FUEL GASES FROM CO-GASIFICATION OF
PULP SLUDGE MIXED WITH BLACK LIQUOR

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แก๊สเชื้อเพลิงที่เกิดจากกระบวนการแกซิฟิเคชันร่วมของกากตะกอนเยื่อกระดาษผสมกับน้ำยางดำ

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งานวิจัยนี้ได้ทำการศึกษาการแจกแจงผลิตภัณฑ์ต่างๆ และประสิทธิภาพทางพลังงานที่เกิด จากกระบวนการแกซิฟิเคชันร่วมของกากตะกอนเยื่อกระดาษผสมกับน้ำยางดำเพื่อเสนอเป็น แนวทางใหม่ในการใช้แทนหม้อไอน้ำในกระบวนการนำสารเคมีกลับมาใช้ใหม่ โดยการทดลองนี้ ใช้เตาปฏิกรณ์แบบเบดนิ่ง โดยมีตัวแปรในการศึกษา ได้แก่ อุณหภูมิ 700, 800 และ 900 องศา เซลเซียส, อัตราส่วนระหว่างอากาศกับเชื้อเพลิง 0.2, 0.4 และ 0.6, อัตราส่วนกากตะกอนเยื่อ กระดาษต่อกับน้ำยางดำ 50:50 และ 40:60, และอัตราการป้อนวัตถุดิบเข้าสู่ระบบ 5 กรัมต่อนาที นอกจากนี้ยังได้ทำการศึกษาผลของตัวเร่งปฏิกิริยา $Ni\text{-}La\text{-}Mg/Al_2O_3$ ที่มีการเตรียมโดยวิธี อิมเพรกเนชั่นร่วมและผสมกับสารตั้งต้นก่อนจะป้อนเข้าสู่ระบบ เพื่อศึกษาผลของตัวเร่งปฏิกิริยาที่ มีต่อกระบวนการเปลี่ยนองค์ประกอบทางเคมีโดยใช้พลังงานความร้อน โดยแก๊สผลิตภัณฑ์หลักที่ ได้จากกระบวนการ ได้แก่ คาร์บอนมอนอกไซด์ คาร์บอนไดออกไซด์ ไฮโดรเจน และมีเทน ซึ่งทำ การวิเคราะห์โดยใช้เครื่องวิเคราะห์แก๊สผลิตภัณฑ์ TCD-NDIR analyzer ในส่วนของถ่านชาร์และ น้ำมันทาร์ที่ได้จากกระบวนการได้ทำการเก็บไว้เพื่อทำการวิเคราะห์โดยน้ำหนัก ผลการวิจัยในชุด การทดลองแบบไม่ใช้ตัวเร่งปฏิกิริยาพบว่า สภาวะที่เหมาะสม คือ อุณหภูมิ 900 องศาเซลเซียส อัตราส่วนระหว่างอากาศกับเชื้อเพลิง 0.2 และอัตราส่วนสารตั้งต้น 40:60 ซึ่งให้ปริมาณแก๊ส ผลิตภัณฑ์ร้อยละ 69.18 โดยน้ำหนัก อัตราส่วนโดยโมลของ H_2/CO เท่ากับ 0.96 ค่าความร้อนของ ผลิตภัณฑ์แก๊ส 5.91 เมกะจูลต่อลูกบาศก์เมตร และค่าประสิทธิภาพเชิงความร้อนร้อยละ 79.55 ใน ชุดของการทดลองแบบใช้ตัวเร่งปฏิกิริยา พบว่า ตัวเร่งปฏิกิริยา ส่งผลให้ปริมาณแก๊สผลิตภัณฑ์ เพิ่มขึ้นร้อยละ 10 โดยประมาณ ค่าความร้อนของผลิตภัณฑ์แก๊ส และค่าประสิทธิภาพเชิงความร้อน อยู่ในช่วง 3.78-6.73 เมกะจูลต่อลูกบาศก์เมตร และร้อยละ 46.02-90.13 ตามลำดับ และในชุดการ ทดลองแบบไม่ใช้ตัวเร่งปฏิกิริยาอยู่ในช่วง 3.37-5.91 เมกะจูลต่อลูกบาศก์เมตร และร้อยละ 34.63-79.55 ตามลำดับ จากผลการวิจัยนี้พบว่า กระบวนการแกซิฟิเคชันร่วมสามารถเป็นทางเลือกที่จะ แปรสภาพของเสียไปเป็นผลิตภัณฑ์เชื้อเพลิงที่มีประโยชน์ได้

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CHANATTAPA SIRINAWIN: FUEL GASES FROM CO-GASIFICATION OF PULP SLUDGE MIXED WITH BLACK LIQUOR. ADVISOR: ASST. PROF. VIBOON SRICHAROENCHAIKUL, Ph.D., CO-ADVISOR: DUANGDUEN ATONG, Ph.D. 132 pp.

In this research, product distribution and energy efficiency from co-gasification of pulp sludge mixed with black liquor has been suggested as a relatively new technology that can be used in addition to recovery boiler in the chemical recovery process. This research was carried out in a fixed bed reactor. The operating parameters including temperature of 700, 800 and 900°C, equivalence ratio (ER) of 0.2, 0.4 and 0.6 and ratio of pulp sludge to black liquor of 50:50 and 40:60 at feeding rate of 5 g/min were examined. In addition, Ni-La-Mg/Al_2O_3 catalyst was prepared by co-impregnation method and mixed with raw material before feeding into system to study its effect on thermochemical conversion reaction. Major gaseous products such as CO, CO_2, H_2 and CH_4 were analyzed by TCD-NDIR analyzer. Char and tar residue were collected and calculated by measured weight. The results of non-catalytic cases indicated that the optimal condition was temperature of 900°C, ER of 0.2 and raw material ratio 40:60 with gas yield of 69.18%, H_2 to CO ratio of 0.96, lower heating value of 5.91 MJ/m^3 and cold gas efficiency of 79.55%. For catalytic cases, it was found that the catalyst can improve the percentage of gas yield around 10 wt%. Lower heating value and cold gas efficiency of catalytic cases were 3.78-6.73 MJ/m^3 and 46.02-90.13% while those obtained from non catalytic trials were 3.37-5.91 MJ/m^3 and 34.63-79.55%, respectively. From these results, co-gasification process can be considered as alternative option for conversion pulp sludge mixed with black liquor to usable fuel products.

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CHAPTER I
INTRODUCTION

1.1 Introduction

It can undeniably be said that pulp and paper has a very significant part in our everyday life. Pulp and paper is used in all aspects of life, from tissue paper to lunch box, from writing paper to movie tickets and from dinner menu to birthday card. Paper is used in studying, working, commercial trading, communications and so on. Paper consumption each year therefore reaches approximately 2,000,000 tons or 34 kilograms per person per year (Pollution Control Department, 2009). Furthermore, Paper demand is consecutively increase 15 percent per year. In response to such an ever-increasing demand for paper, the pulp and paper manufacturers have to continuously increase their production rate, accelerating the level of resource consumption as well. To produce 1 ton of paper, tree 17 trees, electricity 1,000 kilowatt per hour, furnace oil 300 liters, water 100 tons and chlorine 5 kilograms are required (Pollution Control Department, 2009). Therefore, wastes are consequently generated from such manufacturing process, severely affecting the environment where they are not properly managed.

Black liquor and sludge are significant wastes from pulp and paper industry that cause high level of pollution. The essential components of black liquor are the remaining substances from the digestive process where the cellulose fibers have been cooked out from the wood such as alkali lignin, polysaccharides, wood extractives, and residual inorganic pulping chemicals (Marklund, 2009; Sricharoenchaikul et al., 2001). Normally, the pulp and paper industry treats black liquor via chemical recovery process. In the chemical recovery process, weak black liquor (with solid content of less than 20%) from digester will pass through multiple-effect evaporators, where excess water is removed (more than 50%), before passing through conventional combustion at recovery boiler (Sricharoenchaikul, 2009). Then, recovered chemicals and heat are obtained and used in the industry. As for the sludge from wastewater treatment system, it generally consists of the solid residue recovered from the wastewater stream of pulping and paper making process (Scott and Smith, 1995). Sludge is produced at two steps in the wastewater treatment process. Primary sludge is recovered at the primary clarifier and secondary sludge from secondary clarifier.

Then the primary sludge is mixed with the secondary sludge prior to dewatering and disposal. Generally, the pulp and paper industry treats the sludge by dumping them into the landfill. Though variety of treatment processes can be used to manage black liquor and sludge, gasification process has been suggested as a relatively new technology that can be used in addition to recovery boiler in the chemical recovery process of pulp and paper industry (Hammond, 2002).

Gasification is a partial oxidation (reaction) process that convert hydrocarbons, biomass, or various wastes into synthesis gas (primarily hydrogen, H_2 and carbon monoxide, CO) which can be used to produce electricity and valuable products such as chemicals, fertilizers, substitute natural gas, hydrogen, steam and transportation fuels (Gasification technologies council, 2008). In the pulp and paper industry, gasification process has several advantages over combustion. For example, more electricity can be produced per unit of black liquor mass consumed in gasification process than from combustion in recovery boiler. When gasifiers are used instead of recovery boiler, the possibility of smelt-water explosions is eliminated. Moreover, sulfur and sodium can be separated during gasification process (Hammond, 2002).

Accordingly, co-gasification of pulp sludge mixed with black liquor is the new approach for black liquor management and sludge treatment. This process can convert black liquor and sludge into more valuable products, and offers several advantages over combustion process and disposal into the landfill. Furthermore, co-gasification of pulp sludge mixed with black liquor also contributes to environmental friendliness such as lower CO_2 emission, wastewater discharge and solid waste.

In biomass gasification, tar formation is a major problem which may condense in downstream piping system or heat exchanger and cause fouling, plugging, and corrosion of the equipment. Catalytic hot gas conditioning can be applied to resolve this problem. It offers several advantages over physical removal methods such as reducing wastewater, reforming of tars and adjusting the composition of gas products. Ni catalyst is widely used to increase performance in gasification process. It has been extensively investigated because of the metal availability and economic considerations (Djaidja et al., 2006; Garcia et al.,2000; García et al., 2001; Martínez et al., 2002; Miyazawa et al., 2006; Li et al., 2009). Addition of magnesium can change Ni/Al_2O_3 catalytic properties and enhance steam adsorption capability and solid solutions of NiO/MgO stabilize nickel as well as prevent catalyst sintering. For

lanthanum, it improves the stability of the catalyst and decreases carbon formation (Garcia et al., 2000).

In this research, fuel products from co-gasification of pulp sludge mixed with black liquor was carried out in a fixed bed reactor. The effect of temperature, equivalence ratio (ER), ratio of pulp sludge to black liquor and $Ni\text{-}La\text{-}Mg/Al_2O_3$ catalyst, which have influence on the products, were examined. These variables were investigated to determine the optimal condition and the performance of catalyst on co-gasification to transform pulp sludge mixed with black liquor into valuable products.

1.2 Objective

1. To study the production of fuel gases from co-gasification of pulp sludge mixed with black liquor.

2. To study the effect of temperature, equivalence ratio (ER), ratio of pulp sludge to black liquor and $Ni\text{-}La\text{-}Mg/Al_2O_3$ catalyst, which have influence on the products.

3. To determine the optimal condition of co-gasification to transform pulp sludge that mixed with black liquor into fuel products.

1.3 Hypothesis

Pulp sludge and black liquor have heating value and molecule that can transform into valuable products through gasification process.

1.4 Scope of the study

This research is a study of thermochemical conversion of wastes produced by the pulp and paper industry in Thailand. The wastes are pulp sludge and black liquor. Sludge from wastewater treatment system is collected after passing the sludge belt press, while black liquor, in which eucalyptus is used as a raw material, is collected after evaporation process.

- Co-gasification of mixed wastes was carried out in a fixed bed reactor.
- The operating temperatures are at 700, 800 and 900°C.
- The equivalence ratios (ER) are 0.2, 0.4 and 0.6.
- The proportions of pulp sludge mixed with black liquor are 50:50 and 40:60.
- Catalyst is $Ni\text{-}La\text{-}Mg/Al_2O_3$ prepared by co-impregnation method.
- Nitrogen is used as carrier gas and oxygen is used as oxidizing gas.
- The gaseous products are mainly CO, CO_2, H_2 and CH_4.

1.5 Expected outcome

1. Synthesis gas from pulp sludge mixed with black liquor is an innovative renewable energy source.

2. Black liquor and sludge recovery can reduce air and water pollution release into the environment.

3. Co-gasification of black liquor and sludge can reduce wastes from pulp and paper production process.

4. The pulp and paper industry will have available a new approach for black liquor management and sludge treatment.

CHAPTER II
THEORY AND LITERATURE REVIEW

The objectives of this research are to study fuel gases production and to determine the optimal condition of co-gasification of pulp sludge mixed with black liquor in a fixed bed reactor. Theory and literature review are following:

2.1 Biomass

Biomass is the plant material that can be used as renewable energy source. Biomass resources include wood and wood wastes, agricultural crops and their waste by-products, municipal solid waste (MSW), animal wastes, waste from food processing and aquatic plants and algae. Biomass can be converted to energy via conversion processes, so it differs from other alternative energy source (Demirbaş, 2001).

2.1.1 Components of biomass

The major components of biomass are cellulose, hemicellulose and lignin (McKendry, 2002; Kirubakaran et al., 2009).

- Hemicellulose is a mixture of polysaccharides that found with cellulose. An average molecular weight of hemicellulose is <30,000. Hemicellulose differs from cellulose, in consisting primarily of xylose and other five-carbon monosaccharides. Biomass contains hemicellulose about 20-40 percent by weight. Hemicellulose represented by xylan decomposes between 220-320°C

- Cellulose is a glucose polymer with an average molecular weight of around 100,000. Cellulose is the largest fraction of the biomass. Biomass contains cellulose about 40-50 percent by weight. Cellulose decomposes between 250-360°C

- Lignin can be regarded as a group of amorphous, high molecular-weight, chemically related compounds. Lignin gradually decomposes between 80-500°C but it mostly decomposes at 350-450°C (Bartkowiak and Zakrzewski, 2004).

2.1.2 Biomass conversion process

Biomass conversion process can be divided into biochemical conversion process and thermochemical conversion process (McKendry, 2002).

- Biochemical conversion process that commonly used are fermentation and an-aerobic digestion (AD).

- Thermochemical conversion that commonly used are combustion, pyrolysis, gasification and liquefaction/hydrothermal upgrading.
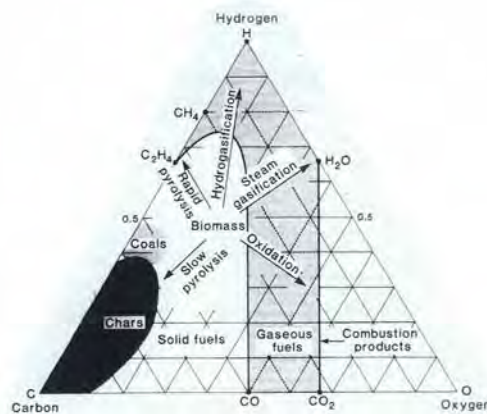
Figure 2.1 Thermochemical conversion of biomass (Probstein and Hicks, 1982)

- Pyrolysis occurs in the absence of oxygen. The products of pyrolysis are gases, liquids, and a carbonaceous char. The products depend on the biomass properties. The main product of slow pyrolysis is char, whereas the liquid and gaseous products are increased with rapid pyrolysis. Pyrolysis usually use temperatures below 600°C

- Gasification is a partial oxidation of the carbon constituent. The gaseous products of gasification, such as carbon monoxide, carbon dioxide and hydrogen, are determined by the calorific value of the raw material. The temperatures ranges of gasification are 800-1100°C.

- Combustion occurs with air containing sufficient oxygen to completely oxidize the hydrocarbon. The products of combustion are carbon dioxide, water vapor and dilute nitrogen. The combustion temperatures are 1500°C or more (Probstein and Hicks, 1982).

2.1.3 Characteristics of biomass for conversion

The most important properties for biomass conversion are (Knoef, 2005):

1) Moisture content

The moisture content of biomass is the quantity of water in the material that expressed as a percentage of the material's weight. For thermochemical conversion process, dry biomass feedstock is better because it produce higher quality gas than wet biomass feedstock.

2) Ash content and ash composition

Ash is the inorganic or mineral content of the biomass, which remains after complete combustion. The amount of ash depends on types of feedstock which would, influence with the reactor design, especially the ash remover system.

3) Elemental composition

The elemental composition of biomass is important because it have influence to the heating value and the level of products emission.

4) Heating value

The heating value is determined by the elemental composition, the ash content of biomass and the moisture content of biomass. The higher heating value (HHV) is the maximum amount of energy that can be obtained for combusting the fuel (water is produced as liquid). HHV is necessary to calculate the efficiency of system. The lower heating value (LHV) is the amount of energy release in case of water escape to atmosphere as a gas and the heat of evaporation of water is not recovered (water as vapor).

5) Bulk density and morphology

The bulk density is the weight of material per unit of volume. It differs for various types of biomass. Biomass of low bulk density is hard to handle, transport and store. Whereas the size and size distribution of biomass are important for determine pressure drop over the bed material, so the uniform size and good particle properties can avoid this problem.

6) Volatile matter content

The volatile matter content in biomass varies between 50 and 80%. The amount of volatiles has an impact on the level of tar production.

7) Feedstock preparation requirement

All types of biomass materials require feedstock preparation due to a large variety in physical, chemical and morphological characteristics.

