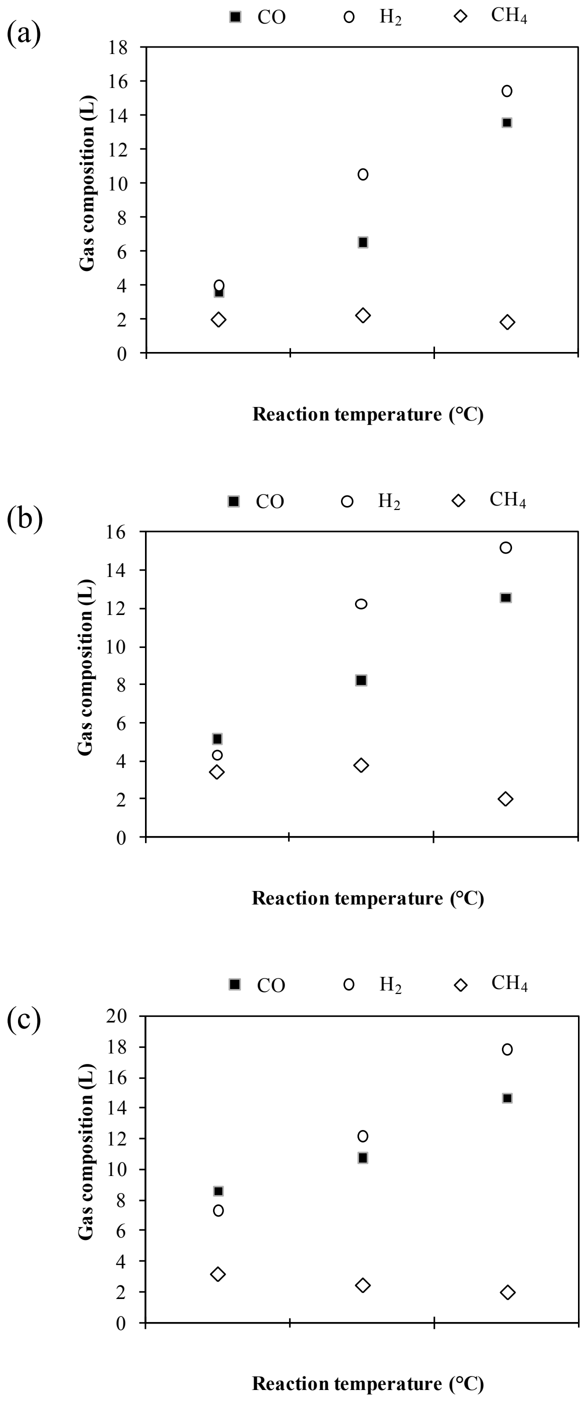


Figure 4.2 Effect of reaction temperature on gas composition from gasification of mixed sample ratio 60:40 at (a) ER of 0.2, (b) ER of 0.4 and (c) ER of 0.6

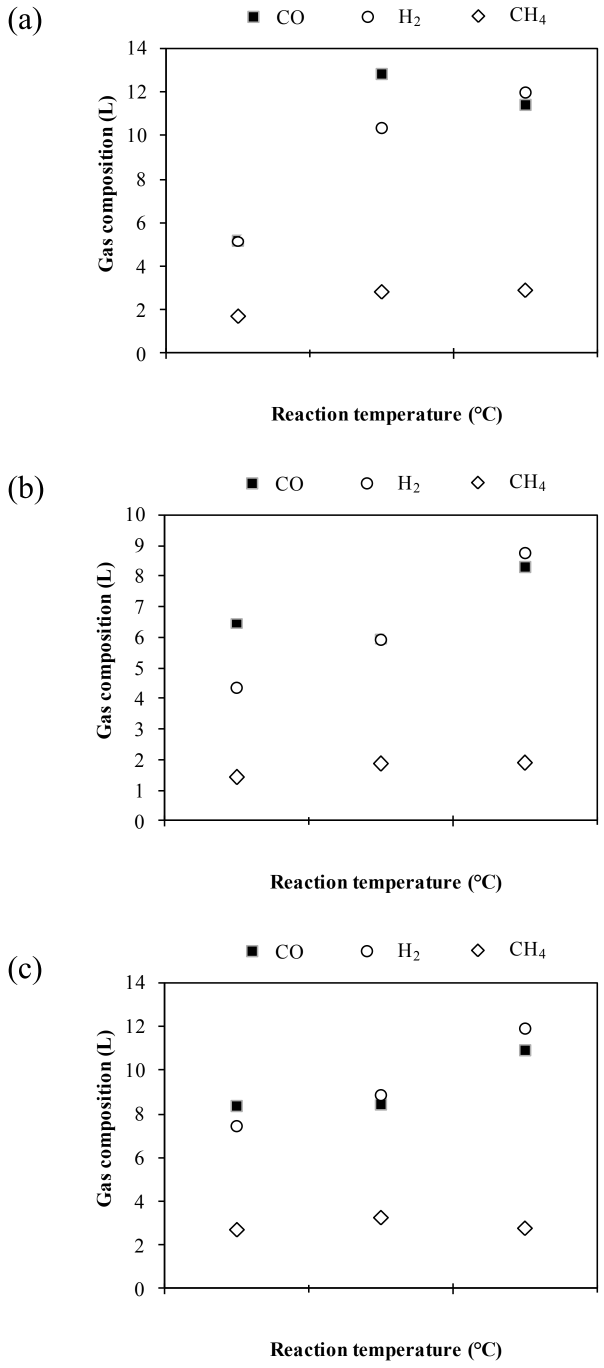


Figure 4.3 Effect of reaction temperature on gas composition from gasification of mixed sample ratio 40:60 (a) ER of 0.2, (b) ER of 0.4 and (c) ER of 0.6

Increasing in temperature favoured the formation of H_2 and CO, since the endothermic reaction, Equations (4.3) and (4.4) were enhanced (Fermoso et al., 2009; Zhou et al., 2009). It can be seen that the major gases are CO_2, CO and H_2. Water gas reaction (Equation (4.3)) is the partial oxidation of carbon by steam, which could come from the difference sources; such as vapor produced from the evaporation of water in material, water vapor associated with the income oxygen, and pyrolysis of material. As the reaction temperature increased, the yield of CO_2 decreased and CO increased because carbon tend to react with CO_2 via Boudouard reaction, Equation (4.4), moving the equilibrium to CO formation. According to the Le Chatelier's principle, higher reaction temperatures favour the reactants in exothermic reactions and the products in endothermic reactions (Carlsson et al., 2010). H_2 yield increased greatly with increasing reaction temperature while CH_4 yield decreased obviously and is smaller than those of other gases. This indicated that methanation reaction, Equation (4.5), did not significantly proceed and CH_4 was produced mainly during the low operating temperature or pyrolysis step.

4.3.2 Effect of reaction temperature on carbon and hydrogen conversion

The carbon and hydrogen conversion is strongly dependent on the gasification reaction temperature (Backman et al., 1993). Conversion of mixed sample to desired gas species along with %C and %H in mixed sample converted to specific gases at various ER. Figure 4.4 presented effect of reaction temperature on total %C and %H conversion from gasification of mixed sample ratio 60:40 at ER of 0.2–0.6. The results suggested that %C conversion as CO of ratio 60:40 seemed to increase sharply with increasing reaction temperature, while %C conversion as CH_4 was almost constant. In parallel, transformation of hydrogen in mixed sample to H_2 was enhanced with increasing reaction temperature. The increase of reaction temperature affected the small increase and decrease of %H conversion as CH_4.