2.2 Black liquor

Black liquor is a major biomass waste from pulp and paper production. It mostly consists of dissolved lignin which the degradation products from reacting. An aqueous solution containing sodium hydroxide and sodium sulfide along with the hemicellulosic and cellulosic hexose and pentose sugars degradation products. The pentose sugars degradation products are present as saccharinic acids, which are anhydrides of the various sugars. Black liquor also consists of some wood extractives and residual inorganic pulping salt (Demirbaş, 2002). Black liquor is comes from cooking process. Then, it will send to reuse by chemical recovery process (see Figure 2.2). The chemical recovery process is important for pulp and paper making process because it can save costs of chemicals that use in pulping process by regenerate them. Furthermore, it can produce energy for use in pulp and paper industry. Weak black liquor, which comes from cooking process, has a solid content under 20%. Then, weak black liquor concentrated by evaporator and change to strong black liquor that has a solid content more than 50% (United Nations Environment Programme, 1996). Next, strong black liquor from the evaporators is burned in a recovery boiler. In this step, organic solids in strong black liquor are burned for produce steam and electricity. The molten organics salts ($Na_2CO_3 + Na_2S$) flow from recovery boiler to dissolving tank, in which they are mixed with the weak white liquor to generate the green liquor. This green liquor is clarified and causticized to recycle the calcium carbonate and to regenerate the white liquor, which returns to the process (Cardoso et al., 2009).
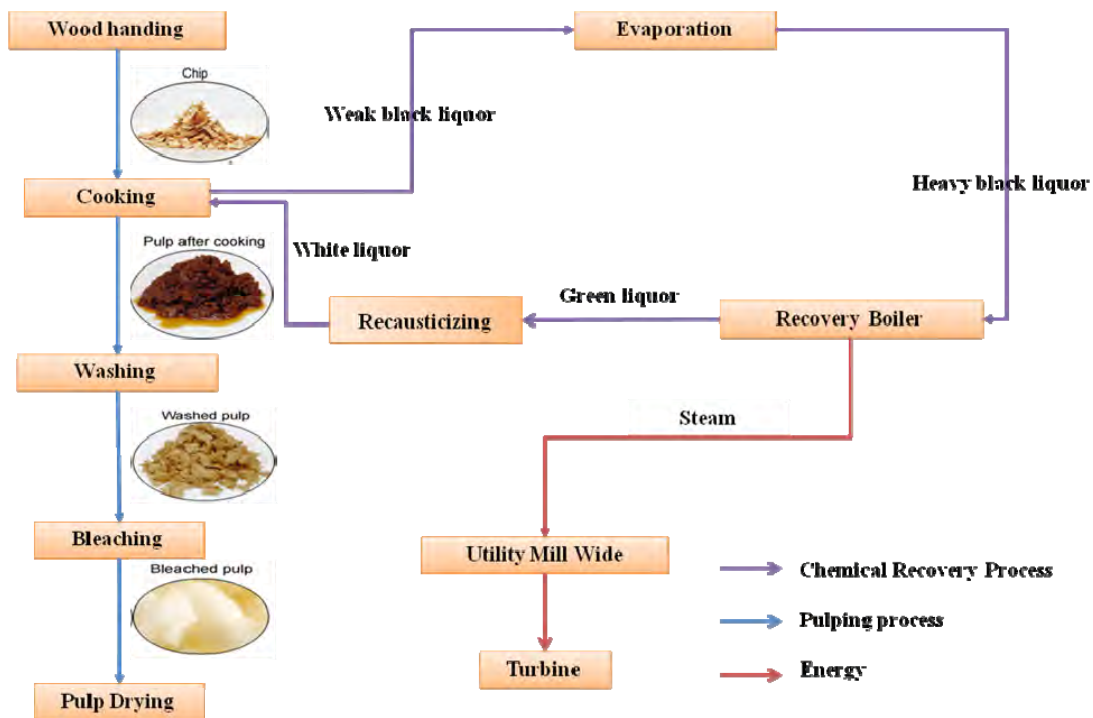
Figure 2.2 Pulping process of pulp and paper industry (Advance Agro (Thailand) Co.,Ltd.)
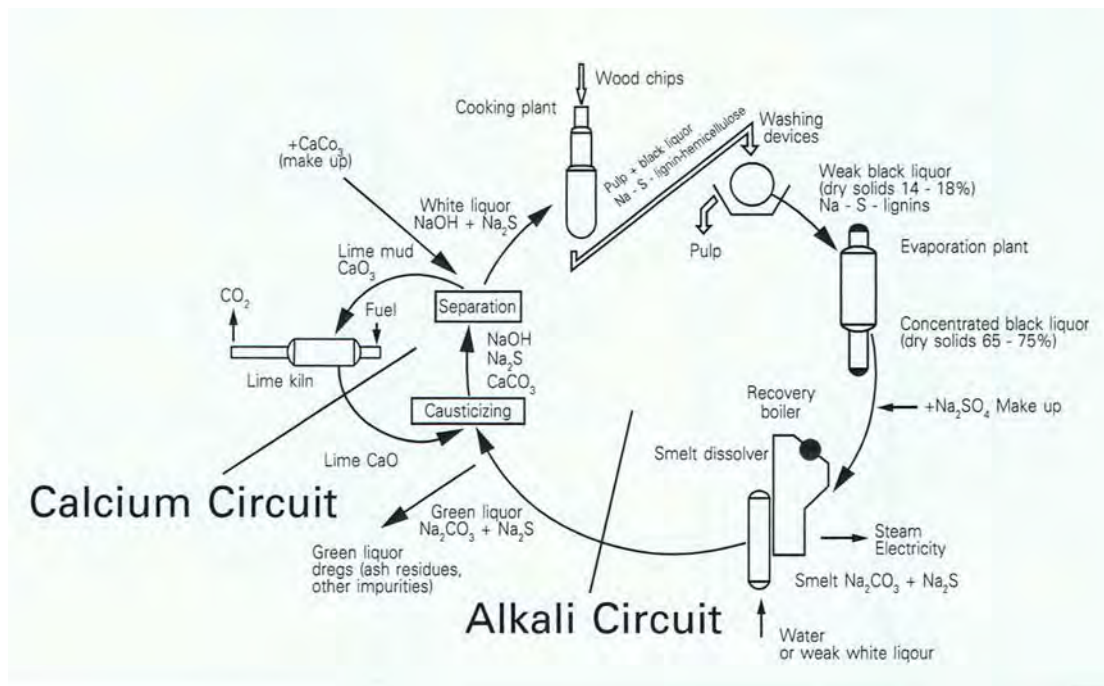
Figure 2.3 Chemical recovery process (Department of Industrial Works, 2007)

2.2.1 Physical properties and chemical composition of black liquor

2.2.1.1 Physical properties

Black liquor is black aqueous, sticky and strong odor. Black liquor is sticky and strong odor because it has high viscosity and has sulfur in its composition. The main structure of black liquor consists of lignin and polysaccharide clusters, salt ions and water, so black liquor can dissolve in water (Cardoso et al., 2009).
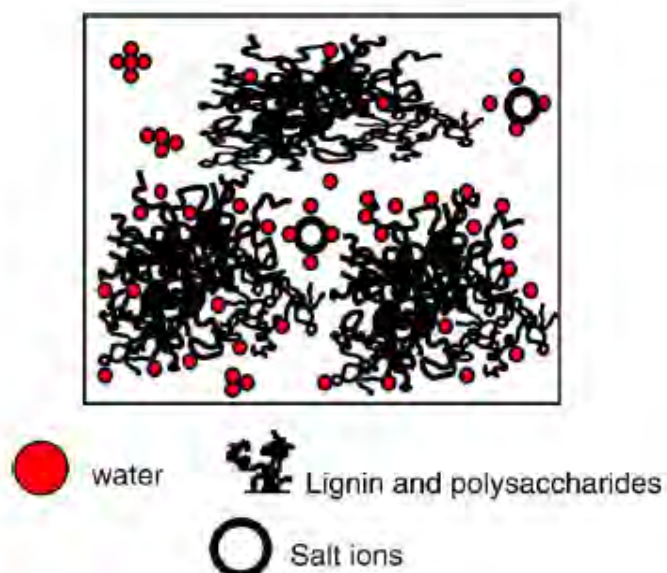
Figure 2.4 Simplified schematic of black liquor structure (Cardoso et al., 2009).

Table 2.1 Physical properties of the eucalyptus and bamboo black liquors (Cardoso et al., 2009)

Type	Eucalyptus	Bamboo
Solid phase density (kg/m^3)	1963 ($\pm$258)	2098
Liquid phase density (kg/m^3)	1005 ($\pm$20)	947
Heating value (kJ/kg)	14593 ($\pm$162)	14673($\pm$226)

2.2.1.2 Chemical composition

The chemical composition of black liquor depends on the type of the raw material processed, i.e. softwoods (such as pine), hardwoods (such as eucalyptus) or fibrous plants (such as bamboo), or depends on the steps in pulping process (Cardoso et al., 2009). Table 2 shows the elemental analysis of different black liquors (dry solids).

Table 2.2 Elemental analysis of different black liquors (dry solids) (Cardoso et al., 2009)

Type of wood / Element (% mass per dry solids)	Fibrous plant (Bamboo)	Softwood (Pine)	Hardwood (Eucalyptus)	Fibrous plant (Straw)
C	35.4	33.9 to 35.8	30.8	39.1
H	3.6	3.3 to 3.6	3.6	4.5
N	0.30	0.06 to 0.07	0.01	1.0
Na	19.3	17.2 to 19.8	21.8	8.8
K	3.3	1.4 to 2.2	1.8	4.1
S	0.2	4.6 to 5.7	3.7	0.8
Cl	1.3	0.3 to 0.9	4.5	3.5
Si	3.8	-	0.1	0.23
Organic/Inorganic	2.30	1.33	1.81	-

Black liquor is a biomass containing a lot of inorganic substances (% dry solids). Inorganic substances in black liquor are mostly come from sodium salts in cooking process and minority from wood chip such as silica potassium. While organic substances in black liquor are mainly come from lignin in wood chip and a few from cellulose and hemicellulose. However, inorganic substances in black liquor are made black liquor sensitive to reaction because of alkali salts catalytic qualification (Sricharoenchaikul et al., 2006).

2.3 Sludge

Sludge is a biomass-residual waste that comes from wastewater treatment system in pulp and papermaking process. It is produced residue solids from wastewater that comes from several steps of pulp and paper making process. Most of wastewater treatment system in pulp and paper industry commonly use activated sludge process because activated sludge process can remove all types of the pollutants relating to the pulp and paper industry. When considering both investment and operating costs,

activated sludge process is efficient, stable, and a competitive combination process, (Pokhrel and Viraraghavan, 2004). In activated sludge process, sludge is produced at two steps (see Figure 2.4). Primary sludge is recovered at the primary clarifier and secondary sludge is comes from the secondary clarifier then it mixed at sludge storage called "mix sludge". After that, mix sludge pass through sludge dewatering process (sludge belt press) called "dewatered sludge". In the sludge dewatering process, the liquid extracted is recycled back to the wastewater stream (Hammond, 2002). Lastly, dewatered sludge is commonly disposed by dumped it into landfill.
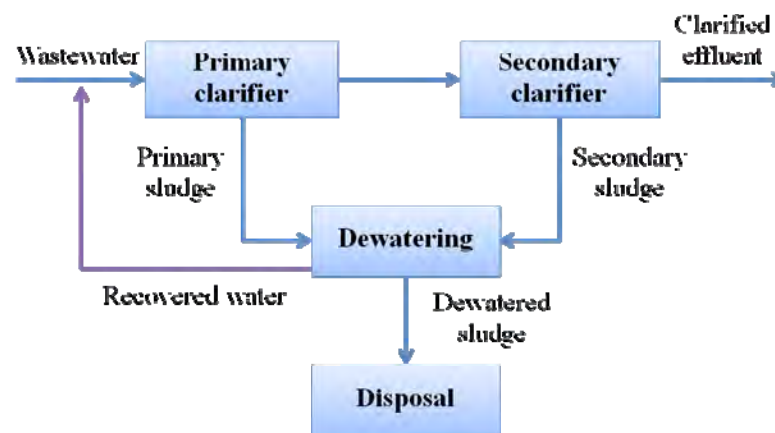
Figure 2.5 Wastewater treatment system (Scott and Smith, 1995)

2.3.1 Physical properties and chemical composition of sludge

Generally, sludge from paper making process is highly fibrous. While sludge from kraft pulping process tends to have higher in sulfur compounds, sludge from deinking process tends to have high ash level. Moreover, sludge from wastepaper recycling process tends to have a lot of solids.

Table 2.3 Physical properties and chemical composition of sludge from different sources (Scott and Smith, 1995)

Source	% Solid	% Ash	% C	% H	% S	% O	% N	Heating value (MJ/kg)
Bleaching process	33.4	1.9	48.7	6.6	0.2	42.4	0.2	20.1
Pulping process	42.0	4.9	51.6	5.7	0.9	29.3	0.9	21.5
Kraft pulping process	40.0	8.0	48.0	5.7	0.8	36.3	1.2	19.8
Deinking process	42.0	20.2	28.8	3.5	0.2	18.8	0.5	12.0
Recycling process	45.0	3.0	48.4	6.6	0.2	41.3	0.5	20.8
Recycled paper process	50.5	2.8	48.6	6.4	0.3	41.6	0.4	20.6
Barking process	54.0	3.5	48.0	6.0	0.1	42.1	0.3	20.3
Wood chipping process	79.5	0.2	49.2	6.7	0.2	43.6	0.1	19.4
Wastepaper recycling process	92.0	7.0	48.7	7.0	0.1	37.1	0.1	25.0

2.4 Thermochemical conversion processes

Thermochemical conversion processes can be subdivided into combustion, pyrolysis, gasification and liquefaction/hydro-thermal upgrading. The thermochemical conversion processes are shown in figure 2.5 (Knoef, 2009), and the main processes, the intermediate energy carriers and the final energy products resulting from thermochemical conversion are illustrated in figure 2.6 (McKendry, 2002).
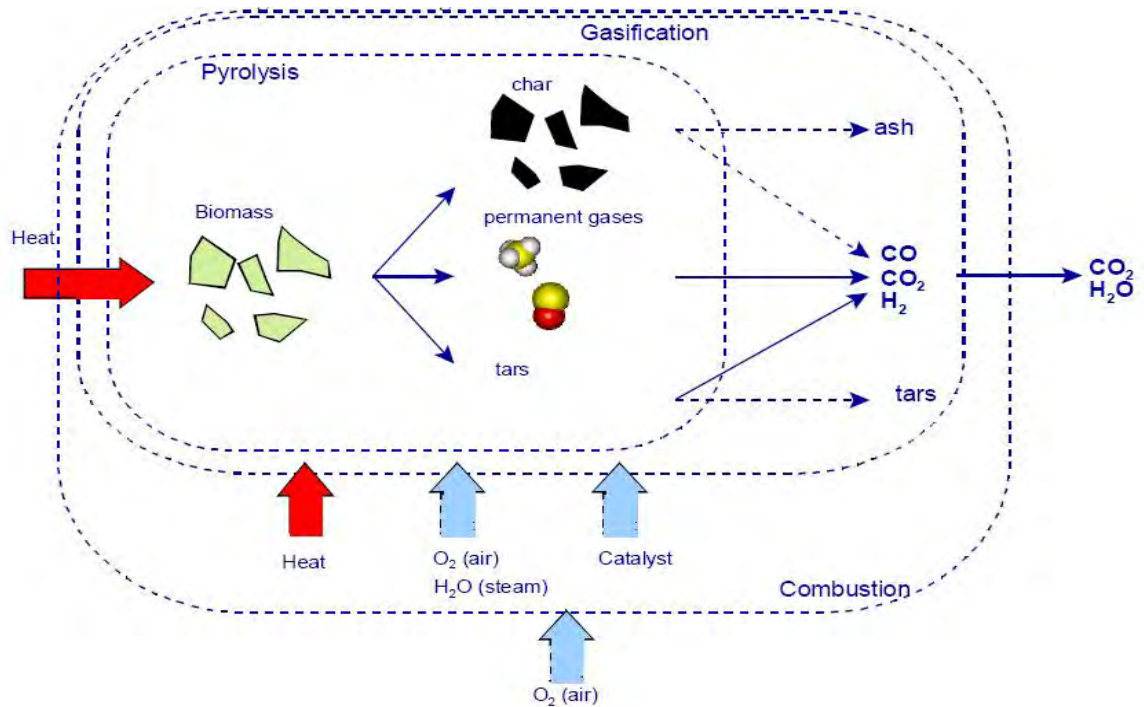
Figure 2.6 Schematic presentation of the thermal conversion process (Knoef, 2009)
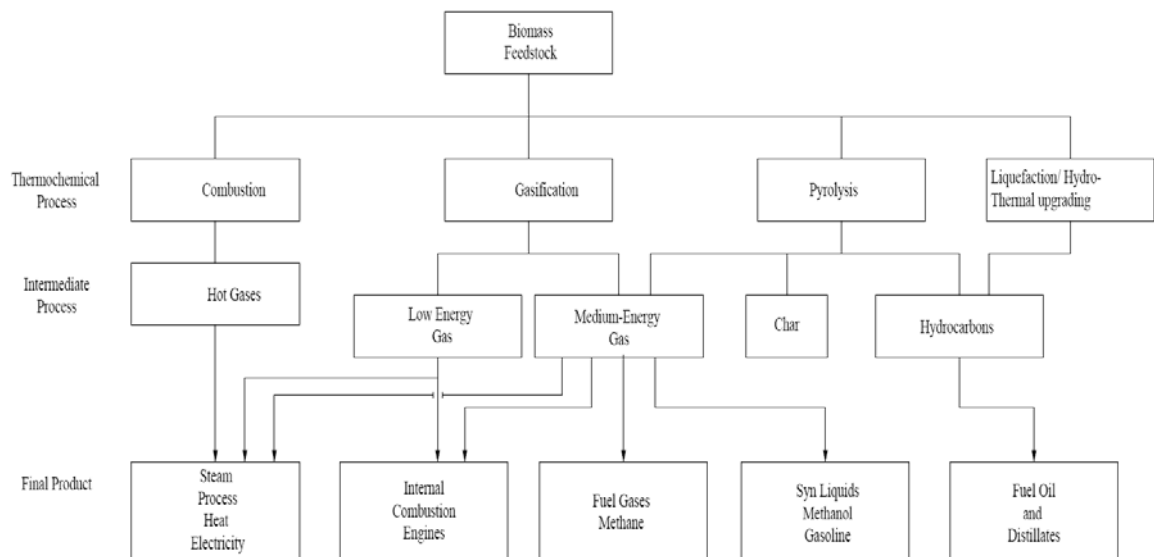
Figure 2.7 Main processes, intermediate energy carriers and final energy products from the thermochemical conversion of biomass (McKendry, 2002)

2.4.1 Pyrolysis

Pyrolysis is the basic thermochemical process that converting hydrocarbons such as coal biomass or various wastes to more useful fuel. In pyrolysis process, raw materials is heated to around 500°C in the absence of oxygen, or partially combusted in a limited oxygen supply, to produce a hydrocarbon rich gas mixture, an oil-like liquid (bio-oil or bio-crude) and a carbon rich solid residue (Demirbaş, 2001).

Pyrolysis is always first step in combustion and gasification process depend on total or partial oxidation of primary product (Bridgwater et al., 1999). A common synonym for pyrolysis is "devolatilizaton". The residue char that remaining is carbon and mineral matter. Furthermore, the term "carbonization" is sometimes used as a synonym from pyrolysis, when has aim to produce the solid char. However, most of synthetic fuel production always interest in liquid and gaseous hydrocarbons (Probstein and Hicks, 1982). The most interest in synthetic fuels production is the rate prediction and amount of volatile yield and product distribution from raw material and set of pyrolysis condition (Probstein and Hicks, 1982). The yields of pyrolysis process depend on the objectives. If objective is to maximize the yield of liquid products, the conditions of pyrolysis process are low temperature, high heating rate, and short gas residence. For high char production, the conditions are low temperature and low heating rate process. If the purpose is to maximize the yield of fuel gas, the conditions are high temperature, low heating rate and long gas residence time (Demirbaş, 2001). Table 4 indicates the product distribution obtain from different modes of pyrolysis process (Bridgwater, 2003).

Pyrolysis of any organic material can be divided into "slow" and "fast" pyrolysis depending on the characteristic time required for heating the material to a specified final pyrolysis temperature and the characteristic pyrolysis reaction time (Probstein and Hicks, 1982).

Table 2.4 Typical product yields (dry basis) obtained by different modes of pyrolysis of wood (Bridgwater, 2003)

Mode of thermochemical process/ Conditions		Liquid (%)	Char (%)	Gas (%)
Fast Pyrolysis	Moderate temperature, short residence time particularly vapor	75	12	13
Carbonisation	Low temperature, very long residence time	30	35	35
Gasification	High temperature, long residence times	5	10	85

2.4.1.1 <u>Fast pyrolysis</u>

Fast pyrolysis is a high temperature process in which organic material is rapidly heated in the absence of oxygen (Bridgwater et al., 1999). It occurs in a time of few seconds or less. The organic material is decomposed and generates mostly vapors and aerosols and some charcoal. After cooling and condensation, a dark brown mobile liquid which has a heating value about half that of conventional fuel oil is formed. When fast pyolysis is compared with the traditional pyrolysis processes for making charcoal, fast pyrolysis is an advanced process, with carefully controlled parameters to give high yields of liquid. The essential features of a fast pyrolysis process for producing liquids are:

• very high heating and heat transfer rates at the reaction interface, which usually requires a finely raw material feed,

• carefully controlled pyrolysis reaction temperature of around 500°C and vapor phase temperature of 400–450°C,

• short vapor residence times of typically less than 2 s,

• rapid cooling of the pyrolysis vapours to give the bio-oil product.

The main product, bio-oil yield, is obtained up to 75 wt.% on dry basis of raw material. The by-product yields, char and gas which are used within the process, so there are no waste streams except flue gas and ash.

A fast pyrolysis process usually use raw material that have water less 10% in order to minimize the water in the liquid oil product (although up to 15% can

be acceptable) and usually grind raw material (to around 2 mm in the case of fluid bed reactors) to give sufficiently small particles to ensure rapid reaction (Bridgwater, 2003).

2.4.2 Gasification

Gasification is the thermochemical process that converts hydrocarbons such as coal, petroleum coke (petcoke), biomass, or various wastes to a synthesis gas (syngas), which can be used to produce electric power and valuable products such as chemicals, fertilizers, substitute natural gas, hydrogen, steam, and transportation fuels, by heating in a gasification medium such as air, oxygen or steam (Gasification Technology Council, 2008; McKendry, 2002). The range of gasification process is typically 800-900°C (McKendry, 2002). The products from gasification process consists of carbon monoxide, carbon dioxide, hydrogen, methane, trace amounts of higher hydrocarbons such as ethane and ethene, water, nitrogen (if air is used as the oxidizing agent) and various contaminants such as small char particles, ash, tars and oils. The gaseous products from gasification process can be produced from raw materials by using partial oxidation or steam gasification process. The partial oxidation can be carried out using air, oxygen, steam or a mixture of these. Gasification by partial oxidation with air produces a poor-quality gas in terms of heating value (~5 MJ/m^3) which is suitable for boiler, engine and turbine operation, but not for pipeline transportation due to its low energy density. Gasification by partial oxidation with oxygen produces a better-quality gas (~10–12 MJ/m^3) which is suitable for limited pipeline distribution and for use as synthesis gas for conversion, for example, to methanol and gasoline. This gas quality can also be produced by pyrolytic or steam gasification, with the process energy being supplied by combustion of by-product char in a second reactor, e.g. a twin fluid bed system. (Bridgwater, 1995; Bridgwater, 2003).

Table 2.5 Modes of thermal gasification (Bridgwater, 2003)

Partial oxidation with air	Main products are CO, CO_2, H_2, CH_4, N_2, tar. This gives a low heating value gas of ~5 MJ/m³. Utilization problems can arise in combustion, particularly in gas turbines.
Partial oxidation with oxygen	The main products are CO, CO_2, H_2, CH_4, tar (no N_2). This gives a medium heating value gas of ~10–12 MJ/m³. The cost of providing and using oxygen is compensated by a better quality fuel gas. The trade-off is finely balanced.
Steam (pyrolytic) gasification	The main products are CO, CO_2, H_2, CH_4, tar. This gives a medium heating value gas of ~15–20 MJ/m³. The process has two stages with a primary reactor producing gas and char, and a second reactor for char combustion to reheat sand which is recirculated. The gas heating value is maximized due to a higher methane and higher hydrocarbon gas content, but at the expense of lower overall efficiency due to loss of carbon in the second reactor.

Gasification occurs in sequential steps:

- drying to evaporate moisture,
- pyrolysis to give gas, vaporized tars or oils and a solid char residue,
- gasification or partial oxidation of the solid char, pyrolysis tars and pyrolysis gases (Bridgwater, 2003).
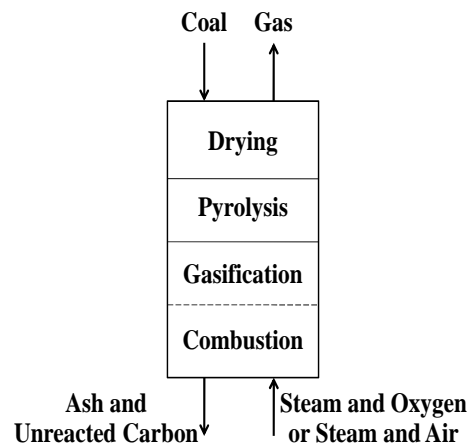
Figure 2.8 Schematic of moving bed gasifier (Probstein and Hicks, 1982)

From figure 2.7, gasification process begins by raw material e.g. coal entering into a gasifier. Then raw material is dried by rising hot gases. Next step, raw material is heated to 300-500°C in the absence of oxidizing gas, the devolatilization or pylolysis reaction is occurred to convert raw material to solid char, condensable hydrocarbons or tar, and gases. The yields from this step are mostly depends on the heating rate and the final temperature. After that, temperatures are sufficiently high for gasification reaction. The gas, liquid and solid products from pyrolysis process react with oxidizing gas to give gaseous product that mostly carbon dioxide, carbon monoxide, hydrogen and methane.

The products from gasification process such as fuel gas have a lot of advantages for use as energy. On the other hand, the various contaminants especially tar is a particular problem. Tar is by-product from gasification or pyrolysis process. Tar will be condensed at low temperature, then it block and foul process equipments like fuel lines, filters, engines and turbines (Han and Kim, 2008). Tar can be destroyed by two basic ways:

- by catalytic cracking using, for example, dolomite or nickel,
- by thermal cracking, for example by partial oxidation or direct contact (Bridgwater, 2003).

2.4.2.1 <u>The principle of gasification reaction</u> (Probstein and Hicks, 1982).

The principle gasification reactions are:

1) <u>Oxygenolysis</u> or reaction with oxygen to form carbon monoxide and carbon dioxide. For this reaction, oxygen is fed into the gasifier, then it used up in the combustion zone and supplies the heat necessary for conversion:

$$C + O_2 \ \rightarrow \ CO_2 \quad \Delta H^\circ_{298} = \text{-393.5 kJ/mol} \qquad (2.1)$$
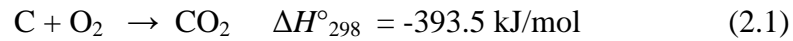
In the oxygen-depleted gasification zone, the raw material is burned in the CO_2 atmosphere according to the Boudouard reaction.

$$C + CO_2 \ \leftrightarrow \ 2CO \quad \Delta H^\circ_{298} = \text{+172.5 kJ/mol} \qquad (2.2)$$
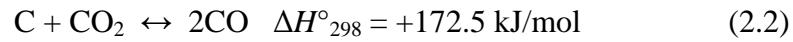
2) Hydrogenolysis or reaction with hydrogen to form methane.

$$C + 2H_2 \ \leftrightarrow \ CH_4 \quad \Delta H^\circ_{298} = \text{-74.8 kJ/mol} \qquad (2.3)$$
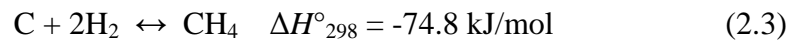
Hydrogen can reacts with the nitrogen and sulfur in the raw material to form ammonia and hydrogen sulfide gases. Normally, hydrogen is added into the system in form of water for increase the hydrogen-to-carbon ratios in the product gases.

3) Hydrolysis or reaction with water. Typically, hydrolysis reaction under gasifier conditions is the endothermic reactions that converts raw material into carbon monoxide and hydrogen.

$$C + H_2O \ \leftrightarrow \ CO + H_2 \quad \Delta H^\circ_{298} = \text{+131.3 kJ/mol} \qquad (2.4)$$
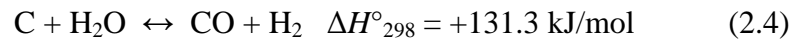
Water and steam is fed into the gasifier to provide oxygen as well as hydrogen, then carbon dioxide is directly form.

$$C + 2H_2O \ \leftrightarrow \ CO_2 + 2H_2 \quad \Delta H^\circ_{298} = \text{+90.1 kJ/mol} \qquad (2.5)$$

or

$$C + H_2O \ \leftrightarrow \ ^{1\!/}_2CO + ^{1\!/}_2CH_4 \quad \Delta H^\circ_{298} = \text{+7.7 kJ/mol} \qquad (2.6)$$

2.4.2.2 Chemical reactions in gasification process

Gasification process can be divided into four stages which can be occurred at the same time or not depended on gasifier types (Knoef, 2005; Turare, 2010).

1) Drying

The water in biomass is removed and converted into steam at temperature above 100°C.

2) Pyrolysis

Biomass fuels are heated in the absence of oxygen to release three kinds of products such as solid (char or charcoal), liquid (pyroligious acid or oil) and gases.

3) Oxidation or combustion

In oxidation or combustion zone, carbon and hydrogen in fuels reacts with oxygen to produce CO_2, steam and heat.

$$C + O_2 \rightarrow CO_2 + 406 \text{ MJ/kmol}$$

$$H_2 + {}^{1/}_2O_2 \rightarrow H_2O + 242 \text{ MJ/kmol}$$
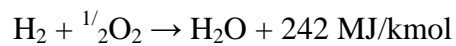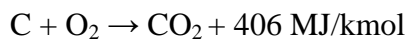
4) Reduction or gasification

In reduction or gasification zone, partial oxygen is added, so this zone is occurred. In this zone, CO_2 and steam react with carbon residue from combustion process and form CO and H_2. The principal reactions in this zone are

Boudouard reaction: $CO_2 + C \rightarrow 2CO - 172.6 \text{ MJ/kmol}$

Water-gas reaction: $C + H_2O \rightarrow CO + H_2 - 131.4 \text{ MJ/kmol}$

Water shift reaction: $CO_2 + H_2 \rightarrow CO + H_2O + 41.2 \text{ MJ/kmol}$

Methane production reaction: $C + 2H_2 \rightarrow CH_4 + 75 \text{ MJ/kmol}$
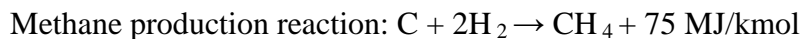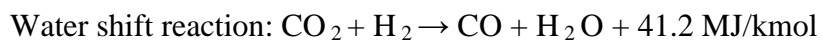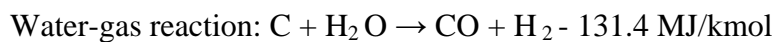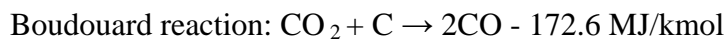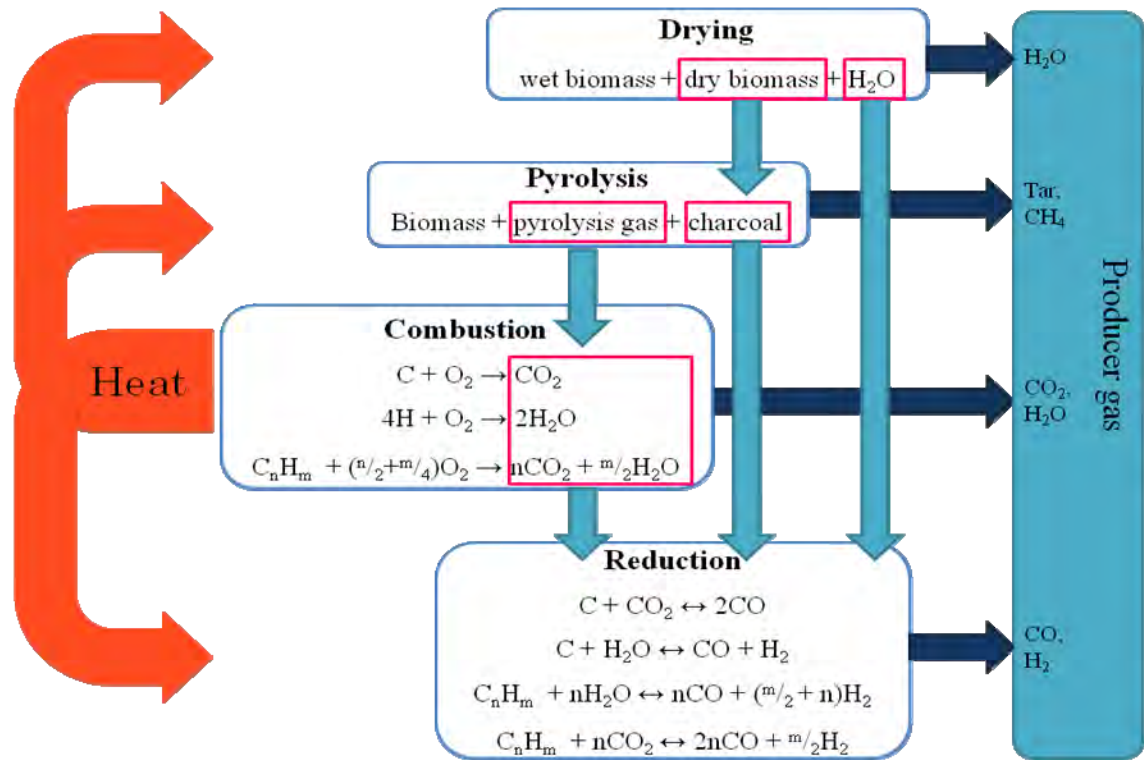
Figure 2.9 Chemical reactions in gasification process (Knoef, 2005)

2.4.2.3 The characteristics of gasifier system (Probstein and Hicks, 1982)

The characteristics of gasifier system can be divided into "independent" characteristic and "dependent" characteristic. The method of supplying heat, the gasifying medium, and the reactor type are the kind of independent characteristics. The other characteristics that often used to classify gasifiers system are dependent characteristics. The dependent characteristics are the solid residue is ash or slag, the raw gas composition and calorific value, and the gasification temperature.

Table 2.6 Lists of independent and dependent gasifier characteristics (Probstein and Hicks, 1982)

Independent	Dependent
1. Method of supply heat - Direct - Indirect	1. Reaction temperature - High - Medium - Low
2. Gasifying medium amount - Steam with air or oxygen - Air - Hydrogen with or without steam - Steam with catalyst	2. Raw gas properties - Composition - H_2/CO ratio - Tar and oil content - Calorific value
3. Reactor type - Moving packed bed - Fluidized bed - Entrained flow - Molten media	3. Solid residue - Ash - Slag - Unconverted carbon

2.4.2.4 <u>Reactor type</u>

Three principle reactor types are used in gasifier design: the moving packed bed (fixed bed), the fluidized bed, and the entrained flow reactor. A fourth type, the molten media reactor, could be grouped together with entrained flow reactor (Probstein and Hicks, 1982). A recent survey of gasifier manufacturers found that 75% of gasifiers system were fixed bed (downdraft), 20% were fluidized beds (including circulating fluidized beds), 2.5% were fixed bed (updraft) and 2.5% were other types (Bridgwater, 2003).

1) <u>Moving bed (Fixed bed)</u> (Probstein and Hicks, 1982).

In the terminology of gasifier technology the term "fixed bed" gasifier refers to a gasifier in which a packed bed of fuel is supported by a grate or by other means and maintained at a constant depth above the support. The fuel moves downward under the action of gravity from the top of the gasifier, through the

gasification and combustion zones, and the residue is discharged at the bottom. This is clearly a "moving packed bed" or more succinctly a "moving bed" reactor.

Moving bed gasifier can separate to countercurrent flow (updraft) or cocurrent flow (downdraft), use either steam and oxygen or steam and air, and the residue may be either slag or dry ash plus any unconverted carbon. The operation often uses undried raw materials that range in size between 3 and 50 mm. They are fed into the top of the gasifier, with the size range that suitable for process. The raw material sizes must be sufficiently large (> 3 mm) for flow with the exiting product gases. If the raw material is too small, it can cause the problem because they tend to clog the bed and offer a high resistance to the upward flowing gases.

The raw material, is fed into gasifier system, being heated. Then it devolatilized, and still lower down gasified. The bottom of the raw material bed is the combustion zone, with the residue of the combustion that cooled by the steam/oxygen or steam/air mixture entering from the bottom before it is discharged. The bed movement is relatively slow, with average velocities on the order of 0.5 m/h in atmospheric steam/air gasifiers and 5 m/h in high pressure steam/oxygen gasifiers. Residence times of the raw material are shorter with the higher velocity beds, and are typically 0.5-1 hour for the high pressure steam/oxygen gasifiers and some ten times longer for atmospheric steam/air gasifier.

Advantage:

• The countercurrent direct contact heat exchange that lead to maximum conversion efficiency with a minimum of heat loss.

Disadvantages:

• The caking and swelling of the raw material are the problems, so it should have oxidative pretreatment such as internal agitation.

• It cannot use fine solid fuel in this reactor type (Probstein and Hicks, 1982).

1.1) Moving/fixed bed, Updraft (Countercurrent)

In the updraft gasifier, the raw material was fed at the top and the air at the bottom of the unit via a grate (Fig. 2.8a) (McKendry, 2002). The raw material is moving downward, then dried by the upflowing hot gas. After that, the raw material is pyrolyzed, char is release in this step. The raw material continues to move down to be gasified. The tars are forms and flow along with with gas products. This

gasifier type contributes high tar content. Then the condensed tars are recycled back to the reaction zones, where they are further crack to gas and char. In the bottom of gasification zone, the solid char from pyrolysis and tar cracking can be oxidized by incoming air and oxygen, and steam can be added to provide a high level of hydrogen in gas.

The advantages of updraft gasifiers are simple construction, high thermal efficiency and high carbon conversion. (Bridgwater, 1995; Bridgwater, 2003).

1.2) Moving/fixed bed, Downdraft (Cocurrent)

In the downdraft gasifier, the raw material is fed in the same direction as the air move (Fig. 2.8b). The maximum of moisture content that can feed into the gasifier is around 35% wet basis (Bridgwater, 2003). The product gases leave the gasifier after passing through the hot zone, and the tars cracking are formed during gasification. This gasifier type gives a clean gas with low tar content and usually with high carbon conversion. The overall energy efficiency of a downdraft gasifier is low, due to the high heat content by the hot gas. The tar content of the product gas is lower than for an updraft gasifier but the particulates content of the gas is high (McKendry, 2002).