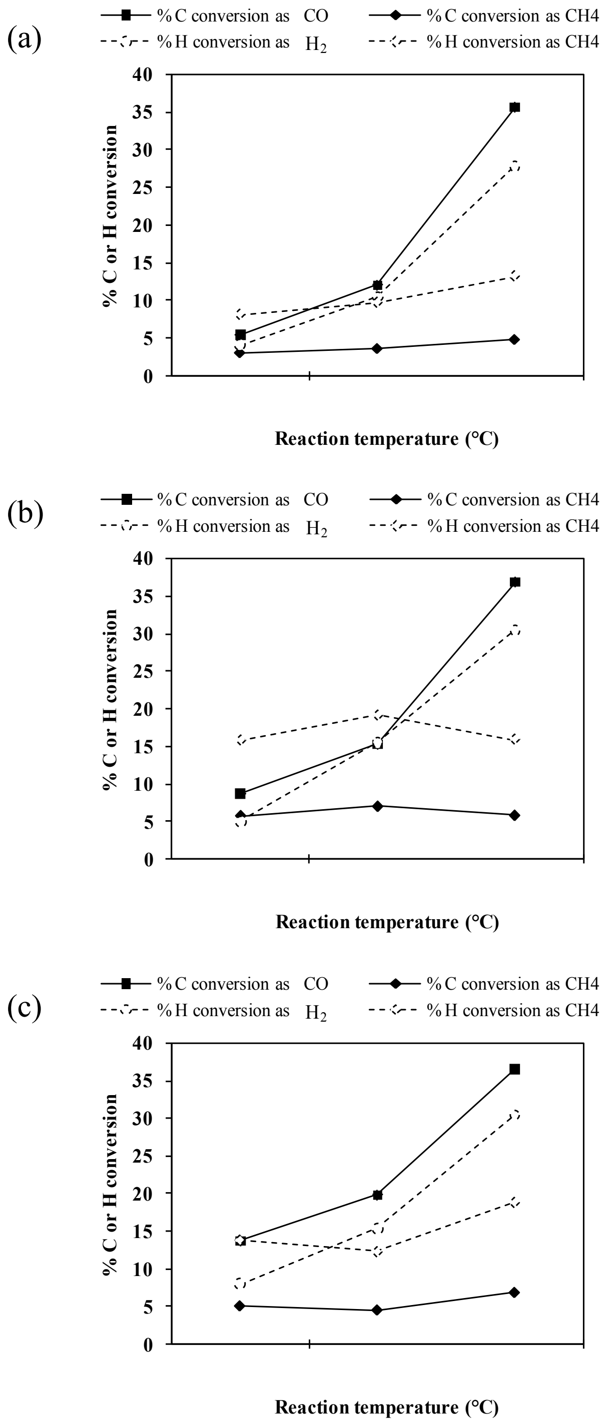


Figure 4.4 Effect of reaction temperature on total %C and %H conversion from gasification of mixed sample ratio 60:40 at (a) ER of 0.2, (b) ER of 0.4 and (c) ER of 0.6

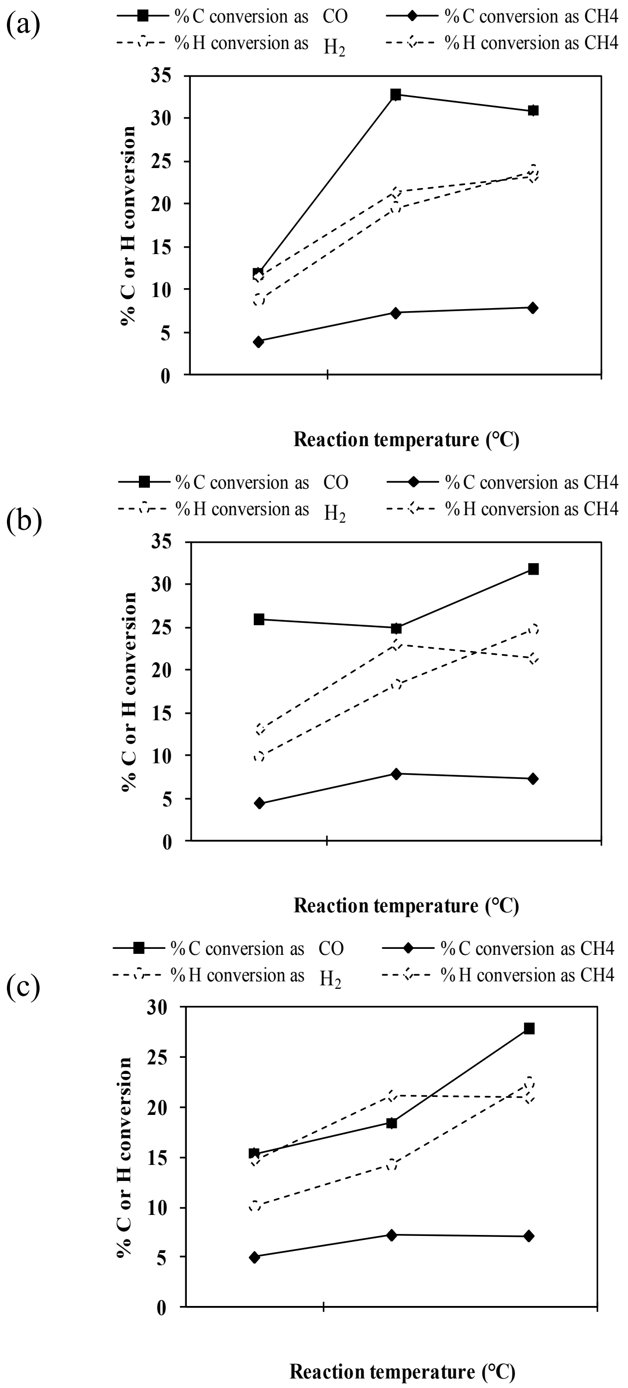


Figure 4.5 Effect of reaction temperature on total %C and %H conversion from gasification of mixed sample ratio 40:60 (a) ER of 0.2, (b) ER of 0.4 and (c) ER of 0.6

Figure 4.5 presented effect of reaction temperature on total %C and %H conversion from gasification of mixed sample ratio 40:60 at ER of 0.2–0.6. The result showed that %C conversion as CO tends to increase with increasing reaction temperature from 700–900 °C. The %C conversion as CH_4 of mixed sample ratio 40:60 was almost constant with increasing reaction temperature. In addition, the transformation of hydrogen in mixed sample to H_2 was improved with increasing reaction temperature. Whereas, the increase of reaction temperature affected the small increase and decrease of %H conversion as CH_4.

From the results of both mixed sample suggested that the optimized reaction temperature for both mixed sample could be 900 °C. Because of this temperature would also greater favors gas yield, gas compositions and carbon conversion.

4.4 Effect of Equivalence Ratio (ER)

4.4.1 Effect of ER on gas composition and carbon and hydrogen conversion

The equivalence ratio (ER) which is defined as the ratio of the amount of oxygen added relative to amount of oxygen required for stoichimetric combustion. In this study, ER was varied from 0.2 to 0.6 through regulating the oxygen flowrate while holding the other parameters unchanged. Figure 4.6 and 4.7 shown the effect of varying ER on gas composition and the conversion of carbon and hydrogen to CO, H_2 and CH_4 of mixed sample (60:40). Results indicated that increasing in ER favored the exothermic reaction, Equations (4.1) and (4.2).

$$\text{Complete oxidation:} \quad C + O_2 = CO_2 \quad +393.8 \text{ kJ/mol} \tag{4.1}$$

$$\text{Partial oxidation:} \quad C + \tfrac{1}{2}O_2 = CO \quad +123.1 \text{ kJ/mol} \tag{4.2}$$

It can be seen that increasing ER significantly increased CO production as shown in Figure 4.6. The increase in ER also influences degree of combustion which char and tar were oxidized to CO or CO_2 as Equations (4.6) and (4.7).

$$\text{Char} \rightarrow CO + CO_2 + H_2 + \text{solid residual} \quad (4.6)$$

$$\text{Tar} \rightarrow \text{light and heavy hydrocarbon} + CO + H_2 + CO_2 \quad (4.7)$$

In case of H_2 and CH_4 contents first increased and then decreased as present in Figure 4.6. They are possible to reduce because CO_2 increased with increasing ER. These trends agree with the results reported by Carlsson, et al (2010). They investigated the influence of operational parameters on product gas composition of black liquor. They explained that CH_4 and H_2 reduced with increasing ER while CO increased.

Sometimes, the increase in oxygen affects the decrease of H_2, CO and CH_4. When O_2 was excessive, H_2, CO and CH_4 were completely combusted, which caused the increase in CO_2 and continuous decreases in CO and H_2.

Figure 4.7 presented effect of ER on total %C and %H conversion from gasification of mixed sample ratio 60:40 at reaction temperature of 700–900 °C. The results suggested that %C conversion as CO of ratio 60:40 seemed to increase with ER increased. While %C conversion as CH_4 was almost constant. In parallel, % H conversion as H_2 was enhanced with increasing ER. The increase of ER affected the increase and decrease of %H conversion as CH_4.

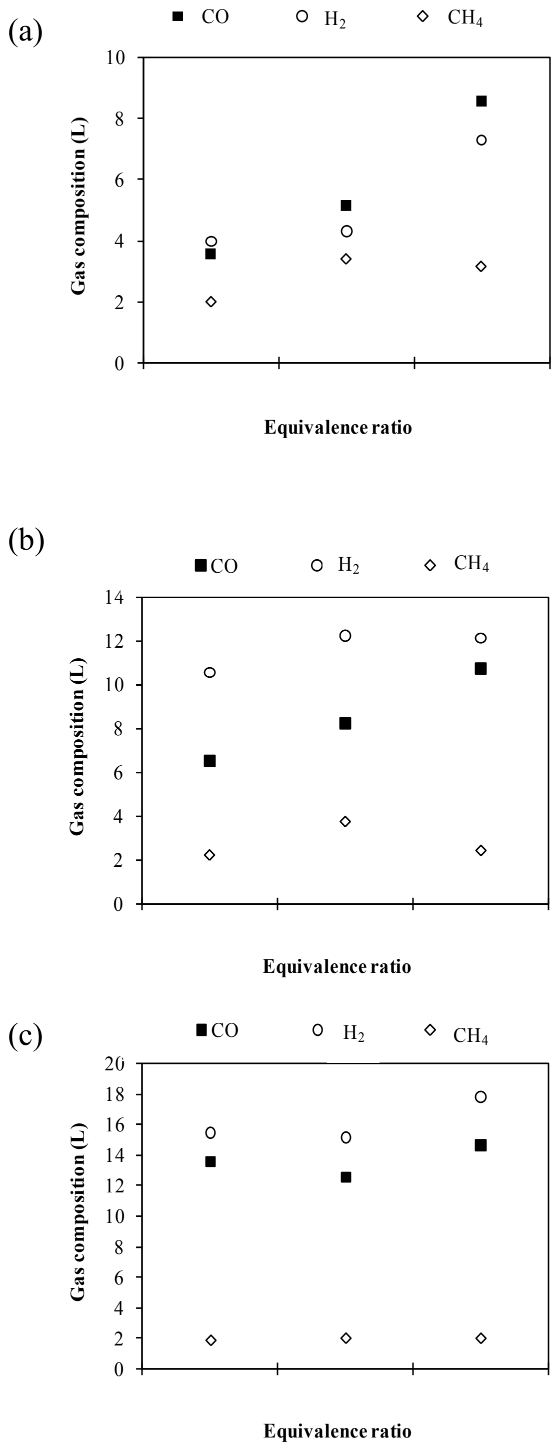


Figure 4.6 Effect of ER on gas composition from gasification of mixed sample ratio 60:40 at (a) 700°C, (b) 800°C and (c) 900°C