The advantages of downdraft gasifiers are simple, reliable and proven for certain fuels. The ash content is low (< 1 wt.%) (Bridgwater, 1995).
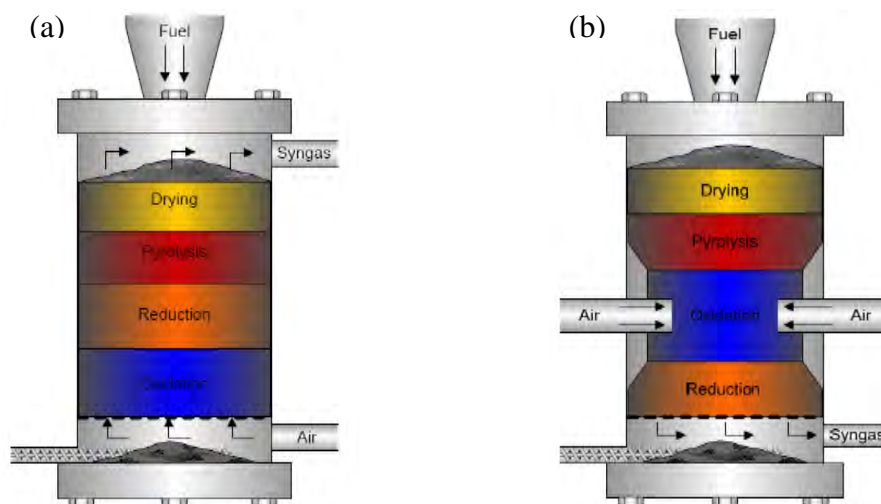
Figure 2.10 Two types of moving bed (fixed bed) (a) updraft gasifier (b) downdraft gasifier (Geurds, 2006)

2) Fluidized bed

In general, fluidized bed gasifiers need raw material in the form of small particles because it is suitable for multi-fuel operation (Bhattacharya and Salam, 2006). Silica sand and alumina and other refractory oxides have been used as fluidizing material to avoid sintering, and catalysts have been used to reduce tars and modify product gas composition (Bridgwater, 1995). When compare fluidized bed gasifiers with fixed bed gasifiers, fluidized bed gasifiers are generally used for applications of larger scale than fixed bed gasifiers (Bhattacharya and Salam, 2006).

The advantage of fluidized bed gasifiers over fixed bed gasifiers is the uniform temperature distribution acheived in the gasification zone. The uniformity of temperature is achieved by using a fine grained material as bed material which air is introduced. The hot bed material is complete mixing in fluidized bed gasifiers (McKendry, 2002).

The fluidized bed reactors in use are two main types (McKendry, 2002):

- Circulating fluidized bed
- Bubbling bed

Advantages:

- Good mixing of the raw material and a uniform temperature bed, with rapid temperature equilibration between the raw material and gases.

- Fluidized bed gasifiers are efficient heat transfer, so the gasification reactions reach equilibrium quickly. Therefore, it will give the high outputs efficiency.

- Fluidized bed gasifiers are no hot spot with formation of fused ash particles.

Disadvantages:

- Most of fluidized bed gasifiers is without oxidative pretreatment or special design configurations, so it difficult to handle caking and swelling of raw material that form larger size particles. The large particle size is difficult to fall, so they can lead to a collapse in the wall of the gasifier.

- Solid in fluidized bed gasifiers is mixed with the product gas, so it hard to remove individually (Probstein and Hicks, 1982).

2.1) Circulating fluidized bed

Circulating fluidized bed gasifiers are often used in the paper industry for the gasification of bark and other forestry residues. The bed material is circulated between the reaction vessel and a cyclone separator, where the ash is removed and the bed material and char returned to the reaction vessel. These gasifiers can be operated at elevated pressures (McKendry, 2002).

The advantages of circulating fluidized bed gasifiers are good temperature and high reaction rates. While disadvantages of circulating fluidized bed is high cost at low capacity (Bridgwater, 2003).

2.2) Bubbling bed

Bubbling gasifiers consist of a vessel with a grate at the bottom for introduce air. Above the grate is the moving bed of fine-grained material that prepare for feed raw material. The raw material is pyrolyzed in the hot bed to form a char with gaseous compounds The high molecular weight compounds being cracked by contact with the hot bed material, giving a product gas with a low tar content, typically <1–3 g/Nm^3(McKendry, 2002).

The advantages of bubbling bed gasifiers are same as circulating fluidized bed gasifiers. Whereas disadvantages of bubbling bed are high particulates in the product gas, moderate tar levels in product gas and some carbon will be loss with ash (Bridgwater, 2003).
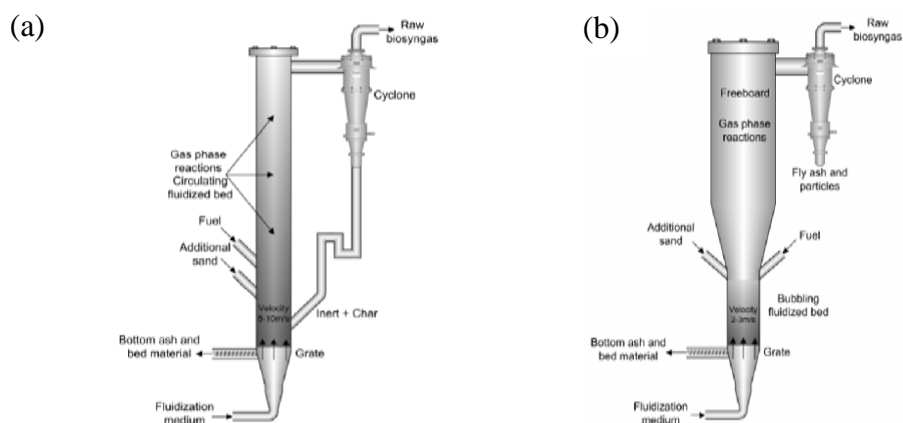
Figure 2.11 Two types of fluidized bed reactors (a) circulating bed (b) bubbling bed (Geurds, 2006)

3) <u>Entrained flow</u>

Entrained flow gasifiers are commonly used for coal because they can be slurry fed in direct gasification mode. Thus, they make solid fuel feeding at high-pressure inexpensive. Nowadays, entrained flow gasifiers can be used for biomass too. In entrained flow gasifiers small fuel particles are fed at top of gasifier and injected in a burner for optimum mixing with steam, oxygen or air (Knoef, 2005). The most important characteristic of entrained flow gasifiers is they operate at the highest temperature. The aim is to gasify the solid fuel rapidly, so the reaction occurred in short residence (~1 second) (Knoef, 2005; Probstein and Hicks, 1982). All of the volatile matter in the solid fuel is oxidized, which leads to relatively high oxygen consumptions at high temperature. Furthermore, at high temperatures methane formation is low, the CO/CO_2 ratio is high, the conversion of the carbon in the solid fuel is high (about 90 to 100 percent), and there are few tars or heavy hydrocarbons in the product gas and no carbon in the slag. The low methane formation makes the entrained flow gasifier suited to hydrogen production (Probstein and Hicks, 1982).

<u>Advantage</u>:

• Entrained flow gasifiers being able to accept any solid fuels and have high output rates, especially with higher pressure operation

<u>Disadvantages</u>:

• Entrained flow gasifiers are not the most efficient thermally because they are cocurrent flow systems.

• The high temperature environment can cause the problem of slag handling and removal (Probstein and Hicks, 1982).

4) <u>Molten media </u>(Probstein and Hicks, 1982)

In molten media gasifiers, the solid fuel is dispersed into a molten carrier, and acts as a heat source. The gasifier is actually an entrained flow type, the solid particles are fed at top of gasifier and injected with steam, oxygen or air into the gasifiers. The solid particles are entrained in the slag. The slag promotes the gasification reaction and certain constituents, such as iron oxide, act as oxygen-transfer agents through oxidation and reduction reactions. Most importantly, molten media gasifiers also react with and adsorbs the sulfur in the solid fuel, as well as retains the ash.

Advantage:

- Molten media gasifiers being able to accept any solid fuels provide an efficient heat sink for the promotion of gasification reaction.

Disadvantages:

- The processes must handle the molten media such as in the case of molten salt, regenerate and recycle an extremely corrosive material.

Table 2.7 Gasifier types and their characteristics (Knoef, 2005)

Gasifier type	Characteristic				
	Temp. (°C)	Tar	Control	Scale (MW)	Feedstock
Updraft	700-900	High	Very easy	< 20	Small ($<$ 5mm)
Downdraft	700-1200	Low	Easy	< 5	Small ($<$ 5mm)
Circulating fluidized bed	< 900	Moderate	Moderate	20-??	Small
Bubbling bed	< 900	Moderate	Moderate	10-100	Small
Entrained flow	~1450	Very low	Complex	> 100	Very fines

2.5 Products of gasification

The products of gasification are depended on the reactor configuration and the oxidizing gas. Ideally, there is complete conversion of all tars, hydrocarbons and char in the gasifier to give fuel gas (Bridgwater, 1995). The major components of products from biomass gasification are CO, H_2, CO_2, CH_4, H_2O, and N_2, in addition to organic (tars) and inorganic (H_2S, HCl, NH_3, alkali metals) impurities and particulates. The ranges of organic impurities are low molecular weight hydrocarbons to high molecular weight polynuclear aromatic hydrocarbons. The lower molecular weight hydrocarbons can be used as fuel in gas turbine or engine applications. The higher molecular weight hydrocarbons are collectively known as ''tar'' (Li and Suzuki, 2009).

$$\text{Biomass} + O_2 \text{ (or } H_2O\text{)} \quad \rightarrow \quad CO, CO_2, H_2O, H_2, CH_4 + \text{other hydrocarbons}$$

$$\rightarrow \quad \text{tar} + \text{char} + \text{ash}$$

$$\rightarrow \quad HCN + NH_3 + HCl + H_2S + \text{other sulfur gases}$$

2.5.1 Gas products

The quantity of gaseous produced depend on the various feed and operations conditions. The essential characteristics of gas products may be summarized as follows (Probstein and Hicks, 1982):

1) Hydrogen and carbon monoxide

Hydrogen and carbon monoxide production increases with decreasing oxygen in the feed, with decreasing pressure, and with increasing temperature. Hydrogen increases and carbon monoxide decreases with increasing steam rates. Moreover, the hydrogen-to-carbon monoxide ratio is increased by oxidizing some of the carbon monoxide following the reaction:

$$CO + H_2O \quad \leftrightarrow \quad CO_2 + H_2 \tag{2.7}$$

The hydrogen-to-carbon monoxide ratio is typically depends on feed composition, although it no affected of temperature and pressure. A gasifier produce a synthesis gas for methanol production that ideally operate with a H_2/CO ratio of 2, and higher for methane production. However, if methane is the desired end product, it may be preferable to produce it directly in the gasifier.

2) Methane production

Methane production is produced at low temperatures and high pressures. Variations in feed conditions do not significantly affect its formation.

3) Carbon dioxide formation

Carbon dioxide formation increases with increasing oxygen in the feed. It also increases with increasing pressure. However, at high temperatures carbon dioxide formation can convert to carbon monoxide.

Table 2.8 Typical product gas characteristics from different gasifiers (Bridgwater, 1995)

Gasifier type	Gas composition (vol.%, dry)					High Heating Value (MJ/m^{-3})	Gas quality	
	H_2	CO	CO_2	CH_4	N_2		Tar	Dust
Fluidized bed with air	9	14	20	7	50	5.4	fair	poor
Updraft with air	11	24	9	3	53	5.5	poor	good
Downdraft with air	17	21	13	1	48	5.7	good	fair
Downdraft with oxygen	32	48	15	2	3	10.4	good	good
Multi-solid fluidized bed	15	47	15	23	0	16.1	fair	poor
Pyrolysis (for comparison)	40	20	18	21	1	13.3	poor	good

2.5.2 Particulates

The quantity of particulate material produced depending on the gasification technology used. Ash and char are particulates that produced from gasification process. Fixed bed gasifiers generally produce a lower particulate load than fluidized bed gasifiers. Conventional cyclones can remove particles above 10 µm, and the particles removed can recycled back to the gasifier if necessary. Filtering devices such as filter bags or sintered ceramic/metallic candles are also used for remove finer particles. These devices have overall removal efficiencies of +99.8% but soot clogging and tar adhering with the ash/char particles is a problem. Clogging can reduced by operate the filter at a temperature >500°C. While at lower temperatures condensed tars on the filter surface can only be efficiently removed by controlled combustion (McKendry, 2002).

2.5.3 Tar

Tars are known as the high molecular weight hydrocarbons (Li and Suzuki, 2009). High molecular weight hydrocarbons are begin to condense at

temperatures <450°C. Tars condensed are partly deposited on the walls of the piping and partly remaining as an aerosol in the gas, so they can causes problems when utilize the gas product.

The tar produced are largely depending on the type of biomass, and they also influenced by the gasification process and the operating conditions. A low viscosity/low reactivity tar produced in gasification with air. While a liquid tar with a low molecular weight produced by gasification with steam. A tar with low oxygen content that mainly consists of hydrocarbons produced with gasification at high temperature. A low tar/ tar-free gas produced by the fixed-bed, downdraft gasifier.

Two strategies can be applied to the removal of tar:

• improvement of the gasification technology so that no/little tar is produced,

• development of tar removal processes.

Mixed Oxygenates	→	Phenolic Ethers	→	Alkyl Phenolics	→	Heterocyclic Ethers	→	PAH	→	Larger PAH
400 °C		500 °C		600 °C		700 °C		800 °C		900 °C
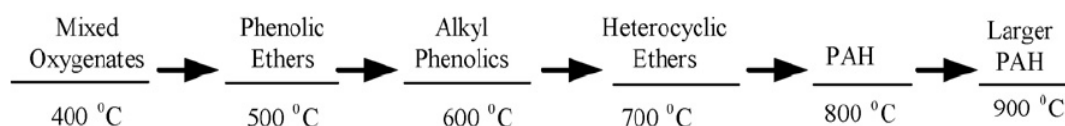
Figure 2.12 Tar formation in different temperature (Elliott, 1988)

Tars can be cracked into lower molecular weight compounds by using catalytic catalytic cracking at 800–900°C or thermal cracking at 900–1100°C. As gasification is usually in the range 800–900°C, thermal cracking requires additional energy to heat the gas, which is usually achieved by introducing a small volume of air to make combustion a part of the gas to raise the temperature. While thermal cracking is an efficiency method to reduce tars. Catalytic cracking is the method that using catalysts such as dolomite, olivine and nickel compounds lead to a uniform and high temperature, which achieve the total cracking of tar.

A very low tar content gas production is best achieved by cooling the gas to 60–80°C with water and using electrostatic precipitators to capture any aerosols. However this method also collects water condensed from the gas phase during cooling, resulting in a wastewater heavily contaminated with dissolved organic substances, which require appropriate treatment and/or disposal (McKendry, 2002).

Table 2.9 Chemical components in biomass tars (Li and Suzuki, 2009)

Gasification technology	Chemical components in tars
Conventional fast pyrolysis (450–500°C)	Acids, aldehydes, ketones, furans, alcohols, complex oxygenates, phenols, guaiacols, syringols, complex phenols
High-temperature fast pyrolysis (600–650°C)	Benzenes, phenols, catechols, naphthalenes, biphenyls, phenanthrenes, benzofurans, benzaldehydes
Conventional steam gasification (700–800°C)	Naphthalenes, acenaphthylenes, fluorenes, phenanthrenes, benzaldehydes, phenols, naphthofurans, benzanthracenes
High-temperature steam gasification (900–1000°C)	Naphthalene, acenaphthylene, phenanthrene, fluoranthene, pyrene, acephenanthrylene, benzanthracenes, benzopyrenes, 226 MW PAHs, 276 MW PAHs

2.6 Synthesis gas

The synthesis gas (syngas) primarily consists of hydrogen and carbon monoxide, which depending upon the specific gasification technology, smaller quantities of methane, carbon dioxide, hydrogen sulfide and water vapor. Syngas can be combusted to produce electric power and steam or used for produce a variety of chemicals and fuels. Syngas generally has a heating value of 250-300 Btu/scf, compared to natural gas at approximately 1,000 BTU/scf. Typically, 70–85% of the carbon in the feedstock is converted into the syngas by gasification process. The hydrogen and carbon content of the feedstock and the type of gasifier determine the carbon monoxide to hydrogen (Gasification Technology Council, 2008).

Methods for production of the synthesis gas are (Littlewood, 1977):

1) The production of water-gas from coke;

2) Production of water-gas by the gasification of soild fuels other than coke;

3) The steam reforming of hydrocarbons;

4) The partial oxidation of hydrocarbons.

Table 2.10 Synthesis gas ratio that produced from processes (Larminie and Dicks, 2000)

Method of Manufacture	H$_2$/CO Ratio	Method of Manufacture	H$_2$/CO Ratio
Oxygen-coke-steam	0.6	Propane-steam	1.33
Air-coke-steam	0.9	Methane-oxygen	1.7
Oxygen-coal-steam	1	Methane-oxygen-steam	2.3
Oxygen-fuel oil-steam	1	Methane-steam	3.0-5.0

2.6.1 Synthesis gas applications

The major components of syngas are hydrogen and carbon monoxide, which can used to produce other products, such as chemicals and fertilizers. The gasification process can produce more than one product, such as the production of electricity, steam, and chemicals (e.g., methanol or ammonia), at a time (co-production or "polygeneration") by design the gasification plant. This polygeneration can be produced by increase the efficiency of gasification process and improve the economics of gasification operations (Gasification Technology Council, 2008).

1) <u>Chemicals and Fertilizers</u>

Gasification plants normally used in the chemical industry. The chemical industry typically uses gasification to produce methanol as well as chemicals such as ammonia and urea for use as nitrogen that basic component in fertilizers. The majority of the operating gasification plants are designed to produce chemicals and fertilizers because the price of natural gas and oil continuous increase.

2) <u>Hydrogen for Oil Refining</u>

One of the two major components of syngas is hydrogen. Hydrogen is used to produce the clean fuels by strip impurities from gasoline, diesel fuel, and jet fuel. Hydrogen is also used to upgrade heavy crude oil. Now, the price of natural gas is increase, so gasification of low residues, such as petroleum coke, asphalts, tars, and some oily wastes, can take place the natural gas for produce hydrogen to run the refinery.

3) Transportation Fuels

Gasification can convert coal and other solid feedstocks or natural gas into transportation fuels, such as gasoline, ultra-clean diesel fuel, jet fuel, naphtha, and synthetic oils. Two basic processes are used to convert coal to motor fuels via gasification.

In the first process, a liquid petroleum is produced from the syngas via the Fischer-Tropsch (FT) reaction. In the second process called "Methanol to Gasoline (MTG)", the syngas is first converted to methanol, and the methanol is converted to gasoline by reacting with catalysts.

4) Transportation Fuels from Oil Sands

The oil sands are consists of recoverable oil (in the form of bitumen) which can use as transportation fuels. Oil sand operators normally use natural gas to produce the steam and hydrogen needed for the mining, upgrading, and refining processes. However, operators have plans to gasify bitumen residues to supply the necessary steam and hydrogen because the feedstock and waste product (the petcoke) gasification can displace expensive natural gas for extract usable energy. In addition, the gasifiers can reduce fresh water usage and wastewater management costs by recycled black water from the mining and refining processes to use in a wet feed system.

5) Substitute Natural Gas

Gasification can also be used to create substitute natural gas (SNG) from coal. Methanation reaction can be profitably convert syngas to methane (CH_4). The substitute natural gas can be used to generate electricity, produce chemicals/fertilizers, or heat homes and businesses, The substitute natural gas will enrich the economics in the country because it can reduce imported natural gas.

6) Power Generation with Gasification

Gasification of feedstock can produce electricity take place oil and natural gas. In case of coal gasification, it can produce electricity too and it can produce syngas with the pollutants removed by "bag house" and/or "scrubber". Thus, the pollutants removed before the syngas is combusted in the turbine.
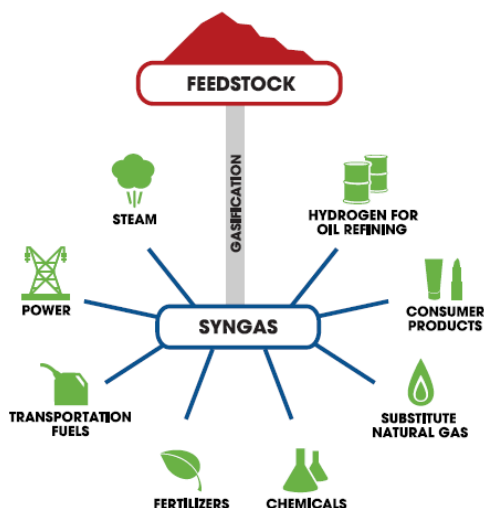
Figure 2.13 Synthesis gas applications from gasification process (Gasification Technology Council, 2008)

2.7 Environmental benefits of gasification process

The gasification process offer several environmental advantages such as reduce air emissions, reduce solids generation, reduce water usage and capture carbon dioxide (Gasification Technology Council, 2008).

2.7.1 Air Emissions

Gasification can achieve greater air emission reductions at lower cost than other technologies. An Integrated Gasification Combined Cycle (IGCC) offers the lowest emissions of sulfur dioxide (SO_x) nitrogen oxides (NO_x) and particulate matter (PM) when compared with other technologies. In addition, more than 95% of the mercury emissions can be removed by gasification process.

2.7.2 Solids Generation

During gasification, all of the carbon in the feedstock is converted to syngas. The mineral material in the feedstock that separates from the gaseous products, and the ash and other inert materials melt and fall to the bottom of the gasifier as a nonleachable material. This material can be used for many construction and building applications. In addition, more than 99% of the sulfur can be removed, and it can be converted into marketable elemental sulfur or sulfuric acid by using this technology.

2.7.3 Water Usage

Gasification uses water to produce electric power from feedstock less than other technologies approximately 14–24%, and water losses during gasification operation less than other technologies about 32–36%.

2.7.4 Carbon Dioxide

In a gasification system, CO_2 can be captured by the water-gas shift reaction before it released to the atmosphere. Moreover, CO_2 can convert to CO by the gasification process. In addition, the "decarbonizing" can reduce carbon in the syngas. Gasification plants manufacturing ammonia, hydrogen, fuels, or chemical products always capture CO_2 as part of the manufacturing process. The environmental benefit of IGCC cycle is to minimize CO_2 emissions more than other technologies (Gasification Technology Council, 2008).
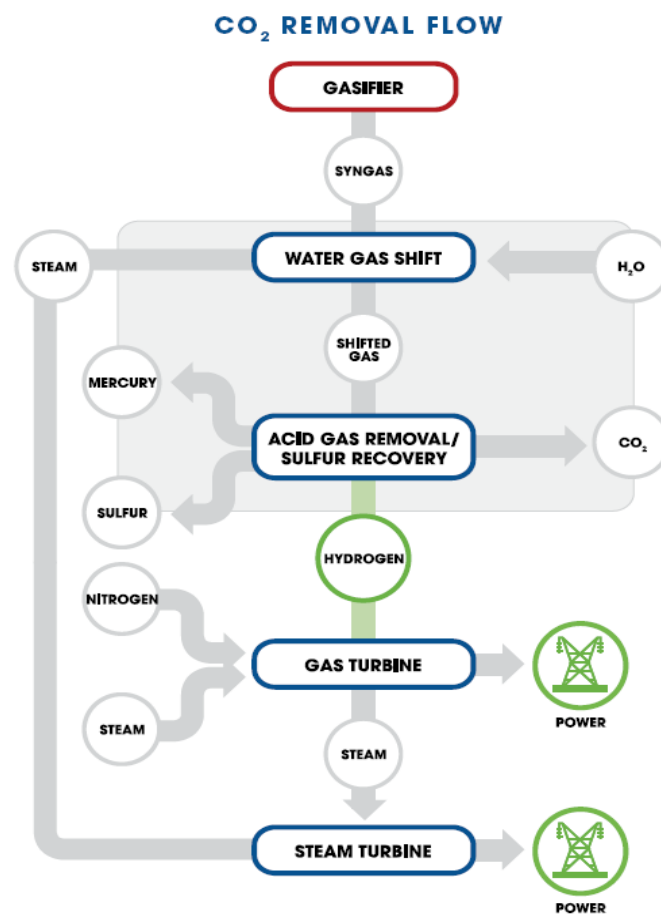
Figure 2.14 CO_2 removal flow by using gasification process (Gasification Technology Council, 2008)

2.8 Catalyst (G.C.Bond, 1987)

The word catalysis comes from two Greek words, the prefix *cata-* means down, and the verb *lysein* means split or break. Thus, catalyst can breaks down the normal forces which inhibit the reactions of molecules. The usually accepted definition of catalyst is that it is *a substance the increases the rate at which a chemical system approaches equilibrium, without being consumed in the process.*

It can be implies that a catalyst can increase the rate only of reaction that is already thermodynamically feasible. It cannot initiate reaction that is thermodynamically impossible. Since the catalyst does not alter the equilibrium constant, but only enhances the forward rate or reverse rate.

2.8.1 Classification of catalytic systems

Catalytic systems can be divided into two categories depending on phase of catalyst and reactants

1) Homogeneous catalysis: the catalyst is the same phase as the reactants and no phase boundary exists

2) Heterogeneous catalysis: a phase boundary separates the catalyst from the reactants. Mostly of heterogeneous catalysis are solid phase. The type of reaction best catalysed by solid depends on its chemical nature. For catalysis, chemical interaction between the catalyst and the reactant- product system must be occurred, but this interaction must not change the chemical nature of the catalyst except at the surface. Thus, surface interaction must be the adsorption of molecules at solid surfaces.

Table 2.11 Catalytic abilities of each heterogeneous catalytic group.

Class	Functions	Examples
Metals	Hydrogenation	Fe, Ni, Pd, Pt, Ag
	Dehydrogenation	
	Hydrogenolysis	
	(Oxidation)	
Semiconducting oxides	Oxidation	NiO, ZnO, MnO_2, Cr_2O_3,
and sulphides	Dehydrogenation	Bi_2O_3,-MoO_3, WS_2
	Desulphurization	
	(Hydrogenation)	
Insulator	Dehydration	Al_2O_3, SiO_2, MgO
Acids	Polymerization	H_3PO_4, H_2SO_4,
	Isomerization	SiO_2-Al_2O_3, Zeolite
	Cracking	
	Alkylation	

The successful catalyst must be able to effect the desired reaction at an acceptable rate under conditions of temperature and pressure during the experiment, and the catalyst must be able to sustain the desired reaction and obtained good yields. Moreover, It should be minimal side reactions, especially minimal leading to poisoning or deactivation through carbon deposition. The deactivation of catalysts because reversible poisoning due to impurities in the reactants or side-reactions, and irreversible physical changes including loss of surface area (sintering or mechanical failure.

2.8.2 Supported metal catalysts

The rate of a catalyzed reaction should be proportional to the surface area of active phase. Since it is necessary to make the particles size as small as possible i.e. maximize the fraction of the atoms that are on the surface for maximize efficiency of the catalysts. The fraction called the *dispersion* or the *fraction exposed*.

The advantages of having the metal particles supported catalysts are following

1) The catalyst is easily and safety handled.

2) It may be used in a variety of reactors, and it can be recovered by filtration if used in a liquid medium.

3) The particles are well separated from each other by sintering

4) The support of catalyst can be prepared by bring promoters into close contact with the metal.
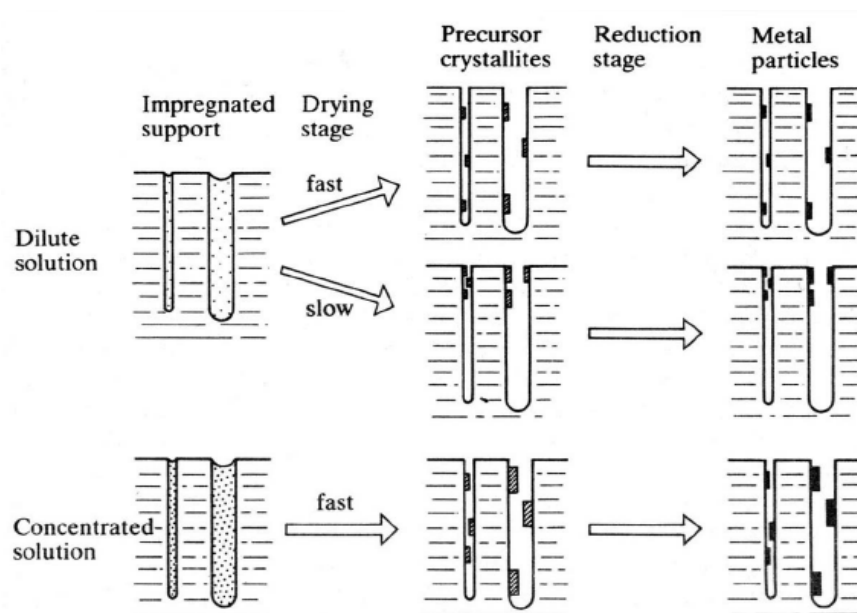
Figure 2.15 Stages in the preparation of supported metals catalyst (G.C.Bond, 1987)

Four general stages for preparing supported metal catalysts are (Impregnation method) (G.C.Bond, 1987):

1) Formation of the precursor to the active phase, usually in an aqueous medium

2) Drying: water is removed by evaporation moist samples. If the drying step is performed slowing, the salt will migrate towards the external surface of the support particle. If it is desired to have a uniform distribution of metal throughout the support, it is better to dry quickly.

3) Calcination (not always necessary): calcinations is to convert the precursor to oxide, which is usually the easiest compound to reduce

4) Reduction: this step is to reduce the precursor to the metallic state. Most of the compounds of the noble metals are quite easily reducible.

2.8.3 Catalytic composition

The composition of heterogeneous catalysts can be divided into three primary components (Bartholomew, C.H., 2006):

1) An active catalytic phase

2) A promoter, which increases activity and/or stability

3) A high surface area support that facilitates dispersion of the active phase
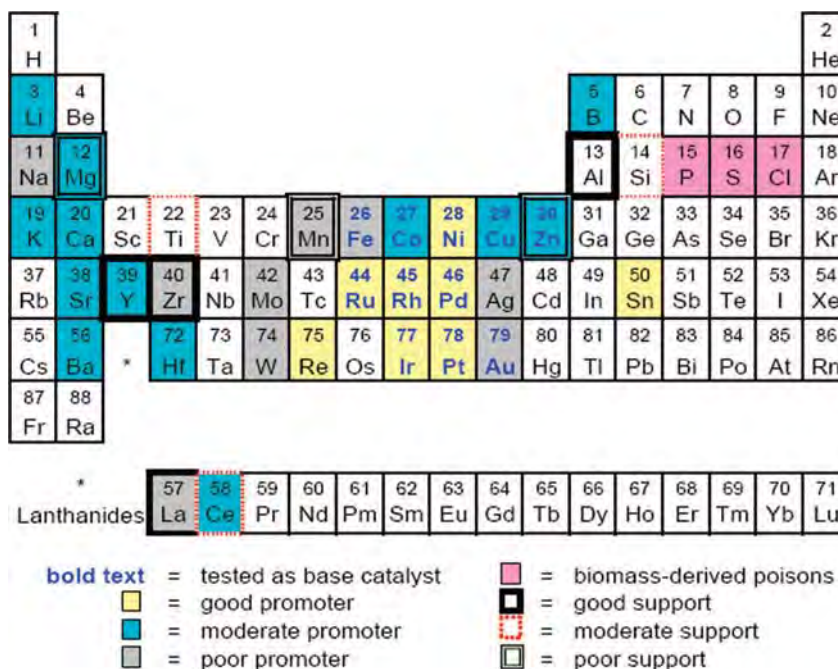
Figure 2.16 Elements investigated for catalytic composition studies (Yung. et al., 2008)

2.8.4 Nickel

The atomic number of nickel or Ni is 28. The density of nickel is 8.908 g/cm^3. Atomic weight of nickel is 58.69 g/mol. Nickel belongs to the transition metals and is hard and <u>ductile</u>. The melting point of nickel is 1,455°C, and the boiling point is 2,913°C. Electronegativity is 1.80. The most common <u>oxidation state</u> of nickel is +2, but compounds of Ni^0, Ni^+, and Ni^{3+} are well known, and Ni^{4+} has been demonstrated. Nickel(II) compounds are known with all common anions, i.e. the sulfide, sulfate, carbonate, hydroxide, carboxylates, and halides. Electron Configuration (Ar) is $3d^8$ $4s^2$.

Nickel-based steam reforming catalysts have been widely used commercially in the petrochemical industry or biomass gasification for methane and naphtha reforming. These Ni catalysts have also shown activity for tar destruction, hydrocarbon reforming, water-gas shift (WGS), and NH_3 decomposition (Dayton, 2002).

2.8.5 Lantanum

Lantanum or La belongs to group 3 of the periodic table and is the first element of the lanthanide series. Atomic number of lantanum is 57, and atomic weight is 138.91 g/mol. The density of lantanum is 6.162 g/cm^3.The melting point of nickel is 920°C, and the boiling point is 3,464°C. Electronegativity is 1.10. Electron Configuration (Xe) is $5d^1\ 6s^2$. Lantanum is good resistance to deactivation by carbon deposition (Yung et al., 2009).

2.8.6 Magnesium

Magnesium is an alkaline earth metal. The atomic number of magnesium is 12 and common oxidation number +2. Atomic weight of magnesium is 24.30 g/mol. The density of magnesium is 1.738 g/cm^3. The melting point is 650°C, and the boiling point is 1,091°C. Electronegativity is 1.31 and Electron Configuration) (Ne) is $3s^2$. Addition of magnesium in catalyst can prevent catalyst sintering (Garcia et al, 2000).

2.8.7 Alumina (Al_2O_3)

Alumina is also known as aluminium oxide with the chemical formula Al_2O_3. The alumina appearance is white granules or powder. The melting point is 2,072°C. The boiling point is 2,977°C. Specific gravity is 4.0.

Alumina can found in α-alumina, β-alumina or γ-alumina. The properties of alumina are hardness, high melting and boiling point, hard to corrode, chemical-resistant and high thermal conductivity but it is an electrical insulator. From alumina properties, it is suitable for use as support in gasification process. Alumina (Al_2O_3) is most commonly used for support commercial Ni steam reforming catalysts. Alumina has work well for natural gas (methane) steam reforming (SMR) catalysts.

2.9 Literature Reviews

Herguido er al. (1992) gasified different biomass materials such as pine sawdust, pine wood chips, cereal straw, and thistles *(Cymra cardunculus)* with steam in a 15-cm^4.d. fluidized bed reactor. The feeding of the biomass to gasfier is carried out continuously. The gas, tar, and char yields, the composition and heating value of the gas produced, and the conversion of carbon for each material have been determined at temperatures between 650 and 780°C (923-1053 K). Silica sand (or dolomite, calcite, etc.) of a correct size has to be used as the supporting bed. The results indicated that temperature is a parameter very important in the process. At low temperatures, under 750°C, the exit gas composition is clearly different for each biomass. Above 750°C the gas composition is near the same for all the biomass used. Tar yields decrease with gasification temperatures and with the steam/biomass ratio. At 750-800°C tar yields are between 2.8 and 5.0 wt%. The size and shape of the biomass have influence on the product distribution. Small particle sizes (like the pine sawdust) or shapes near a plate (like the cereal straw) produce a greater gas yield and a lesser char yield than the bigger particles (chips).

Maschio et al. (1994) studied the influence of the operating conditions on the gasification of biomass in a pilot-plant. The process consisted of a steam gasification carried out in two indirectly-heated reactors in series. The first step of the process, in which a conventional pyrolysis was performed at a temperature ranging from 400 to 600°C, was carried out in an indirectly heated continuous-screw reactor (tube diameter = 200 mm; length = 1500 mm). The second step, in which gasification was performed at an operating temperature ranging from 700-950°C, was carried out in tubular coiled entrained bed reactor (tube diameter = 52 mm; length = 20000 mm). The results found that at lower Water/Biomass ratio a syngas can be obtained, increasing Water/Biomass ratio a hydrogen rich gas can be more produced. The catalyst was used to decrease the operating temperature and reduce the production of tar. The high heating rate achieved in the entrained-bed reactor can cracking of volatiles and minimizes char and tar. The very short residence time in the gasification reactor avoid the problem of softening the ash and the formation of eutectics with the inert-bed solids typical of fluidized-bed gasifiers.

Garcia et al. (2000) studied catalytic steam reforming of bio-oils for the production of hydrogen. The operation conditions were catalytically steam reformed at 825 and 875°C, high space velocity (up to 126,000 h^{-1}) and low residence time (26 ms). This experiment was carried out in a fixed bed reactor. The catalysts were prepared by impregnation of an α-Al_2O_3 support with nickel and additives. Magnesium and lanthanum were used as support modifiers to enhance steam adsorption while cobalt and chromium additives were applied to reduce coke formation reactions. The best results in the laboratory tests were the cobalt-promoted nickel and chromium-promoted nickel supported on MgO-La_2O_3-α-Al_2O_3 catalysts. Magnesium and lanthanum enhanced steam adsorption that facilitated the gasification of surface carbon while cobalt and chromium modified the metal sites forming alloys with nickel and possibly reducing the crystallite size. Carbon conversion to CO and CO_2 decreased slightly with reaction time, the main impact on the decrease of H_2 and CO_2 yields appears to be linked to the ability of the catalyst to enhance the water–gas shift reaction.