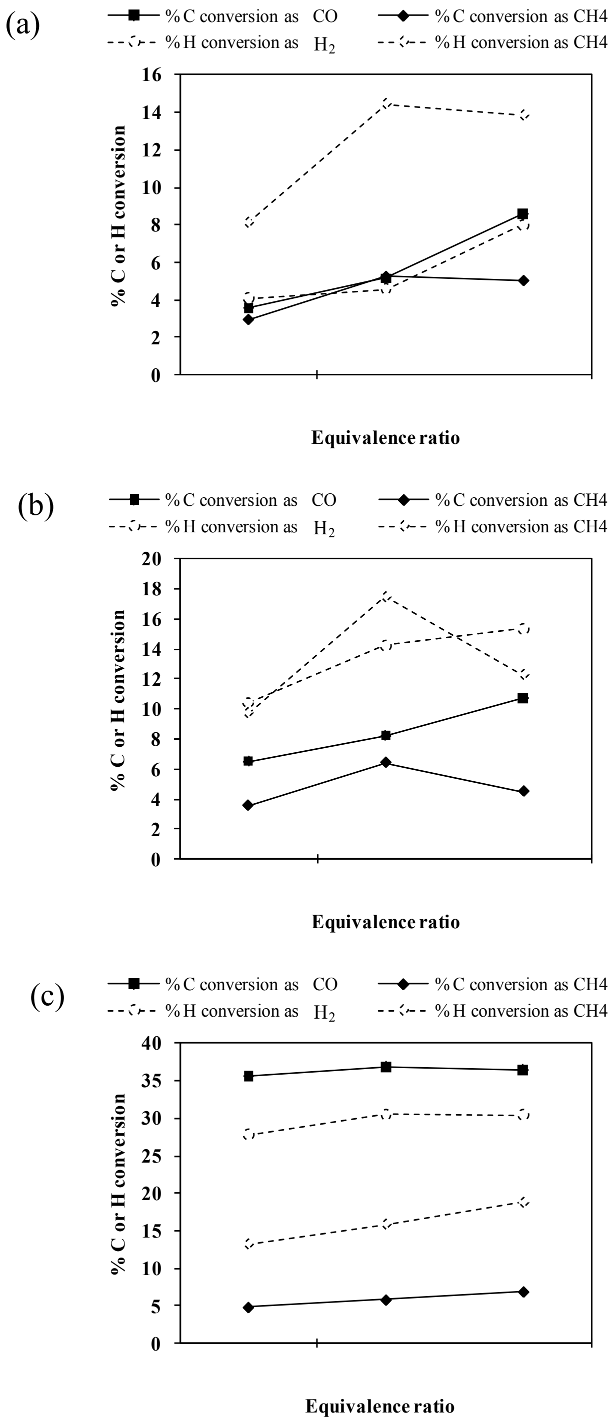


Figure 4.7 Effect of ER on %C and %H conversion as specific gas from gasification of mixed sample ratio 60:40 at (a) 700°C, (b) 800°C and (c) 900°C

The effect of varying ER on gas composition and the conversion of carbon and hydrogen to CO, H_2 and CH_4 of mixed sample ratio 40:60 shown in Figure 4.8 and 4.9. The result of gas composition of ratio 40:60 (Figure 4.8) indicated that CO and H_2 production increased with increasing ER only at 700 °C. At 800 and 900, CO and H_2 production decreased when ER increased from 0.2-0.4. After that, CO and H_2 production increased when ER increased from 0.4-0.6. These results can be explained that the increase in ER also influences degree of combustion which char and tar were oxidized as Equations (4.6) and (4.7). In case of CH_4 contents first decreased and then increased as present in Figure 4.8. The increase in oxygen affects the decrease of H_2, CO and CH_4. When O_2 was excessive, H_2, CO and CH_4 were completely combusted, which caused the increase in CO_2 and continuous decreases in CO and H_2.

Figure 4.9 presented effect of ER on total %C and %H conversion from gasification of mixed sample ratio 40:60 at reaction temperature of 700–900 °C. The results suggested that %C conversion as CO tend to decrease with ER increased. While %C conversion as CH_4 was almost constant. In parallel, % H conversion as H_2 was decreased with increasing ER. The increase of ER affected the increase and decrease of %H conversion as CH_4.

For ratio 40:60, the run time and feed rate was not stable. This problem may be caused by equipments and operating condition which used in this study. From this, the results of ratio 40:60 did not similar with ratio 60:40 and the results have no trend because it depend on the run time and feed rate.

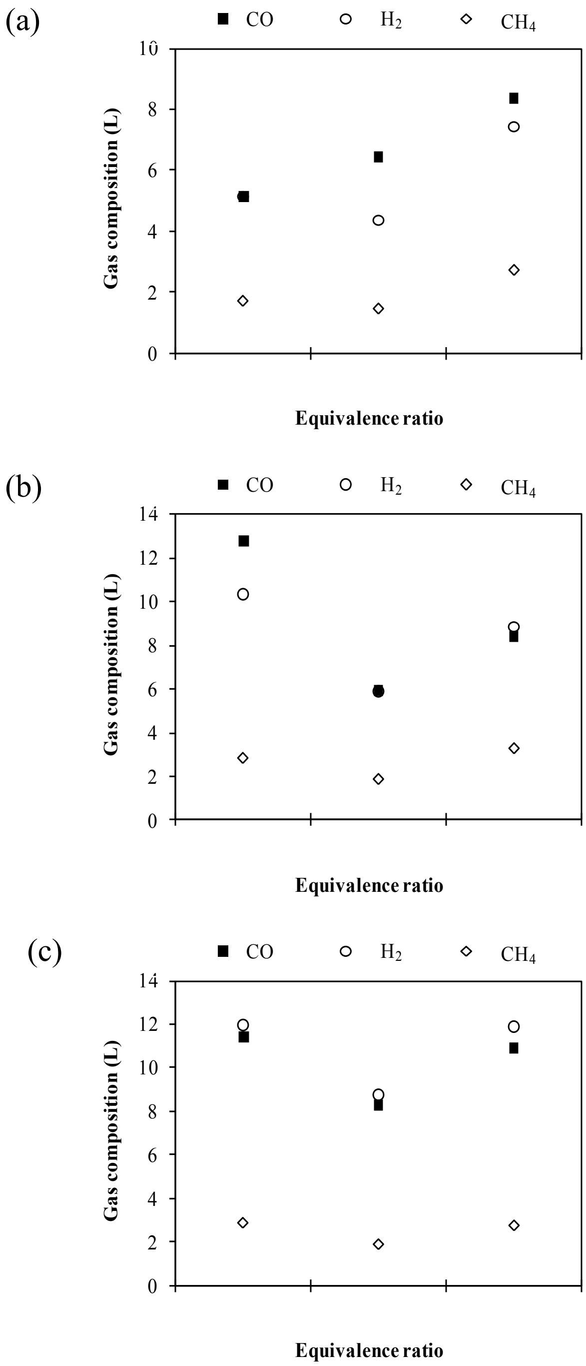


Figure 4.8 Effect of ER on gas composition from gasification of mixed sample ratio 40:60 at (a) 700°C, (b) 800°C and (c) 900°C