Demirbaş (2002) studied pyrolysis and steam gasification of black liquor. The pyrolysis experiments were performed in a stainless steel tube reactor with height 10cm, ID 1.75 cm and OD 1.85. For each pyrolysis run, 5 g samples was used. The samples were pyrolysis in a nitrogenous ambient pressure at different temperatures. The temperature ranges applied for the pyrolyses of black liquor samples were 500–700 K and 500–800 K, respectively. For the steam gasification used a reactor tube (42 mm diameter) placed in a electric furnace. Temperature range between 850 and 1350K, weighed black liquor samples were introduced continuously at the top of the reactor. The total weight of the sample was 3 g. The gaseous products from both direct and catalytic runs of the black liquor samples, CO_2, CO, olefins, H_2 + paraffins and H_2S were analyzed. The residence time of the gas in the hot zone of the reactor was less than 2 s. Water vapor for steam gasification was supplied from a steam generator. K_2CO_3 was used as the catalyst, 10.0% by weight of the black liquor sample, in the catalytic pyrolysis runs. The ratios of water-to-black liquor (Water/Black liquor) were 0.7 and 1.9 in the steam gasification runs. This studied found that the yields of liquid products from the black liquor pyrolysis increase from 17.2% to 26.5% with increasing temperature from 600 to 800 K. The yields of liquid and gaseous products from pyrolysis of the black liquor samples increase with

increasing temperature. The yields of H_2 + paraffins in the gaseous products from the black liquor steam gasification run (Water/Black liquor = 1.9) increase from 38.0% to 50.3% with increasing temperature from 975 to 1325 K. The highest hydrogen rich gas yield was obtained from the catalytic steam gasification run (Water/Black liquor = 1.9) at 1325 K.

Hammond (2002) studied the effects of secondary sludge addition on black liquor gasification, the ratio of 0, 5, 10, and 15% secondary sludge solids that added to hardwood black liquor solids, gasification temperatures at 700 and 900°C and residence times at 0.2, 0.7, and 1.2 seconds. Gasification was performed in a laminar entrained flow reactor. This studied found that both amount and rate of organic carbon conversion increased with temperature, the percentage of sludge addition did not affect percent of feed carbon recovered as organic carbon. Recovery of sulfur in char was higher for the 100/0 (black liquor/secondary sludge) feed than for the 85/15 feed. Recoveries of H_2S were higher for purer (less sludge added) feed stocks for all experiments except those performed 900°C/1.2 seconds residence time. Recoveries of methyl mercaptan, n-propyl mercaptan, carbon disulfide, and ammonia were relatively independent of sludge addition. Recoveries in char of magnesium, vanadium, and aluminum were higher for the 85/15 feed stock.

Chewatanakup (2003) studied synthesis gas by gasification of eucalyptus with the operating temperature of 550-800°C. Eucalyptuses were used as the reactant. Steam was added with feed rate of 0.15-2.100 g/h/g of biomass as gasifying medium for synthesis gas. The effects of temperature, steam feed rate, and amount of catalyst were also studied. This studied found that with low steam feed rate, the ratio between H_2 and CO is about 1:1. In contrast, at high steam feed rate the ratio between H_2 and CO was significantly increased. The same result was also observed for the case of temperature. The ratio between H_2 and CO was increased when temperature in reactor was increased. And the ratio was decreased when temperature was decreased. The ratio of 1:1.612 for H_2 and CO was achieved at 15 g of Eucalyptus 0.15 g/h/g of biomass 550°C. By adding dolomite catalyst with the same condition, it was found that the product has the ratio of H_2 and CO as 1:0.96.

Martínez et al. (2003) studied the addition of lanthanum to co-precipitated Ni–Al catalysts used in the catalytic steam gasification of biomass. The experimental work was carried out at temperature of 700°C, and at atmospheric pressure. Three Ni–Al–La catalysts were prepared, the Ni content being the same in all cases (33 wt%) but with varying amounts of La and Al. The calcinations temperature was 750°C for 3 hours. The results showed that addition of lanthanum to the Ni–Al catalyst resulted in an increase in CO, CO_2, CH_4, C_2 and total gas yields higher than Ni–Al catalyst, while the H_2 yield remained almost unchanged.

Ketcong (2004) studied gasification of eucalyptus wood by nickel/dolomite catalyst. The influence of operating parameters, such as steam/biomass ratio, temperature of the reactor, composition of catalysts and weight of catalysts, were studied. Steam gasification studies were carried out in an atmospheric fixed bed. The gasifier was operated over a temperature in the range of 500-800°C while, varying a catalyst composition from 0 to 10% of nickel loading on dolomite in steam flow rate of 0.01-0.07 g/min/g of biomass and 0 to 1.5g of nickel/dolomite weight. This studied found that the optimum condition is at temperature 700°C, percentage of nickel loading on dolomite 9.32% and a steam flow rate of 0.01 g/min/g of biomass. At this condition, comparing the gasification without and with catalyst, it was found that the percentage of hydrogen increased from 41.23% to 45.26% and carbon monoxide increase from 42.75% to 56.45%. In addition, the proportion of hydrogen and carbon monoxide is 0.58.

Pui-ock (2004) studied of gasification of black liquor for producing gas products such as H_2, CO, CO_2 and CH_4. This research studied the effect of temperature from 600°C to 800°C, steam feed rate from 0.03 to 0.10 ml/s, the percentage of catalyst are 1, 3, 5 and 10 by weight, and studied synthesis gas with the ratio of H_2:CO about 2:1 which will be suitable for methanol production. This studied found that the best of temperature to produced the gas product was 750ºC., the best of steam feed rate to produced the gas product was 0.05 ml/s and the best of percentage of catalyst to produced the gas product was 5 percent by weight. The optimum condition which gave the ratio nearest to 2:1 were temperature of 700ºC, Steam feed rate 0.03 ml/s and the percentage of catalyst was 1 percent by weight.

Xiao et al. (2007) studied air gasification of polypropylene plastic waste in fluidized bed gasifier. This research was determine the effect of the equivalence ratio, bed height and fluidization velocity. Furthermore, the product yield distribution, gas composition, gas heating value and gas yield were studied. The results found that increasing equivalence ratio from 0.20 to 0.45, and increasing bed temperature from 703 °C to 915°C results in greater the formation of the fuel gas and decreased the formation of the tars and char. The decrease in the hydrocarbons content and, therefore, the gas heating value with an increase in the equivalence ratio was also observed. The results indicated that the range of calorific value is 5.2–11.4 MJ/Nm^3 and low tars content, which could be used in many end use applications.

Chuchai (2008) studied gasification of palm shell waste mixed with crude glycerol by partial oxidation with air. Air and mixed waste were introduced into the gasifier from the bottom and the top of a laboratory scale quartz gasifier, respectively. The effects of temperature (700, 800 and 900°C), ratio of palm shell waste to crude glycerol (100:0 and 70:30) and equivalent ratio (ER) of 0-0.6 with total flow rate 15 l/min and feeding rate 5 g/min were investigated. Major gaseous products were CO_2, CO, H_2 and CH_4. Char and tar from the reactions were collected and analyzed. This studied found that the temperature 900°C and ER of 0 appeared to be the optimum conditions for palm shell waste mixed with crude glycerol gasification with respect to the maximum of mole ratio H_2/CO in this study which is 0.37 and also yielding maximum heating value of gas product in this study. The lower heating value obtained from this work are 4.32–17.62 MJ/m^3. Heating value of obtained gas product is high enough to be further utilized without addition auxiliary fuel.

Kumar et al. (2009) studied gasification of distillers grains in fluidized bed by using steam and air as fluidizing and oxidizing agents. The maximum throughput of the system was approximately 1–1.5 kg/h depending on the density of biomass and flow rate of fluidizing agents used. The gasifier tube was made of stainless steel. The lower part of reactor had an inside diameter of 3.81 cm (1.5") and a length of 700 mm. The upper part of reactor had an inside diameter of 6.35 cm (2.5") and a length of 500 mm. The effect of steam to biomass ratio, equivalence ratio and gasification temperature were determined. The operating conditions are temperatures of 650, 750 and 850°C, steam to biomass ratios of 0, 7.30 and 14.29 and equivalence ratios of

0.07, 0.15 and 0.29. The results showed that temperature was the most influential factor. Increasing the temperature resulted in increases in hydrogen and methane contents, carbon conversion and energy efficiencies. Increasing temperature, the energy efficiency increased from 10–70% at 650°C to 22–82% at 750°C and 28–96% at 850°C. Increasing equivalence ratio decreased the hydrogen content but increased carbon conversion and energy efficiencies. The steam to biomass ratio was optimal in the intermediate levels for maximal carbon conversion and energy efficiencies.

Sricharoenchaikul (2009) studied the feasibility of using supercritical waster gasification technique to convert black liquor into valuable products. Operating parameters such as pressure, temperature, feed concentration, and reaction time, which would yield the highest conversion and energy efficiencies were studied. Reaction was performed in a quartz capillary heated in a fluidized bed reactor. Results indicated that pressure between 220 and 400 atm has insignificant influence on the gas products and extent of carbon conversion. Increasing temperature and residence time between 375–650°C and 5–120 s resulted in greater gas production, overall carbon conversion, and energy efficiency. Maximum conversion to H_2, CO, CH_4, and C_2H_X was achieved at the highest temperature and longest residence time. The results showed that the highest of carbon conversion is 84.8%, gas energy content is 9.4 MJ/m3 and energy conversion ratio is 1.2. Higher carbon conversion and energy conversion ratio were obtained with more dilute liquor, energy content was lower with higher solid contents.

From literature reviews, it can be concluded that black liquor and sludge can be used to transform to fuel products via thermochemical conversion process. Temperature, equivalence ratio (ER) and raw material ratio are parameters which have influence on the products. Temperature is a parameter very important in the gasification process. A greater gas yield and a lesser solid and liquid yield produced at higher temperature. Addition of catalyst can also be improving the performance of gasification process.

CHAPTER III
EXPERIMENTAL

This research deal with pulp sludge from wastewater treatment system mixed with black liquor. Both wastes were obtained from local pulp and paper manufacturer. Fuel gases from co-gasification of these wastes were investigated.

3.1 Materials

3.1.1 Black Liquor

Black Liquor was obtained from local pulp and paper manufacturer. This plant was using *Camaldulensis* eucalyptus as raw material. Black liquor was come from cooking process. Then, it will send to reuse by chemical recovery process. In this research, black liquor was collected after pass evaporation process, called "strong black liquor" because it has a solid content of more than 50%.

3.1.2 Sludge from wastewater treatment system

Sludge was supplied from local pulp and paper manufacturer. Sludge was come from wastewater treatment system. In activated sludge process, sludge was produce from two steps. These two steps were the primary clarifier called "primary sludge", and the secondary clarifier called "secondary sludge". Sludge used in this research was mix sludge because it came from primary sludge mixed with secondary sludge. This sludge was collected after passing through sludge belt press called "dewatered sludge".

3.1.3 Alumina balls, Al_2O_3

Alumina balls were used as bed material to distribute heat to raw materials. Its approximate size is 1 mm.

3.1.4 Ni-La-Mg/Al_2O_3 catalyst

Ni-La-Mg/Al_2O_3 was used as catalyst. It prepared by co-impregnation method.

3.1.5 Nitrogen gas

Nitrogen 99.99% was used as carrier gas. It was supplied from Thai Industrial Gases Public Company Limited, Thailand.

3.1.6 Oxygen gas

Oxygen 99.5% (purified oxygen) was used as oxidizing gas. It was supplied from Bangkok Industrial Gases Public Company Limited, Thailand.

3.1.7 Hydrogen gas

Hydrogen gas 99.99% was used to reduce catalyst. It was supplied from Bangkok Industrial Gases Public Company Limited, Thailand.

3.2 Equipments

3.2.1 Fine Grinder

Fine grinder was used to grind dewatered sludge to suitable particle for mixed with black liquor.

3.2.2 Grinder

Grinder was applied to grind catalyst to proper size for sieve.

3.2.3 Sieve

Sieve was used to select proper size of pulp sludge that mixed with black liquor for feed into system, and applied to select proper size of catalyst to mix with raw material. Sieve had diameter 8 inch and aperture size 2.0 mm, 10 mesh and diameter 8 inch and aperture size 150 micron, 100 mesh, respectively.

3.2.4 Feeder

Feeder was made from a funnel connect with silicone tube that connect with acrylic pipe to feed raw material into the reactor.

3.2.5 Rotameter

Rotameters were used to control the rate of oxidizing gas and carrier gas that flow through the reactor.

3.2.6 Pressure gauge

Pressure drop between the top and bottom of the reactor was continuously measured by pressure gauge for determine stability of each run.

3.2.7 Gas pre-heater

Gas pre-heater was applied to warm up inlet gases before fed into the reactor.

3.2.8 Temperature controller

Temperature controller was applied to control temperature of electrical furnace during experiment.

3.2.9 Electrical furnace

Electrical furnace was applied to contribute heat to reactor during the experiment. The electrical furnace was supplied from Suan Luang Engineering Ltd., Part.

3.2.10 Stainless Tube

Stainless tube was used in this research as a reactor. The upper part of stainless tube has 46 mm outside diameter, 40 mm inner diameter, and the lower part has 25 mm outside diameter, 19 mm inner diameter. The height of stainless tube was 1100 mm.

3.2.11 Cyclone and collector

Cyclone was used to trap solid particles into collector. Cyclone and collector were made from quartz.

3.2.12 Chiller

Chiller was supplied to produce cold water to control temperature and used for heat exchanging in condensers.

3.2.13 Condensers and collectors

Tar from the reaction was trapped by condenser into collectors before enter to gases analyzer. Condensers and collectors were made from quartz.

3.2.14 Gas Washer

Gas washer used to clean gases before entering to gases analyzer.

3.2.15 Gas flow meter

Gas flow meter was used to measure the rate of gas flow during experiment.

3.2.16 Analyzer (MRU GmbH model SWG$^{200\text{-}1}$)

Gas product was analyzed by online gas analyzer (MRU GmbH, SWG$^{200\text{-}1}$) which capable of continuous real time qualification of CO_2, CO, H_2 and C_xH_y (as CH_4). For CO_2, CO and CH_4 analyses, non dispersive infrared sensor (NDIR) technique was applied. H_2 analysis was performed by dedicated thermal conductivity detector (TCD).

3.2.17 Stop-watch

Stop-watch was used to collect time data for calculated the quantity of gas products.

3.2.18 A scale

A scale was used to measure weight of char and tar that produces during run system (2 decimal places), and used to measure catalyst (4 decimal places).

3.2.19 Oven

Oven was used to dry black liquor and sludge for analyze proximate analysis, ultimate analysis, and heating value analysis, and used to dry catalyst too.

3.2.20 High temperature furnace

High temperature furnace was applied to calcine catalyst after it dried, and reduced it after calcined.

The procedure of co-gasification system

Before the operation, alumina 85 g was put in stainless steel reactor, which equivalence to approximately 100 mm in bed height. Then, reactor was put into electrical furnace. Electrical furnace equipped with temperature controller, was used to supply heat to alumina bed in the reactor. Chiller was used to produce cold water for heat exchanging in the condensers. Then, nitrogen gas and oxygen gas was fed into the bottom of reactor at the determined ratio by using rotameters to control rate of inlet gases flow. Gas pre-heater was applied to warm up inlet gases before fed into the reactor. Pressure drop between the top and bottom of reactor was continuously measured by pressure gauge for determine stability of the run. After that, pulp sludge mixed with black liquor at determined ratio was fed via feeder into reactor. Then, thermal cracking reaction occurred in the system and transformed raw materials into gaseous products. Gaseous products were moved to the upper part of reactor, while most of the residual solid fell to bottom of the reactor. The gaseous products moved into cyclone and collector that used for trap the residual solid particles entrained in gaseous products, so solid yield is collected in the reactor and collector under cyclone. It is collected for further analysis and calculated by measure weight. Next, gaseous products passed through condensers for heat exchange where the liquid product was condensed into collectors. Liquid yield is tar mixed with water from raw material. Liquid yield from the process is collected and calculated by measure weight. Finally, the gaseous products were separated into two flows. One was passed though washer to clean gaseous products before entered to TCD-NDIR analyzer and gas yield were calculated by difference from solid and liquid yield (total was 100 wt.%). Another

was passed though gas flow meter for measurement of outlet gases flow rate then ventilated through exhaust.

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┌─────────────────────────────────────────────┐
│         Put alumina balls as bed in reactor         │
└─────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────┐
│         Put reactor into electrical furnace         │
└─────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────────────────┐
│ Open temperature controller for contribute and control heat in system │
└─────────────────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────┐
│      Open chiller for heat exchange in condensers      │
└─────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────┐
│   Feed nitrogen and oxygen gas into the bottom of reactor   │
│       by using rotameters to control inlet gases       │
└─────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────────────────┐
│ Open gas pre-heater to warm up inlet gases before fed into the reactor │
└─────────────────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────┐
│     Feed raw materials into system by using feeder     │
└─────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────────────────┐
│  Record gaseous products that shown on analyzer screen every minute  │
└─────────────────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────┐
│   Measure the residual solid and liquid by using A scale   │
└─────────────────────────────────────────────┘
```

Figure 3.1 Procedure of co-gasification experiment

The diagram of co-gasification system is shown in Figure 3.2
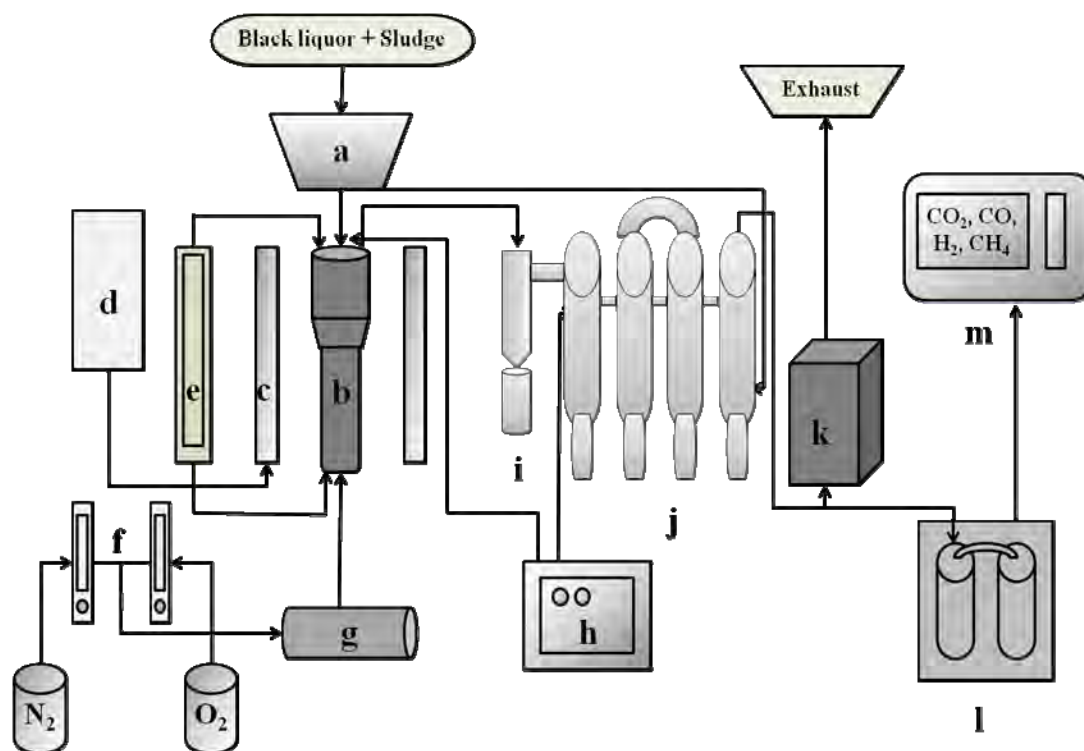
Figure 3.2 Schematic of co-gasification system: (a) Feeder (b) Stainless tube reactor (c) Electrical furnace (d) Temperature controller (e) Pressure gauge (f) Rotameters (g) Gas pre-heater (h) Chiller, (i) Cyclone (j) Condensers (k) Gas flow meter (l) Gas washers (m) Gas analyzer

The procedure of catalytic preparation

1.   Measure weight of $Ni(NO_3)_2.6H_2O$(Merck, $\geq 99\%$), $La_2(NO_3)_2.6H_2O$ (Merck, $\geq 96\%$), $Mg(NO_3)_2.6H_2O$(Fluka, $\geq 99\%$) and α-Al_2O_3(Indal, 99.5%, 1.8 µm, 3.9 g/cm^3) by using a scale.

2.   Bring $Ni(NO_3)_2.6H_2O$, $La_2(NO_3)_2.6H_2O$ and $Mg(NO_3)_2.6H_2O$ to dissolve by distilled water.

3.   Dip Al_2O_3 support into metal salt solution.

4.   Dry it at 110°C, 24 hours.

5.   Calcine catalyst in high temperature furnace at 850°C, 2 hours.

6.   Crush and sieve to 100 mesh.

7.   Reduce Ni-La-Mg/Al_2O_3 in high temperature furnace at 700°C, 2 hours by using H_2 gas at 10 mL/min.

8.   Keep catalyst in desiccator.