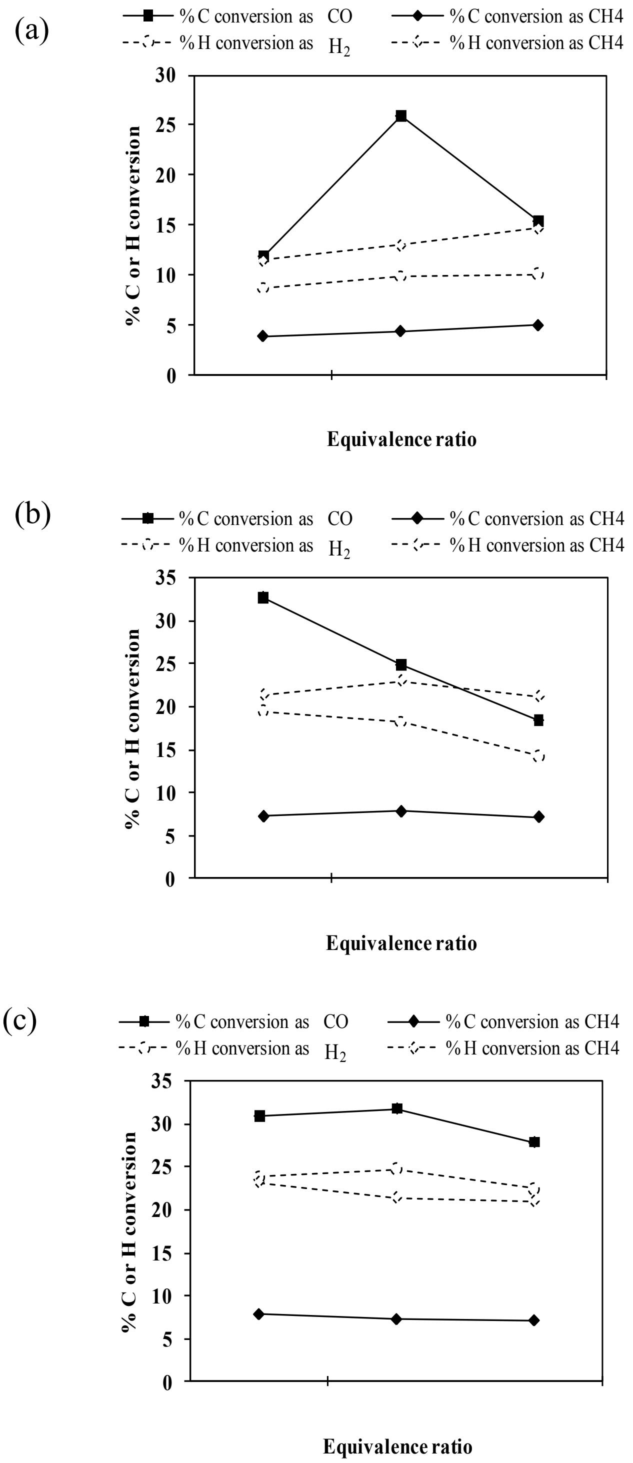


Figure 4.9 Effect of ER on %C and %H conversion as specific gas from gasification of mixed sample ratio 60:40 at (a) 700°C, (b) 800°C and (c) 900°C

4.5 Effect of ER and reaction temperature on H_2/CO ratio and syngas production

Product gases in which the major active components are carbon monoxide and hydrogen is called a synthesis gas (syngas). These two compounds can be utilized to form various value added products. Selectivity of products manufactured from syngas depends on hydrogen to carbon monoxide ratio. Figure 4.10 exhibited that H_2/CO ratio tends to decrease with increasing ER.

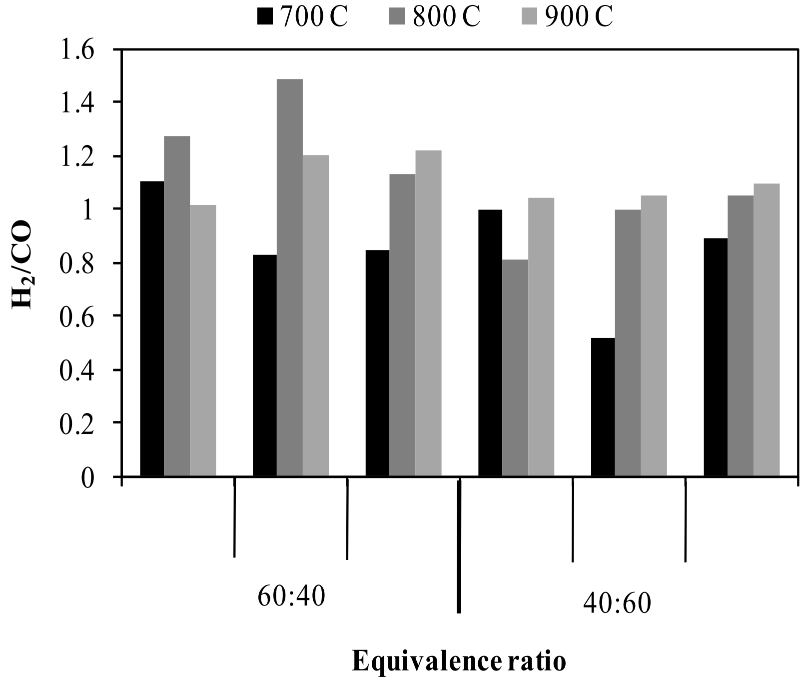


Figure 4.10 Effect of temperature and ER on H_2/CO from gasification of both mixed samples

This implies that excessive of O_2 and increasing in reaction temperature did not improve the quality of the syngas and H_2/CO. The result is similar to the work of Zhou et al.(2009) who gasified biomass (rice husk, sawdust and camphor wood) in entrained-flow gasifier with oxygen as gasifying agent using high operating temperature (1000-1400°C) at the feeding rate ranged from 1 to 2 g/min. They found that the injection of O_2 into the gasifier could strengthen the gasification and improve carbon conversion, but reduce the gas LHV and H_2/CO ratio. Formation of syngas with the H_2/CO ratio of 1:1 to 2:1 can be used as a feedstock to produce methanol and other synthesis fuels by Fisher-Tropsh reaction. H_2/CO ratio obtained from this study between 0.52-1.48. The maximum H_2/CO of 1.48 was achieved from mixed sample (60:40) at 800°C and ER of 0.4.

Syngas production was calculated by the sum volume of H_2 and CO that produced in the experiments. Syngas production, Figure 4.11, increased with reaction temperature and ER. Because of H_2 and CO production increased with increasing reaction temperature and ER that explained in section 4.3 and 4.4. In present work, the highest syngas production equals to 32.43 L obtained when gasified mixed sample (60:40) at 900°C and ER of 0.6.

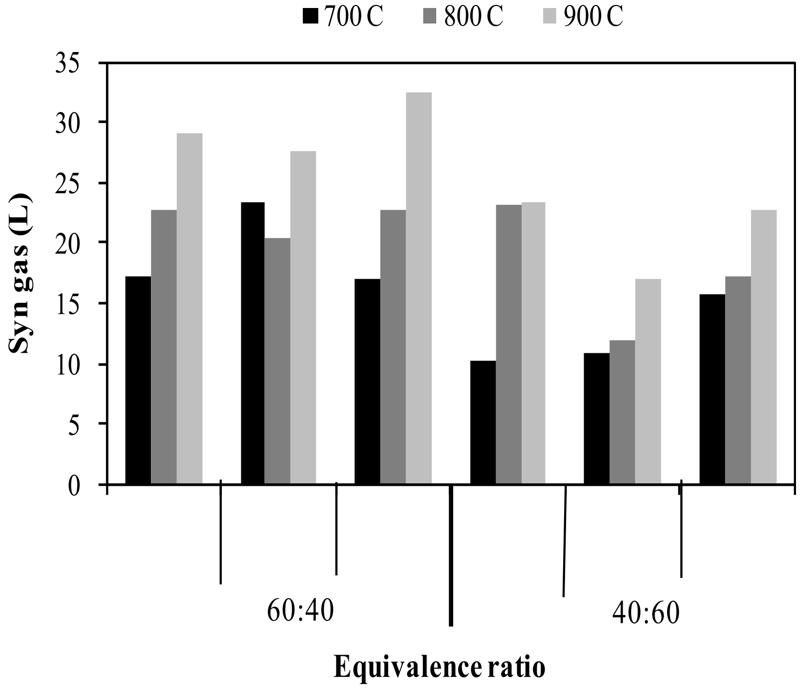


Figure 4.11 Effect of temperature and ER on syngas production from gasification of both mixed samples

4.6 Lower heating value (LHV) of gas and cold gas efficiency

The heating value of a gasification gas is perhaps the most influential characteristic for design purposes and energy efficiency calculation. The dominant combustible gases produced by gasification of mixed sample are CO, H_2 and CH_4. Figure 4.12 presented lower heating value of gas and cold gas efficiency of mixed sample (ratio 60:40) at operating temperature of 700-900°C and ER of 0.2-0.6.

The result from the plots of ratio 60:40 indicated that LHV and cold gas efficiency increase with temperature and ER. Higher temperature (900°C) is beneficial for increasing of product gas heating value and cold gas efficiency. These agree with the results reported by Tavasoli et al (2009) who studied effect of temperature on LHV from gasification of corn and wheat dry distiller grain using a fixed-bed micro reactor at 700-900 °C. They found LHV increased for both biomasses with increasing temperature.

For mixed sample ratio 40:60, Figure 4.13, the maximum LHV was obtained at ER of 0.4 while at a higher ER of 0.6, more CO_2 is formed, mostly due to the combustion of carbon and CO by oxygen as Equations (4.1) and (4.8), respectively.

Complete oxidation: $C + O_2 = CO_2 \quad +393.8\ \text{kJ/mol} \qquad (4.1)$

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \quad + 283.9\ \text{kJ/mol} \qquad (4.8)$$

For the case of ER equals to 0.6, LHV decreased because large amount of non-combustible CO_2 was produced. Typically, the LHV of gas should be more than 3.7 MJ/m^3 for produced gas may be burned without additional of complement fuel (Sricharoenchaikul et al, 2008). The LHV obtained in this study ranging from 1.59-5.66 MJ/m^3. Such product gas that obtained from this study can be readily utilized by combustion. The highest LHV and cold gas efficiency of the gasification of mixed sample (60:40) were achieved at 900°C and ER of 0.6. The maximum LHV and cold gas efficiency of the gasification of mixed sample (40:60) was gained at 900°C, ER of 0.6 and at 900°C, ER of 0.4, respectively.

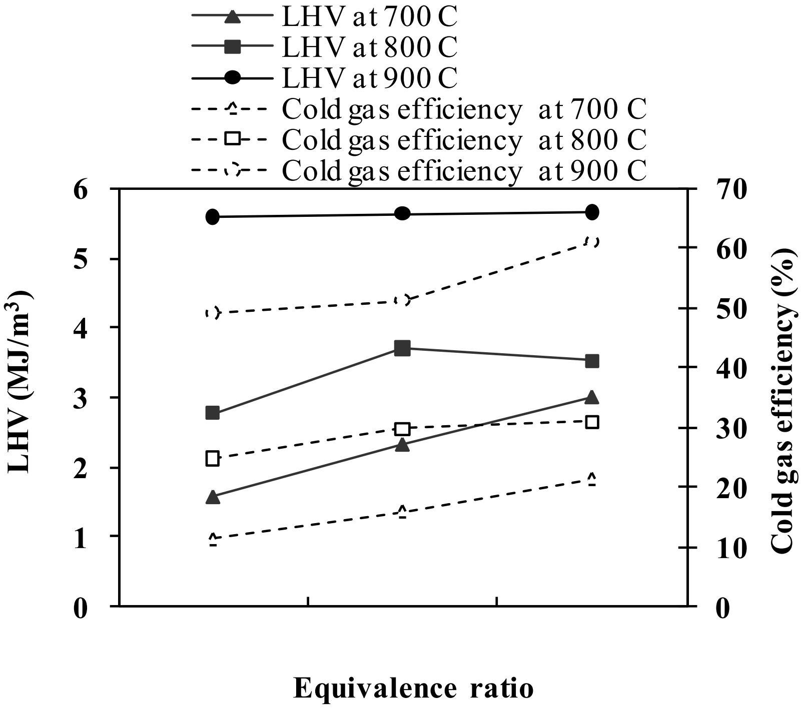


Figure 4.12 Effect of temperature and ER on LHV and cold gas efficiency from gasification of mixed sample (ratio 60:40)

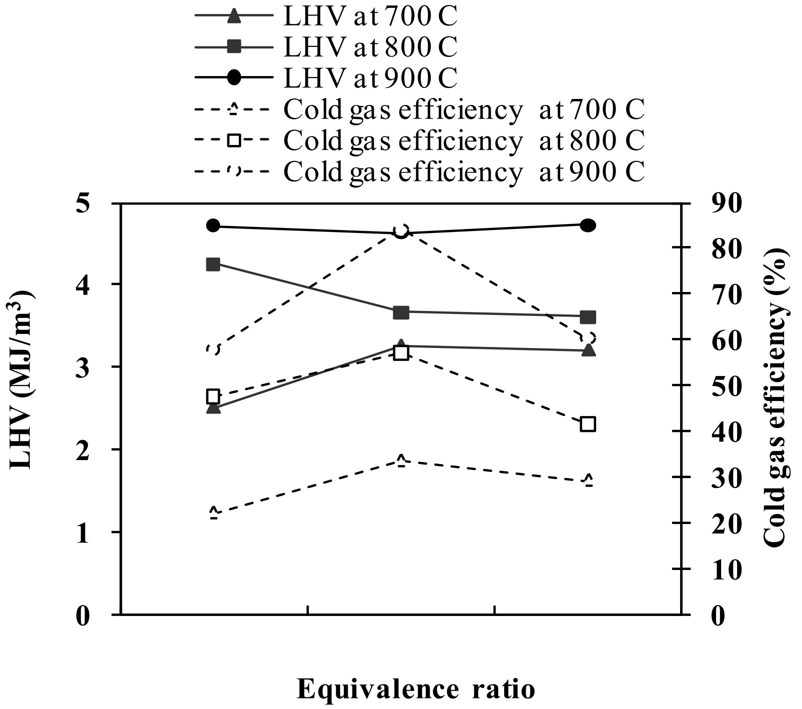


Figure 4.13 Effect of temperature and ER on LHV and cold gas efficiency from gasification of mixed sample (ratio 40:60)

4.7 Analysis of char

4.7.1 Ultimate analysis of char

Chemical analysis of char produced is the measurement of total carbon, hydrogen, nitrogen and sulfur content in char. Char from gasification was analyzed by using CHNS analysis. The plots in Figure 4.14 and 4.15 are comparisons between the compositions of char from the two mixed sample during gasification at reaction temperature of 700–900°C and ER of 0.2–0.6. The ultimate analysis of char which gasified at various conditions was shown in Table 4.2.

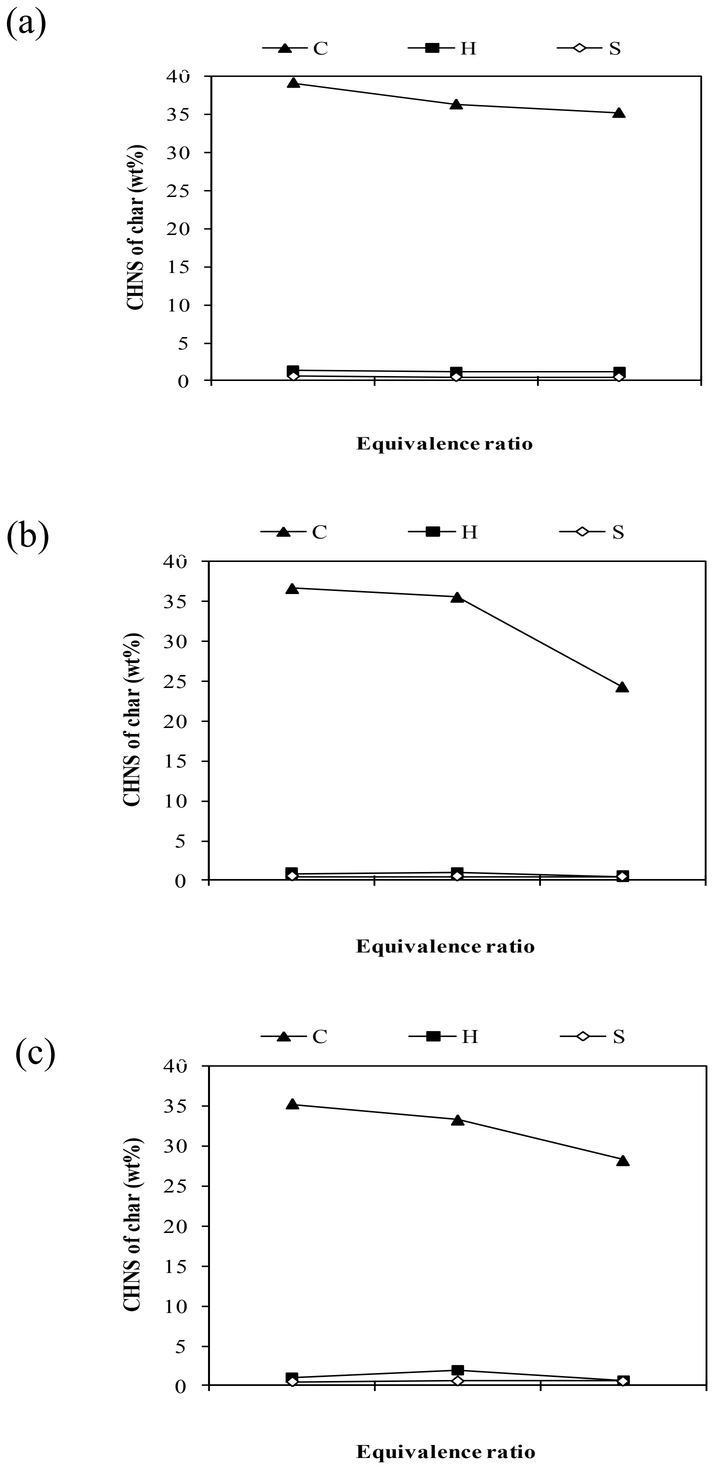


Figure 4.14 The composition of char from gasification of mixed sample (ratio 60:40) (a) 700°C (b) 800°C and (c) 900°C