```
┌─────────────────────────────────────────────────────────────────────┐
│  Measure weight of Ni(NO₃)₂.6H₂O, La₂(NO₃)₂.6H₂O, Mg(NO₃)₂.6H₂O       │
│                                                                       │
│            and α-Al₂O₃ at determined percentage                       │
└─────────────────────────────────────────────────────────────────────┘
```

$$\text{Measure weight of } Ni(NO_3)_2.6H_2O, \ La_2(NO_3)_2.6H_2O, \ Mg(NO_3)_2.6H_2O \text{ and } \alpha\text{-}Al_2O_3 \text{ at determined percentage}$$

$$\text{Dissolve } Ni(NO_3)_2.6H_2O, \ La_2(NO_3)_2.6H_2O \text{ and } Mg(NO_3)_2.6H_2O \text{ by distilled water}$$

$$\text{Dip } Al_2O_3 \text{ support into metal salt solution}$$

$$\text{Dry it at } 110°C, \ 24 \text{ hours}$$

$$\text{Calcine at } 850°C, \ 2 \text{ hours}$$

$$\text{Crush and sieve to } 100 \text{ mesh}$$

$$\text{Reduce at } 700°C, \ 2 \text{ hours by using } H_2 \text{ gas at } 10 \text{ mL/min}$$

$$\text{Keep in desiccator}$$

Figure 3.3 Procedure of catalytic preparation by co-impregnation method

3.3 Instrument

- Thermal properties

Thermal degradation of raw materials was studied by Thermogravimetric Analyzer (TGA) to determine quantity of volatiles, fixed carbon, and ash at heating rate 20°C/min under inert atmosphere (N_2) and air of 20 ml/min flow rate. This research used the METTLER TOLEDO TGA model TGA/SDTA 851 with STARe software version 8.1 for data evaluation. CHNS analysis technique (Leco TruSpec® CHNS (micro) Analyzer) was applied to determine CHNS/O composition. Heating value (HV) analysis was investigated by using Automatic Bomb Calorimeter; Leco model AC-350. Moreover, elemental compositions were analyzed by using X-ray fluorescence spectrometer**.**
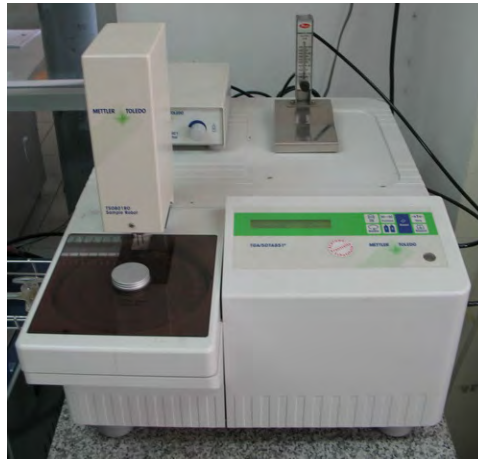
Figure 3.4 Thermogravimetric Analyzer (TGA) instrument

Figure 3.5 Automatic Bomb Calorimeter instrument

3.4 Variables

In this research, total input flow rates were depending on reaction temperatures in order to yielded relatively constant gas hold time for each run. Raw material feed rate is 5 g/min and alumina balls are 85 g (approximate high 100 mm in the lower part of reactor). Followings variables were adjusted to transform pulp sludge that mixed with black liquor into valuable products. For example,

3.4.1 Temperature

The range of temperature was varied to study the effect of temperature for the gasification reaction and gaseous products. The ranges of operating temperature that varied in this experiment were 700, 800 and 900°C.

3.4.2 The ratio of pulp sludge and black liquor

The ratio of pulp sludge and black liquor was varied to study the effect of pulp sludge and black liquor ratio to the reaction in this experiment. The ratios of pulp sludge and black liquor that varied in this experiment were 50:50 and 40:60.

3.4.3 Equivalence Ratio

In this research, air to fuel ratio (equivalence ratio) was varied to identify the effect of equivalence ratio to the gasification reaction. The ranges of equivalence ratio were 0.2, 0.4 and 0.6.

3.4.4 Ni-La-Mg/Al$_2$O$_3$catalyst

Ni-La-Mg/Al$_2$O$_3$ catalyst was carefully mixed with raw material at 20 wt.% (1g/min). It used to compare the results of non-catalytic with catalytic cases.

3.5 Procedure

3.5.1 Study theoretical and collected data about pulp and paper industry, raw materials and gasification process

3.5.2 Design and plan the experiment

- Determine controlled variable and varied variable. For example, study the optimal ratio of pulp sludge and black liquor by mixed dry sludge (after grind) with black liquor. The ratio that was studied was 50:50 and 40:60.

- Analysis of raw materials and products.

3.5.3 Analyze the qualification of pulp sludge and black liquor

3.5.3.1 Proximate analysis

- Analyze black liquor, sludge and char to measure moisture content, volatile matter, fixed carbon and ash by using Thermogravimetric Analyzer (TGA), and using standard method from International Standard Organization (ISO).

- Methodology
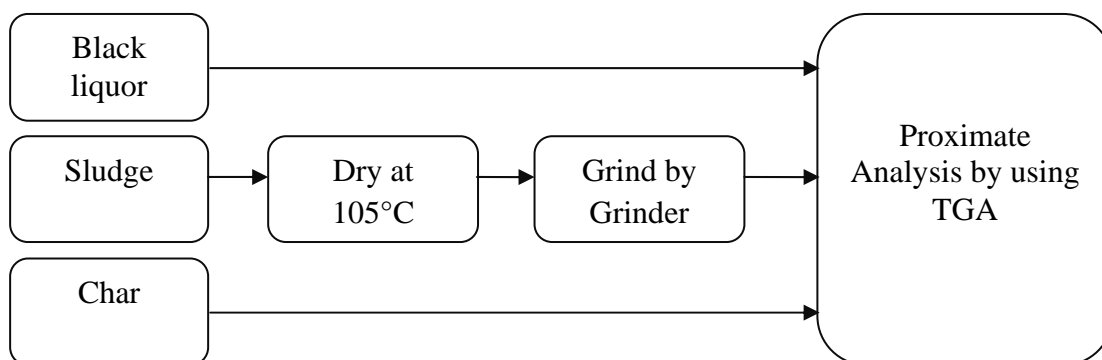
Figure 3.6 Flow chart of proximate analysis

3.5.3.2 Ultimate analysis

- Analyze percentage of Carbon(C), Hydrogen(H), Nitrogen(N), Sulfur(S) and Oxygen(O); by different; in black liquor and sludge by using CHNS analysis technique at 1100°C under oxygen atmosphere and carrier gas is helium gas and CHNS/O analyzer (Leco TruSpec® CHNS (micro) Analyzer).

- Methodology
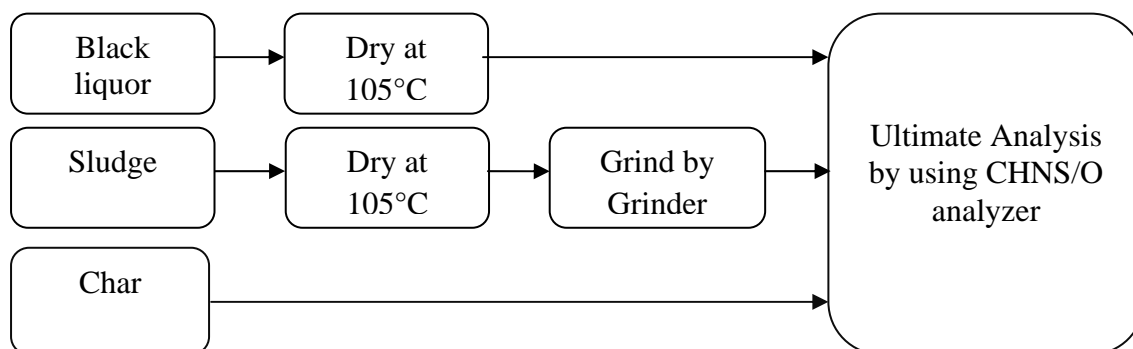
Figure 3.7 Flow chart of ultimate analysis

3.5.3.3 Heating value analysis

- Analyze heating value (HV) of black liquor and sludge by using Automatic Bomb Calorimeter; Leco model AC-350 and using standard method following ASTM D240. Find heating value from combustion reaction of sample by using water as receiver of heating energy (Calculate heating value from the temperature of water that increased).

- Methodology

```
┌──────────┐     ┌──────────┐                              ┌─────────────────┐
│  Black   │ ──▶ │  Dry at  │ ───────────────────────────▶ │                 │
│  liquor  │     │  105°C   │                              │  Heating Value  │
└──────────┘     └──────────┘                              │  Analysis by using │
┌──────────┐     ┌──────────┐     ┌──────────┐             │  Bomb Calorimeter │
│  Sludge  │ ──▶ │  Dry at  │ ──▶ │ Grind by │ ──────────▶ │                 │
│          │     │  105°C   │     │ Grinder  │             │                 │
└──────────┘     └──────────┘     └──────────┘             └─────────────────┘
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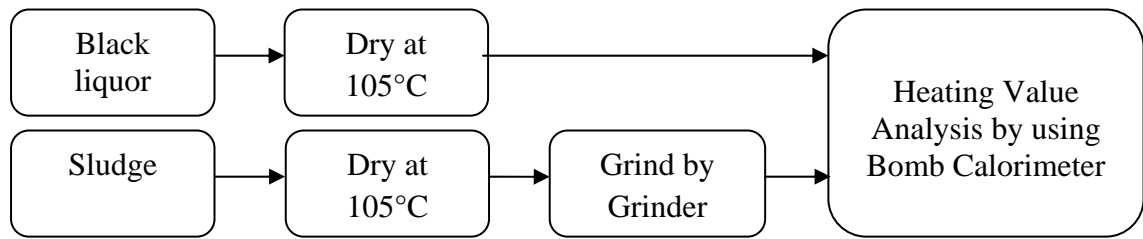
Figure 3.8 Flow chart of heating value analysis

3.5.3.4 Elemental analysis

- Analyze elemental composition of black liquor, sludge and char by using X-ray fluorescence spectrometer, XRF (Philips PW-2404, 4kW).