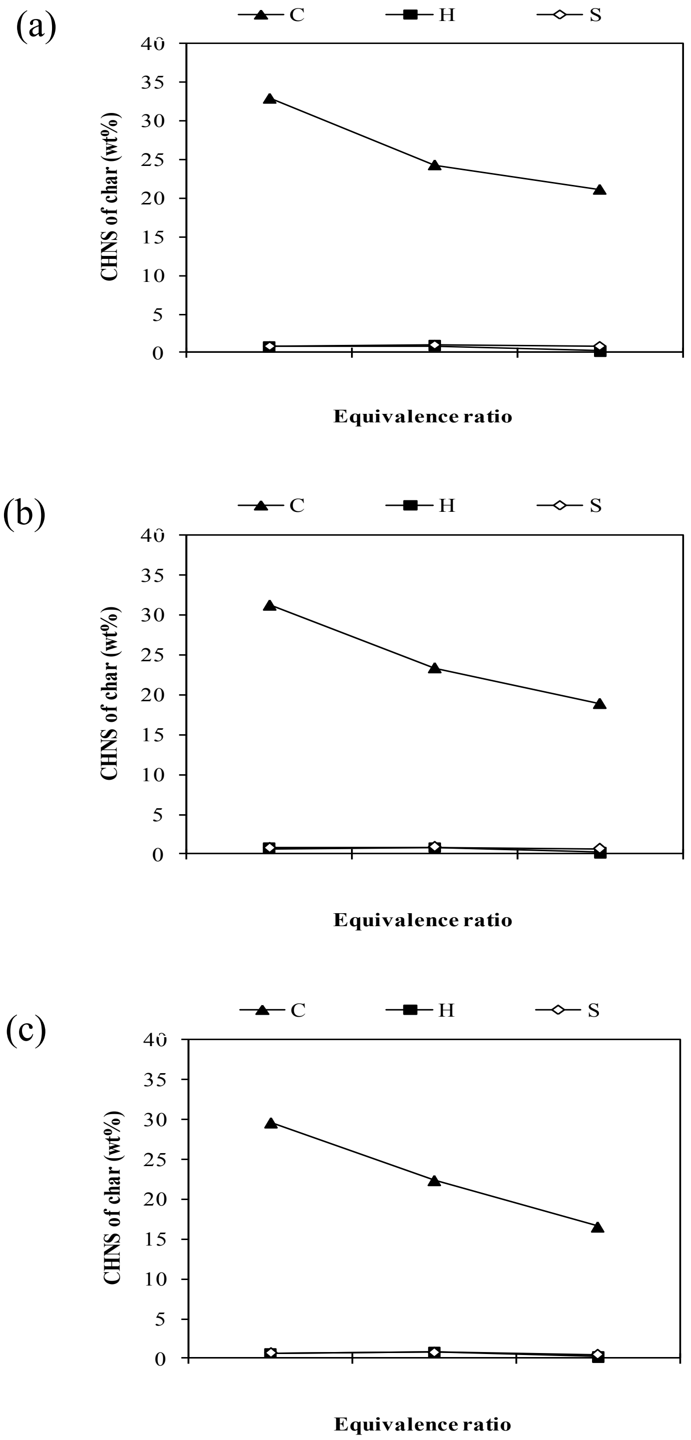


Figure 4.15 The composition of char from gasification of mixed sample (ratio 40:60) (a) 700°C (b) 800°C and (c) 900°C

Table 4.2 The ultimate analysis of char

Mixed sample ratio (BL:EU)	Temperature (°C)	Equivalence ratio	C (wt%)	H (wt%)	N (wt%)	S (wt%)
60:40	700	0.2	39.20	1.34	0.00	0.61
		0.4	36.40	1.20	0.00	0.53
		0.6	35.30	1.13	0.00	0.51
	800	0.2	36.70	0.91	0.00	0.50
		0.4	35.60	0.93	0.00	0.48
		0.6	24.30	0.54	0.00	0.43
	900	0.2	35.30	0.99	0.00	0.53
		0.4	33.30	1.96	0.00	0.61
		0.6	28.30	0.65	0.00	0.59
40:60	700	0.2	33.00	0.74	0.00	0.83
		0.4	24.30	0.89	0.00	1.02
		0.6	21.10	0.23	0.00	0.84
	800	0.2	31.30	0.70	0.00	0.77
		0.4	23.40	0.84	0.00	0.90
		0.6	18.90	0.22	0.00	0.67
	900	0.2	29.60	0.65	0.00	0.71
		0.4	22.40	0.78	0.00	0.77
		0.6	16.60	0.22	0.00	0.50

BL refers to Black Liquor.

EU refers to Eucalyptus bark residue.

The effect of reaction temperature on the element compositions for both mixed sample char shown that the carbon content in char at the lowest reaction temperature (700°C) was higher than the highest reaction temperature (900°C) at the same ER. The carbon content in char was decreased with increasing reaction temperature. The increase of reaction temperature affected the risen transformation of carbon in mixed sample into gas, condensable organic matter and tar. This result was related with the enhancement of gas yield and %C conversion which reported above. When carbon converted, the carbon content in char residual was decreased. These agree with the results reported by Frederick et al. (1994) who studied volatiles and char carbon yields during black liquor pyrolysis. They found that the char carbon content was rapid decreased with increasing temperature. Sricharoenchaikul et al. (2003) found that the char carbon content was decreased with increasing reaction temperature during black liquor gasification with CO_2. In addition, they concluded the effect of gasifying agents on char carbon was significant at reaction temperature above 800°C.

Similar the results of the effect of ER on the element compositions of mixed sample 60:40 and 40:60 char, the carbon content in char decreased greatly with increasing ER. The risen of ER influenced the reaction of carbon in mixed sample with O_2 added which carbon was transformed as gas, condensable organic matter and tar. Thus the amount of carbon in char was decreased with increasing ER. The carbon remained in char of mixed sample ratio of 40:60 was lower than the carbon remained in mixed sample ratio 60:40. The result explained that the carbon in char of mixed sample ratio of 40:60 could be converted to gas, condensable organic matter and tar more than char of mixed sample ratio of 60:40. Because of mixed sample ratio of 40:60 has more amount of eucalyptus proportion which carbon was more decomposed than carbon in black liquor. On the other hand, the change in the hydrogen and sulfur contents with increasing reaction temperature and ER tend to decrease but there were no significant difference. Nitrogen content was no appeared in char residual of both mixed samples. The result shown that all of nitrogen content in mixed sample may be vaporizing at this range of reaction temperature and ER. The remaining of carbon content in char are shown that this char can reuse and recommended for use as a feedstock in gasification process in further work.

4.7.2 XRF of char

After gasification, some of the carbon from organic matter and most of the inorganic matter remains in char residue. The remaining solid contains the residual non-volatile organic together with most of the inorganic matter. The char residues from both mixed sample gasification at various conditions were studied about the type and quantity of matter in char by using XRF. The results of XRF of raw materials and both mixed sample char reported in Table 4.3–4.5. The results suggested that black liquor contained more Na, S, Cl and K than eucalyptus bark. While eucalyptus bark contained more Si and Ca than black liquor as shown in Table 4.3.

Table 4.3 XRF of raw materials

Compounds	Black liquor	Eucalyptus bark
O	-	-
Na	25.84	0.05
Mg	0.07	0.44
Al	0.02	0.47
Si	0.25	2.42
P	0.04	0.34
S	5.56	0.24
Cl	3.77	0.62
K	20.23	1.82
Ca	0.26	10.13
Ti	-	0.22
Br	0.03	0.01
Rb	0.1	0.05
Sr	-	-
Ba	-	-
Mo	0.01	-

Table 4.4 and Table 4.5 presented that the main inorganic remained in char as sodium (Na), potassium (K), sulfur (S), chloride (Cl) and calcium (Ca). The results indicated that the most of Na, S, Cl and K remained in char came from black liquor. After gasification at various conditions of both mixed sample, the small amount of Na, S, Cl and K content in char are loss. It shown that the range of reaction temperature (700–900°C) and ER (0.2–0.6) used in this work were not effluence to the quantity of Na, S, Cl and K.

Table 4.4 XRF of mixed sample ratio 60:40

Compounds	Mixed sample ratio 60:40								
	700°C			800°C			900°C		
	ER=0.2	ER=0.4	ER=0.6	ER=0.2	ER=0.4	ER=0.6	ER=0.2	ER=0.4	ER=0.6
O	50.52	48.12	50.29	51.7	51.02	47.27	49.34	44.86	43.1
Na	25.36	25.85	25.79	25.3	24.99	26.53	24.71	27.44	27.3
Mg	0.26	0.3	0.28	0.29	0.29	0.3	0.28	0.36	0.28
Al	0.14	0.17	0.15	0.15	0.16	0.23	0.15	0.17	0.22
Si	0.61	0.75	0.67	0.77	0.83	0.99	0.61	0.78	0.96
P	0.1	0.11	0.12	0.11	0.11	0.1	0.11	0.12	0.12
S	4.05	4.53	4.1	4.53	4.22	5.7	5.08	6.39	6.4
Cl	3.61	3.82	3.6	3.57	3.61	3.42	3.76	3.88	4.15
K	10.55	11.23	10.29	9.43	10.17	9.82	10.86	10.85	11.73
Ca	4.68	4.95	4.59	4.04	4.47	5.54	4.99	5.06	5.6
Ti	0.02	0.04	0.02	0.02	0.03	0.03	-	0.03	0.03
Br	0.02	0.02	0.01	0.01	0.01	-	-	-	0.02
Rb	0.05	0.06	0.05	0.05	0.05	0.03	0.06	0.02	0.05
Sr	0.03	0.03	0.03	0.02	0.02	0.02	0.03	0.01	0.02
Ba	-	-	-	-	-	-	-	-	
Mo	-	0.01	-	-	0.01	0.02	-	0.02	0.01

Table 4.5 XRF of mixed sample ratio 40:60

Compounds	Mixed sample ratio 40:60								
	700°C			800°C			900°C		
	ER=0.2	ER=0.4	ER=0.6	ER=0.2	ER=0.4	ER=0.6	ER=0.2	ER=0.4	ER=0.6
O	45.27	48.23	51.2	42.63	49.76	40.53	47.05	45.31	43.3
Na	20.77	21.38	21.99	22.47	22.82	22.23	20.76	20.96	21.29
Mg	0.83	0.78	0.73	0.67	0.98	0.88	1.01	0.9	0.95
Al	0.4	0.38	0.36	0.52	0.53	0.79	0.5	0.43	0.43
Si	8.11	7.88	7.65	8.6	8.31	11.94	8.24	7.66	8.45
P	0.8	0.77	0.64	0.7	0.77	0.95	0.98	0.94	1.03
S	4.31	3.53	2.75	6.85	6.13	4.66	3.74	5.04	5.41
Cl	3.03	2.73	2.43	3.03	1.73	2.18	2.61	3.05	2.95
K	7.67	7.02	6.36	7.18	3.83	6.15	6.63	7.09	7.17
Ca	8.57	7.12	5.7	7.14	5.07	9.29	8.27	8.46	8.78
Ti	0.09	0.09	0.08	0.15	0.06	0.24	0.09	0.08	0.09
Br	0.02	0.02	0.01	-	-	0.01	-	0.01	0.02
Rb	0.04	0.03	0.02	0.02	0.01	0.03	0.02	0.03	0.03
Sr	0.04	0.03	0.03	0.02	0	0.05	0.03	0.04	0.04
Ba	0.06	0.06	0.05	-	-	0.08	0.07	-	0.06
Mo	-	-	-	0.02	0.01	-	0.01	-	0

The effect of reaction temperature on the vaporization of inorganic in black liquor was explained by Wåg et al. (1997) that a substantial loss of Na and K from the black liquor char has been found to occur at temperatures of 900°C and above. From the reason above, it indicated that this range of reaction temperature (700– 900°C) which used in this work is suitable for choosing as the gasification reaction temperature. In addition, the small decrease of Na and S in both mixed sample char, which compared with raw materials, shown that the Na and S contained in char can be recovered for reused as pulping chemical.

CHAPTER V

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

Raw materials contained high content of volatile and carbon and low ash content which should be a good candidate for production of fuel via thermochemical process. From the environmental point of view, mixed sample contained low nitrogen and sulfur contents. The utilization of this mixed sample would help a reduction in NO_x and SO_x emission thus lessen environment pollution.

5.1.1 The raised reaction temperature and ER of mixed sample gasification conducted an increase in gas yields and a decrease in solid and liquid yields. The highest gas yield obtained at the highest reaction temperature and ER of 900°C and 0.6, respectively. The optimized reaction temperature for both mixed sample could be 900 °C. Due to this temperature would also greater favors gas yield, gas compositions and carbon conversion. The gas composition result can be seen that increasing ER significantly increased CO production while CH_4 and H_2 reduced. The carbon conversion increased with increasing ER while hydrogen conversion decreased.

5.1.2 The excessive of O_2 did not improve the quanlity of syngas which concerned on H_2/CO ratio. H_2/CO ratio obtained from this study between 0.52-1.48. The maximum H_2/CO was achieved from mixed sample of 60:40 at 800°C and ER of 0.4. The syngas production increased with reaction temperature and ER. In present work, the highest syngas production equals to 32.43 L obtained when gasified mixed sample 60:40 at 900°C and ER of 0.6.

5.1.3 The highest temperature (900°C) is beneficial for increasing of product gas heating value. The gas LHV obtained in this study ranging from 1.59-5.66 MJ/m^3. Such product gas that obtained from this study can be readily utilized by combustion. The maximum gas LHV is obtained from mixed sample ratio of 60:40 that gasified at reaction temperature 900, ER of 0.4.

5.1.4 Analysis of char found that the carbon content in char decreased with increasing reaction temperature and ER because of the risen transformation of carbon in mixed sample into gas, condensable organic matter and tar. The remaining of carbon content in char shown that this char can reuse and suggested for use as a feedstock in gasification process for the further work. In addition, reaction temperature and ER did not effluence to the quantity of Na and S. The range of reaction temperature (700–900°C) which used in this work is suitable for choosing as the gasification reaction temperature. In addition, the small decrease of Na and S in both mixed sample char shown that the Na and S contained in char can be recovered for reused as pulping chemical.

From all of results it suggested that the gasification of mixed sample may be considered as an appropriate option for conversion black liquor and eucalyptus bark residues to various fuel gases.

5.2 Recommendations

Based on the results of this study, some recommendations for future studies can be proposed.

5.2.1 The conditions of this work varied only reaction temperature and ER. Future work should concern the other variables, which are important parameters, could improve the quantity and quality of fuel gases. such as;

- Residence time
- Type of biomass material used
- The catalyst added
- The usage of stream and pressure
- The pyrolysis condition (to compare the result from gasification process) etc.

5.2.2 Black liquor that used in this work can be corrosive the stainless reactor. The element matters of stainless may be contaminating in char residues. The evaluation of char Future work should change type of reactor. For example, the use of reactor that made from alumina or quartz. This development can reduce this problem.

5.2.3 Future work should study form and quantity of element matter in the remaining char during gasification. This study will support the exactly utilization of char.

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APPENDICES

APPENDIX A

APPENDIX A.1

The calculation of % C, % H conversion as specific gases

This is an example of % C, % H conversion for mixed sample ratio of 60:40 gasified at reaction temperature of 900°C and ER of 0.2.

Mixed sample feed rate 5 g/min
% Moisture content 30%
(% moisture content depend on mixed sample ratio)
Thus, % solid in mixed sample 70 %

Actual dry mixed sample feed (70 x 5)/100 = 3.5 g/min
% C in mixed sample 28.1%
% H in mixed sample 3.42%
So, C in mixed sample (28.1 x 3.5)/100 = 0.9835 g C/min
H in mixed sample (3.42 x 3.5)/100 = 0.1197 g H/min

<u>%C conversion as CO</u>

vol% of CO from analyzer 18.80%
Total gas flow out 3.8 L/min
So, volume of CO (18.80 x 3.8)/100
= 0.7143 L/min
= 0.7143/24.45 L/ mole = 0.0292 mole/min
= 0.0292 x 28 g = 0.8180 g/min
To find C in volume of CO (in gram)
CO 28 g contain C 12 g C
CO 0.8180 g/min contain C 0.351 g C/min
%C conversion as CO = (C in CO/C in mixed sample) x 100
= (0.351/0.9835) x 100
= 35.65%

%C conversion as CH_4

vol% of CH_4 from analyzer 2.54 %

Total gas flow out 3.8 L/min

So, volume of CH_4 (2.54 x 3.8)/100

= 0.0965 L/min

= 0.0965/24.45 L/mole = 0.0039 mole/min

= 0.0039 x 16 g = 0.0632 g/min

To find C in volume of CH_4 (in gram)

CH_4 16 g contain C 12 g C

CH_4 0.0632 g/min contain C 0.047 g C/min

%C conversion as CH_4 = (C in CH_4/C in mixed sample) x 100

= (0.047/0.9835) x 100

= 4.82%

%H conversion as H_2

vol% of H_2 from analyzer 21.42%

Total gas flow out 3.8 L/min

So, volume of H_2 (21.42 x 3.8)/100

= 0.8141 L/min

= 0.8141/24.45 L/mole = 0.0333 mole/min

= 0.0333 x 2 g = 0.07 g/min

To find H in volume of H_2 (in gram)

H_2 2 g contain H 1 g H

H_2 0.07 g/min contain H 0.033 g H/min

%H conversion as H_2 = (H in H_2/H in mixed sample) x 100

= (0.033/0.1197) x 100

= 27.82%

%H conversion as CH_4

vol% of CH_4 from analyzer 2.54%
Total gas flow out 3.8 L/min
So, volume of CH_4 (2.54 x 3.8)/100
= 0.0965 L/min
= 0.0965/24.45 L/mole = 0.0039 mole/min
= 0.0039 x 16 g = 0.0632 g/min

To find H in volume of CH_4 (in gram)
CH_4 16 g contain H 4 g H
CH_4 0.0632 g/min contain H 0.016 g H/min

%H conversion as CH_4 = (H in CH_4/H in mixed sample) x 100
= (0.016/0.1197) x 100
= 13.19%

APPENDIX A.2

The volume calculation of specific product gases

This is an example of the volume calculation of specific product gases for mixed sample ratio of 60:40 gasified at reaction temperature of 900°C and ER of 0.2.

Total gas flow out	3.8 L/min
Run time	19 min

Thus,

Total volume of product gas (L) = Total gas flow out (L/min) x Run time (min)
= 3.8 L/min x 19 min
= 72.21 L

%CO average from analyzer	18.80
$\%H_2$ average from analyzer	21.42
$\%CH_4$ average from analyzer	2.54

Thus, volume of CO = (%CO average x Total volume of gas (L))/100
= (18.80 x 71.21 L)/100
= 13.57 L

volume of H_2 = ($\%H_2$ average x Total volume of gas (L))/100
= (21.42 x 71.21)/100
= 15.47 L

volume of CH_4 = ($\%H_2$ average x Total volume of gas (L))/100
= (2.54 x 71.21)/100
= 1.83 L

APPENDIX A.3

The LHV calculation of product gases

This is an example of the LHV calculation for mixed sample ratio of 60:40 gasified at reaction temperature of 900°C and ER of 0.2.

Volume of CO	0.7143	L/min
Volume of H_2	0.8141	L/min
Volume of CH_4	0.0965	L/min
Total gas flow out	3.8	L/min

$$\text{LHV of product gas} = \frac{[(12.64 \text{ x vol CO}) + (10.82 \text{ x vol } H_2) + (35.72 \text{ x vol } CH_4)]}{\text{Total gas flow out (L/min)}}$$

$$= \frac{[(12.64 \text{ x } 0.7143) + (10.82 \text{ x } 0.8141) + (35.72 \text{ x } 0.0965)]}{3.8}$$

$$= 5.60 \text{ MJ/m}^3$$

APPENDIX A.4

The cold gas efficiency calculation of product gases

This is an example of the cold gas efficiency calculation for mixed sample ratio of 60:40 gasified at reaction temperature of 900°C and ER of 0.2.

LHV of product gas 5.60 L/min
Volume of product gases 72.2 L
= 72.2 L/1000 = 0.0722 m^3
LHV of mixed sample 9.95 MJ/Kg
Mass of mixed sample feed 82.62 g
= 82.26/1000 = 0.0826 Kg

$$\text{cold gas efficiency} = \frac{\sum LHV_i \text{ x } V_i}{LHV_{feed} \text{ x } M}$$

where LHV_i is lower heating value of product gas I (MJ/m^3), V_i is volume of product gas i (m^3), LHV_{feed} is lower heating value (MJ/kg) of material feed, and M is mass of material feed (kg).

$$\text{Thus, cold gas efficiency} = \frac{5.60 \text{ x } 0.722}{9.95 \text{ x } 0.0826}$$

$$= 49.158\%$$

APPENDIX B

Table B-1 The products distribution from the gasification of mixed sample ratio 60:40

Reaction temperature (°C)	Equivalence ratio	Solid (wt%)	Liquid (wt%)	Gas (by difference)
700	0.2	49.01	30.97	20.02
	0.4	43.85	28.65	27.50
	0.6	39.11	30.76	30.13
800	0.2	28.44	25.22	46.34
	0.4	25.98	26.08	47.94
	0.6	23.61	26.08	50.31
900	0.2	23.13	7.20	69.67
	0.4	20.39	7.06	72.55
	0.6	15.60	9.45	74.95

Table B-2 The products distribution from the gasification of mixed sample ratio 40:60

Reaction temperature (°C)	Equivalence ratio	Solid (wt%)	Liquid(wt%)	Gas(by difference)
700	0.2	26.68	11.50	61.82
	0.4	26.91	5.93	67.16
	0.6	23.09	13.58	63.33
800	0.2	26.35	17.91	55.74
	0.4	24.24	14.42	61.33
	0.6	25.42	8.17	66.42
900	0.2	19.82	8.89	71.30
	0.4	27.52	8.17	64.31
	0.6	14.89	13.44	71.67

Table B-3 The % C and % H conversion as specific gases at various conditions of mixed sample ratio 60:40

Reaction temperature (°C)	Equivalence ratio	Gas flow out (L/min)	% C conversion as		% H conversion as	
			CO	CH_4	H_2	CH_4
700	0.2	3.00	5.36	2.96	4.07	8.12
	0.4	3.10	7.98	5.27	4.56	14.43
	0.6	3.20	13.69	5.05	7.98	13.82
800	0.2	3.20	12.01	3.55	10.44	9.71
	0.4	3.40	14.00	6.40	14.23	17.52
	0.6	3.70	19.79	4.49	15.34	12.29
900	0.2	3.80	35.65	4.82	27.82	13.19
	0.4	4.10	36.88	5.80	30.48	15.87
	0.6	4.20	36.50	6.87	30.41	18..81

Table B-4 The % C and % H conversion as specific gases at various conditions of mixed sample ratio 40:60

Reaction temperature (°C)	Equivalence ratio	Gas flow out (L/min)	% C conversion as		% H conversion as	
			CO	CH_4	H_2	CH_4
700	0.2	3.60	11.85	3.90	8.70	11.48
	0.4	4.20	25.91	4.40	9.85	12.98
	0.6	4.40	15.36	4.99	10.08	14.70
800	0.2	4.90	32.71	7.23	19.49	21.30
	0.4	5.10	24.84	7.79	18.23	22.95
	0.6	4.20	18.42	7.17	14.26	21.12
900	0.2	4.70	30.88	7.85	23.81	23.14
	0.4	4.80	31.78	7.24	24.70	21.34
	0.6	4.30	27.88	7.10	22.43	20.93

Table B-5 The volume of specific product gas at various conditions of mixed sample ratio 60:40 and 40:60

Mixed sample ratio (BL:EU)	Reaction Temperature (°C)	Equivalence ratio	Volume of gas (L)			
			CO	H_2	CH_4	syngas
60:40	700	0.2	3.58	3.97	1.98	7.55
		0.4	5.16	4.30	3.41	9.46
		0.6	8.57	7.30	3.16	15.87
	800	0.2	6.52	10.55	2.22	17.07
		0.4	8.25	12.25	3.77	20.50
		0.6	10.72	12.13	2.43	22.85
	900	0.2	13.57	15.47	1.83	29.04
		0.4	12.56	15.16	1.97	27.73
		0.6	14.63	17.80	1.97	32.43
40:60	700	0.2	5.15	5.14	1.69	10.29
		0.4	6.45	4.36	1.44	10.81
		0.6	8.35	7.44	2.71	15.79
	800	0.2	12.80	10.35	0.00	23.15
		0.4	5.94	5.92	1.86	11.86
		0.6	8.41	8.84	3.27	17.25
	900	0.2	11.41	11.94	2.90	23.36
		0.4	8.29	8.75	1.89	17.04
		0.6	10.91	11.91	2.78	22.82

BL refers to Black Liquor.
EU refers to Eucalyptus bark residue.

Table B-6 The lower heating value of product gases, cold gas efficiency and H_2/CO ratio of mixed sample ratio 60:40 and 40:60

Mixed sample ratio (BL:EU)	Reaction Temperature (°C)	Equivalence ratio	Lower heating value of product gases (MJ/m^3)	Cold gas efficiency	H_2/CO
60:40	700	0.2	1.59	11.27	1.10
		0.4	2.33	15.96	0.83
		0.6	3.00	21.44	0.85
	800	0.2	2.77	24.97	1.27
		0.4	3.71	29.85	1.48
		0.6	3.53	30.91	1.13
	900	0.2	5.60	49.16	1.14
		0.4	5.64	51.13	1.21
		0.6	5.66	61.11	1.22
40:60	700	0.2	2.52	22.11	1.00
		0.4	3.26	33.50	0.52
		0.6	3.21	29.23	0.89
	800	0.2	4.25	47.61	0.81
		0.4	3.66	57.14	1.00
		0.6	3.61	41.51	1.05
	900	0.2	4.72	57.97	1.05
		0.4	4.63	83.98	1.06
		0.6	4.73	60.36	1.09

BL refers to Black Liquor.
EU refers to Eucalyptus bark residue.

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2. Wanvipa Kripittayakorn, Duangduen Atong, Sildara Thassanaprichayanont and Viboon Sricharoenchaikul. *Fuel Gases Production from Gasification of Black Liquor Mixed with Eucalyptus Bark using Fixed Bed Reactor.* The poster presentation and published in The International Conference of Solid Waste 2011 Moving Towards Sustainable Resource Management (ICSWHK 2011), Hong Kong SAR, China, May 2–6, 2011. Organized by Hong Kong Baptist University and Sino-Forest Applied Research Centre for Pearl River Delta Environment.