- Methodology

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┌────────────────────────────┐                 ┌─────────────────┐
│ Black liquor, Sludge, Char  │ ──────────────▶ │ Elemental Analysis │
│                            │                 │  by using XRF   │
└────────────────────────────┘                 └─────────────────┘
```
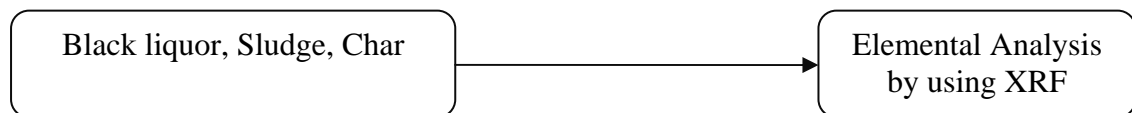
Figure 3.9 Flow chart of elemental analysis

3.5.4 Analyze the optimal condition of the reaction

3.5.4.1 Raw materials preparation

1. Dry sludge from wastewater treatment system to remove excess water.

2. Crush sludge by fine grinder.

3. Store sludge in close containers to protect it from moisture

4. Mix sludge with strong black liquor

5. Crush sludge that mixed with black liquor by fine grinder.

6. Select size of sludge that mixed with black liquor by using sieve (aperture size 2 mm, 10 mesh).

3.5.4.2 Preparation of gasification system

1. Input oxidizing gas and carrier gas (total flow depend upon temperature used) from bottom of reactor. Air to fuel ratio was set to 0.2. In this experiment Al_2O_3 was used as bed material.

2. Set reactor temperature at 700°C at atmosphere pressure. Waiting for temperature increased to 700°C.

3. Feed sludge that mixed with black liquor, the ratio of sludge that mixed with black liquor was 50:50, 5 g/min (every minute) into reactor by feeder.

4. Analyze gaseous products by using gases analyzer until the production of gases are stable (approximate 30 minute).

5. Measure gas flow rate by using gas flow meter.

6. Collect char and tar that residue from process for further analysis.

7. Repeat the experiment by changed temperature to 800 and 900°C.

8. Repeat the experiment by changed the ratio of pulp sludge that mixed with black liquor to 40:60.

9. Repeat the experiment by change air to fuel ratio into 0.4 and 0.6.

3.5.5 Examine the results to determine the highest yields conversion and the highest energy efficiency, discussion and draw conclusion from finding

The flow chart of the entire experimental procedure is shown in Figure 3.10
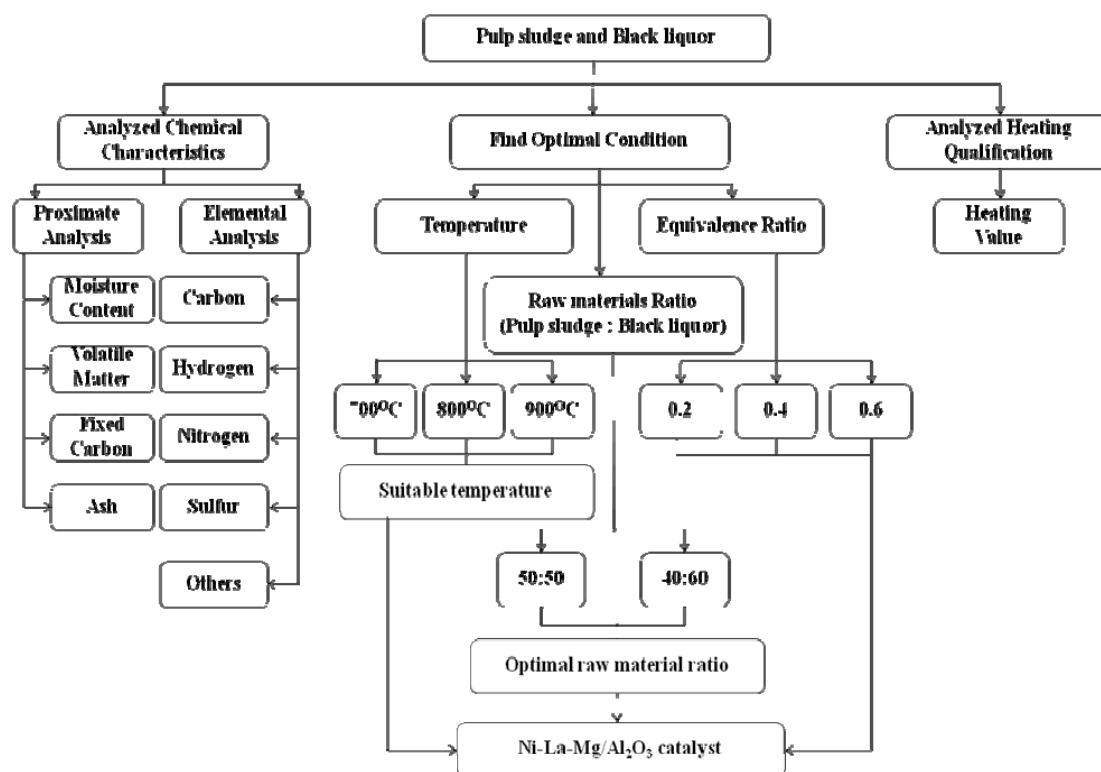
Figure 3.10 Flow chart of the entire experimental procedure

CHAPTER IV
RESULTS AND DISCUSSION

This research studied fuel gases such as CO, CO_2, H_2 and CH_4 from co-gasification process of pulp sludge that mixed black liquor in a fixed bed reactor. The variables in this study were the effect of temperature, equivalence ratio (ER), ratio of pulp sludge to black liquor. After that, the suitable conditions were chosen to add Ni-La-Mg/Al_2O_3 catalyst. These variables were examined to determine the optimal condition and the performance of catalyst on conversion process.

In this research, the optimal condition and the performance of catalyst on co-gasification to transform pulp sludge that is mixed with black liquor into valuable products were determined. It can be reported into 3 parts

Part 1   Study on the qualification of pulp sludge and black liquor

1) Proximate analysis of pulp sludge mixed with black liquor was performed following the standard method from International Standard Organization (ISO) to measure moisture content, volatile matter, fixed carbon and ash.

2) Ultimate analysis was analyzed to determine the percentage of carbon, hydrogen, nitrogen and sulfur of the sample by CHNS analysis and using Leco TruSpec® CHNS (micro) as analyzer.

3) Heating value analysis was performed by using Bomb calorimeter (Leco model AC-350) to determine the higher (gross) heating value of raw material following ASTM D240.

4) Elemental analysis was used to determine the elemental compositions of raw materials by using X-ray fluorescence technique.

Part 2   Study on the characteristics of Ni-La-Mg/Al_2O_3 catalyst

Part 3   Study on fuel products from co-gasification of pulp sludge mixed with black liquor. The effect of temperature, equivalence ratio, ratios of pulp sludge to black liquor and Ni-La-Mg/Al_2O_3 catalyst on products distribution, gas composition and quality, and energy efficiency were determined.

Part 4   Study on the qualification of char from co-gasification of pulp sludge mixed with black liquor.

4.1 The qualification analysis of pulp sludge and black liquor

Chemical compositions of pulp sludge and black liquor were examined by proximate analysis, ultimate analysis, heating value analysis and elemental analysis. The results were shown in Table 4.1- 4.6.

Table 4.1 Proximate analysis of pulp sludge and black liquor (Thermogravimetric analyzer, TGA)

Proximate Analysis	Pulp	Black	Pulp sludge : Black liquor	
(wt.%)	sludge	liquor	50 : 50	40 : 60
Moisture content	5.99	37.52	19.66	23.62
Volatile matter	58.93	45.16	67.04	59.68
Fixed carbon	30.87	16.05	12.64	16.16
Ash	4.21	1.27	0.66	0.54

From the results of proximate analysis, it was found that pulp sludge and black liquor have the composition of ash 4.21 and 1.27 percent by weight, respectively. The ash content in these raw materials is very small when compared with other biomass. This composition is inorganic substances such as $Na_2CO_3+Na_2S$ (smelt) in black liquor, which cannot be decomposed by combustion process. The compositions of moisture content, volatile matter and fixed carbon of pulp sludge and black liquor are 95.79 and 98.73 percent by weight, respectively. These compositions are organic substances, which can be degraded into gaseous products. Moisture can be released by chemical reactions during gasification process. The volatile matter mainly derived from cellulose and hemicelluloses, which can be converted to gaseous products in gasification process. The fixed carbon is the carbon that converted to char or other solid carbonaceous. This carbon was mainly derived from lignin in raw materials. The fixed carbon is difficult to vaporize unless at high temperature (Asadullah et al., 2007). From these results, the chemical compositions of pulp sludge and black liquor are mainly consists of organic substances, which can be converted to gaseous product. Thus, pulp sludge mixed with black liquor is suitable for co-gasification process.

Table 4.2 Ultimate analysis of pulp sludge and black liquor (CHNS/O analyzer)

Ultimate Analysis (wt.%)	Pulp sludge	Black liquor	Pulp sludge : Black liquor	
			50 : 50	40 : 60
Carbon	35.00	30.51	32.76	32.31
Hydrogen	4.65	4.48	4.57	4.55
Nitrogen	3.42	1.13	2.28	2.05
Sulfur	0.96	2.39	1.68	1.82

From the results of ultimate analysis, it was indicated that pulp sludge has carbon and hydrogen 35.00 and 4.65 percent by weight, respectively. Black liquor has carbon and hydrogen 30.51 and 4.48 percent by weight, respectively. Pulp sludge and black liquor have carbon and hydrogen as main compositions. Pulp sludge and black liquor can be converted these compositions into gaseous products that have carbon and hydrogen in their compositions. This result can be indicated that pulp sludge and black liquor are suitable for produce synthesis gas.

Table 4.3 Higher heating value of pulp sludge and black liquor (Bomb calorimeter)

Sample	Higher heating value (HHV), MJ/kg
Pulp sludge	13.87
Black liquor	13.07
Pulp sludge : Black liquor of 50 : 50	13.47
Pulp sludge : Black liquor of 40 : 60	13.39

From the results of heating value analysis, pulp sludge and black liquor have higher heating value close to others biomass that used as raw material for gasification process in the present (Table 4.4). The heating values of these materials are very interesting for further study about energy production. Because of this reason, pulp sludge and black liquor are proper for use as fuels in gasification process.

Higher heating value is the heating that not including heat of vaporization. Higher heating value can be transformed into lower heating value that including heat of vaporization by using equation (4.1) or (4.2).

Higher heating value = Lower heating value + (5.72 ✕ (9H + M)) kcal/kg   (4.1)

= Lower heating value + (23.95 ✕ (9H + M)) kJ/kg   (4.2)

*Remark   H is a percentage of hydrogen in biomass

M is a percentage of moisture content in biomass

From equation (4.1) or (4.2), the results the lower heating value (from calculation) were illustrated in Table 4.4

Table 4.4 Lower heating value of raw material (Calculate)

Sample	Lower heating value (LHV), MJ/kg
Pulp sludge	12.75
Black liquor	11.98
Pulp sludge : Black liquor of 50 : 50	11.89
Pulp sludge : Black liquor of 40 : 60	11.69

The higher heating value (HHV) is the maximum amount of energy that can be obtained from combusting the fuel (water is produced as liquid) and this HHV is necessary to calculate the gasifier efficiency. However, mostly the water escape to the atmosphere as a gas, and the heat of evaporation of the water is not recovered. The amount of energy released in this case (water as vapor) is referred to as the lower heating value (LHV). In gasification process, the water vapor is condensed and the heat of vaporization recovered, therefore the efficiency can be over 100% when fuels are rated on HHV value (Knoef, 2005). Thus, LHV is better than HHV for calculate energy efficiency in gasification process.

Table 4.5 Chemical compositions of pulp sludge and black liquor compared with others biomass (Energy for Environment, http://ete.or.th)

Biomass	Proximate analysis (wt.%)					Ultimate analysis (wt.%)					Heating value analysis (MJ/kg)	
	Moisture content	Volatile matter	Fixed carbon	Ash	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen	HHV	LHV
Pulp sludge	**5.99**	**58.93**	**30.87**	**4.21**	**35.00**	**4.65**	**3.42**	**0.96**	**-**	**13.87**	**12.75**
Black liquor	**37.52**	**45.16**	**16.05**	**1.27**	**30.51**	**4.48**	**1.13**	**2.39**	**-**	**13.07**	**11.98**
Cassava rhizome	59.40	31.00	8.10	1.50	18.76	2.48	0.32	0.04	17.50	7.45	5.49
Eucalyptus bark	60.00	28.00	9.56	2.44	18.60	2.12	0.15	0.02	16.68	6.81	4.97
Palm fiber	38.50	42.68	14.39	4.42	30.82	3.74	0.84	0.08	21.61	13.13	11.40
Corncob	40.00	45.42	13.68	0.90	28.19	3.36	0.12	0.03	27.42	11.30	9.62
Rice husk[**]	6.65	60.90	13.34	19.11	38.00	4.73	0.37	0.09	50.20	13.23	12.05
Rice straw[**]	6.71	58.64	11.09	23.55	44.40	5.00	0.60	0.10	30.80	11.54	10.30

*Garivait, 2006

Table 4.6 Elemental analysis of pulp sludge and black liquor (X-ray fluorescence technique)

| Raw material	Black liquor	Sludge
Na	25.84	0.29
Cl	3.77	0.43
K	20.23	0.31
Ca	0.26	7.07

Data from Table 4.6 showed that black liquor contains a lot of sodium and potassium. These two elements can cause serious operating problems because chloride (Cl^-) and potassium (K^+) ions tend to combine with sodium ion (Na^+) to form a salt. This salt can build up on the wall of equipment, plugging and corroding them (especially, scaling of downstream heat exchangers) (Cardoso et al., 2009). For pulp sludge, it contains a lot of silica and calcium. Calcium is the most abundant mineral that found in wood. It was used as raw material in pulping process. Furthermore, a large quantity of calcium is added in the pulping and bleaching processes (McGovern et al., 1983). From these reason, pulp sludge contains a lot of calcium.

4.2 The characteristics of Ni-La-Mg/Al$_2$O$_3$ catalyst

This catalyst was prepared by loading of nickel, lanthanum and magnesium 10 wt.%, 5 wt.% and 5 wt.%, respectively. The surface area of Ni-La-Mg/Al$_2$O$_3$ catalyst measured by Brunauer–Emmett–Teller (BET) method is 7.74 m^2/g. This surface area is little because surface area of Al$_2$O$_3$ supported is small (7.39 m^2/g). However, this surface area is high when compared with Garcia et al. (2000) reported. They prepared by impregnation method and calcination at same temperature. Their surface area of catalysts are around 2.7-4.9 m^2/g.

Figure 4.1 showed SEM analysis of catalyst. From this image found that this catalyst has irregular shape and small particle size less than 1 μm like loose powder. It could not be observed metal loading on support by this analysis method. The X-ray elemental analysis was also used to identify the amount of elemental compositions approximately. This method found that the catalyst consisted

of nickel, lanthanum and magnesium about 12.57 wt.%, 4.36 wt.% and 7.21 wt.%, respectively.
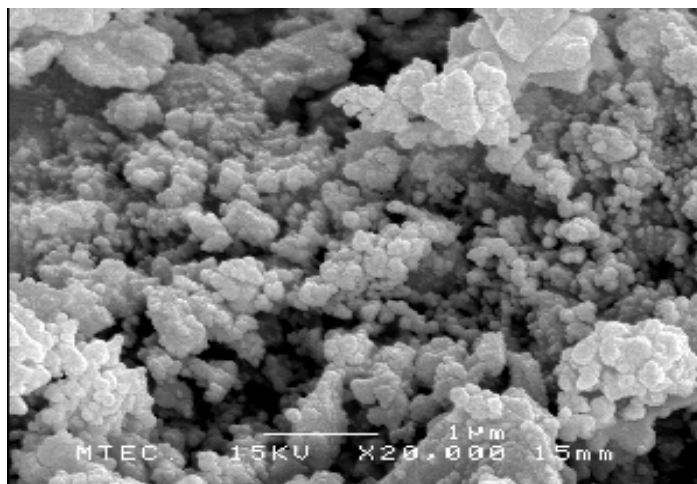
Figure 4.1 SEM analysis of 10Ni5La$_2$O$_3$5MgO/Al$_2$O$_3$ after reduction.

The catalyst sample patterns showed diffraction lines of Al$_2$O$_3$, La(AlO$_3$), MgO, Ni and NiO (Figure 4.2). The Al$_2$O$_3$ Corundum found three major peaks at about 35°, 43° and 57° for 2θ. Furthermore, it found peaks at about 26°, 38°, 52°, 66° and 68° for 2θ. The XRD of catalyst found that this catalyst mainly consists of Al$_2$O$_3$ that used as catalyst support. The peak of Ni was indicated at about 44° for 2θ, whereas the signal of phase NiO was observed at about 37° and 43° for 2θ. The peaks assigned to MgO appeared at about 42° and 62°. Peaks of La(AlO$_3$) placed at about 23° and 33°. For La(AlO$_3$) patterns may be due to the interaction between the basic properties of La$_2$O$_3$ promoter and the acidic hydroxyl groups of alumina support. This compound phase indicated stronger degree of interactions between alumina support and promoter. It might contribute to improve the stability of the catalyst.
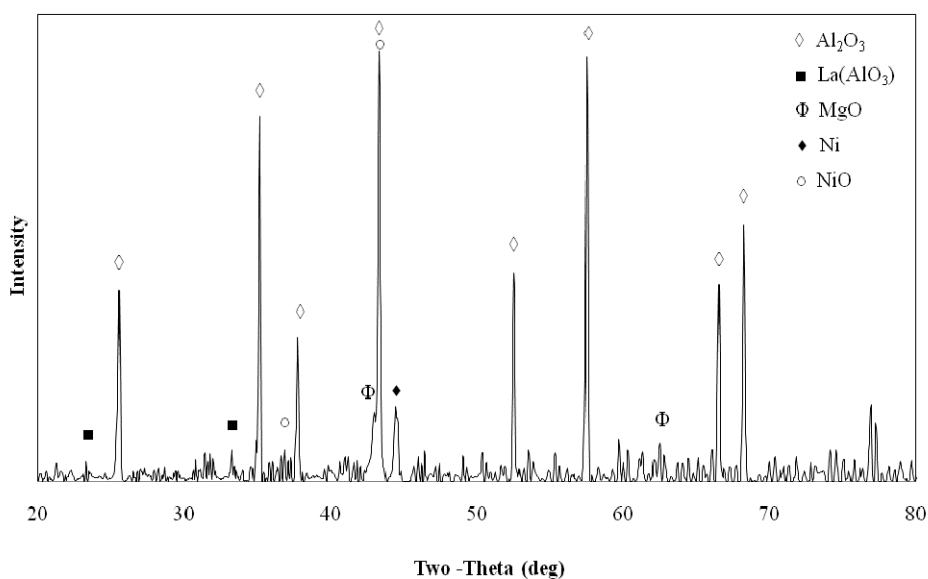
Figure 4.2 X-ray patterns of catalysts calcined at 850°C. (◊) Al_2O_3, (■) $La(AlO_3)$, (Φ) MgO, (♦) Ni and (○) NiO

4.3 Co-gasification process of pulp sludge mixed with black liquor

In this research, co-gasification process of pulp sludge mixed black liquor was carried out in a fixed bed reactor using alumina balls as supporting material and feeding rate of 5 g/min. During each run, reaction temperature increased with heating rate of 10°C/min. Thermocouple in temperature controller was used to measure and control temperature during the experiment. The reaction time was approximately 30 minute and stable operation could be obtained with in 5 minute after start feeding raw material by observing steady gas production. Major gaseous products such as CO, CO_2, H_2 and CH_4 were analyzed. Solid and liquid yields were calculated by measured weight (Figure 4.3).

This part was seperated into non catalytic and catalytic cases. The effect of temperature, equivalence ratio, ratio of pulp sludge to black liquor and Ni-La-Mg/Al_2O_3 catalyst was studied.
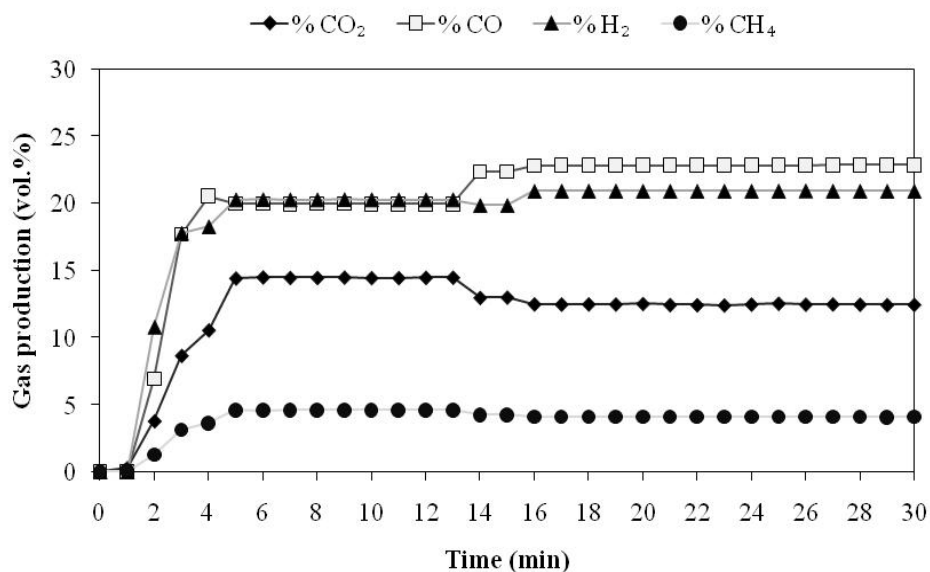
Figure 4.3 Typical gas distribution during co-gasification of pulp sludge mixed with black liquor.

4.3.1 Effect of temperature, equivalence ratio and ratio of raw material on product distribution

In this research, the effect of temperature, equivalence ratio and ratio of raw material on product distribution, carbon conversion, hydrogen conversion and the ratio between H_2 to CO at different conditions was studied. The conditions are temperature of 700, 800 and 900°C, equivalence ratio of 0.2, 0.4 and 0.6, and ratio of pulp sludge mixed with black liquor of 50:50 and 40:50.

Generally, complete gasification is achieved and reduction of carbon dioxide to carbon monoxide is occurred at temperature above 500°C (Kirubakaran et al., 2007). This experiment start the operating temperature at 700°C because the melting point of inorganic salts in black liquor (about 30 wt.%) is around 700-750°C (Backman et al., 1993). For operating temperature was used at 900°C because the volatilization of sodium in black liquor and the influence of gas composition such as CO increased rapidly when increasing temperature from 800°C to 900°C (Backman et al., 1993 and Sricharoenchaikul et al., 2002). Furthermore, Hammond (2002) who studied gasification of black liquor with addition of secondary sludge also varies temperature of 700 and 900°C. The equivalence ratio is defined as the air-to-fuel weight ratio used divided by the air-to-fuel weight ratio of stoichiometric combustion (Narváez et al.,

1996). Normally, raw material (especially biomass) is converted into gas giving the highest energy density of gas at equivalence ratio of 0.25 (Knoef, 2005). From this reason, this experiment vary equivalence ratio from 0.2 to 0.6.

Solid yield from co-gasification process is collected in the reactor and collector under cyclone. Solid residue from the process is collected for further analysis and calculated by measure weight. Liquid yield is tar mixed with water from raw material. This mixed waste produces a lot of liquid more than others biomass because black liquor contains a lot of water. Liquid yield from the process is collected from collectors under condensers and calculated by measure weight. For gas yield was calculated by difference (total is 100 wt.%). Percentage of carbon and hydrogen conversion are calculated from percentage of CO, CO_2, H_2 and C_xH_y (as CH_4) at time that stable yields (see calculate in Appendix B).

Product yields from co-gasification of mixed wastes vary greatly depend on operating conditions. The results indicated that product yields improved with higher reaction temperature and lower equivalence ratio. Product yields from the ratio of pulp sludge mixed with black liquor of 40:60 are higher than 50:50 (Figure 4.4a and 4.4b).

At higher temperature, gas yields increased while solid and liquid yields decreased. Increasing temperature results in more volatile matter released from biomass particle. Furthermore, char could change to gas products at higher temperature due to Boudouard and primary water-gas reaction, equation (4.3) and (4.4) (Ioannidou et al., 2009). Greater temperature, weight loss of solid yield (char) may also come from the reactions that occur within the char after devolatilization is complete (temperature above 200°C). These reactions can reduce sulfate and carbonate in raw material and form CO and CO_2, equation (4.12), (4.13), (4.14) and (4.15) (Sricharoenchaikul et al., 2003). Also, tar can be cracked and reformed at greater temperature owing to tar cracking reaction, equation (4.16) (Lapuerta et al., 2008 and Narváez et al., 1996). These results are similar to reported of Chen et al. (2003) who studied the effect of reactor temperature (500°C to 950°C) on biomass pyrolysis/gasification for product gas production. This studied reported that higher temperature leads to greater gas yield and lower solid and liquid yield. When temperature enlarged from 800 to 900°C, products distribution of two material ratios are very close to 900°C, so it should be considered that co-gasification of pulp sludge

mixed with black liquor at 800°C is better than 900°C. Temperature of 800°C is better than 900°C because it use less energy than 900°C and distributes same percentage of products.
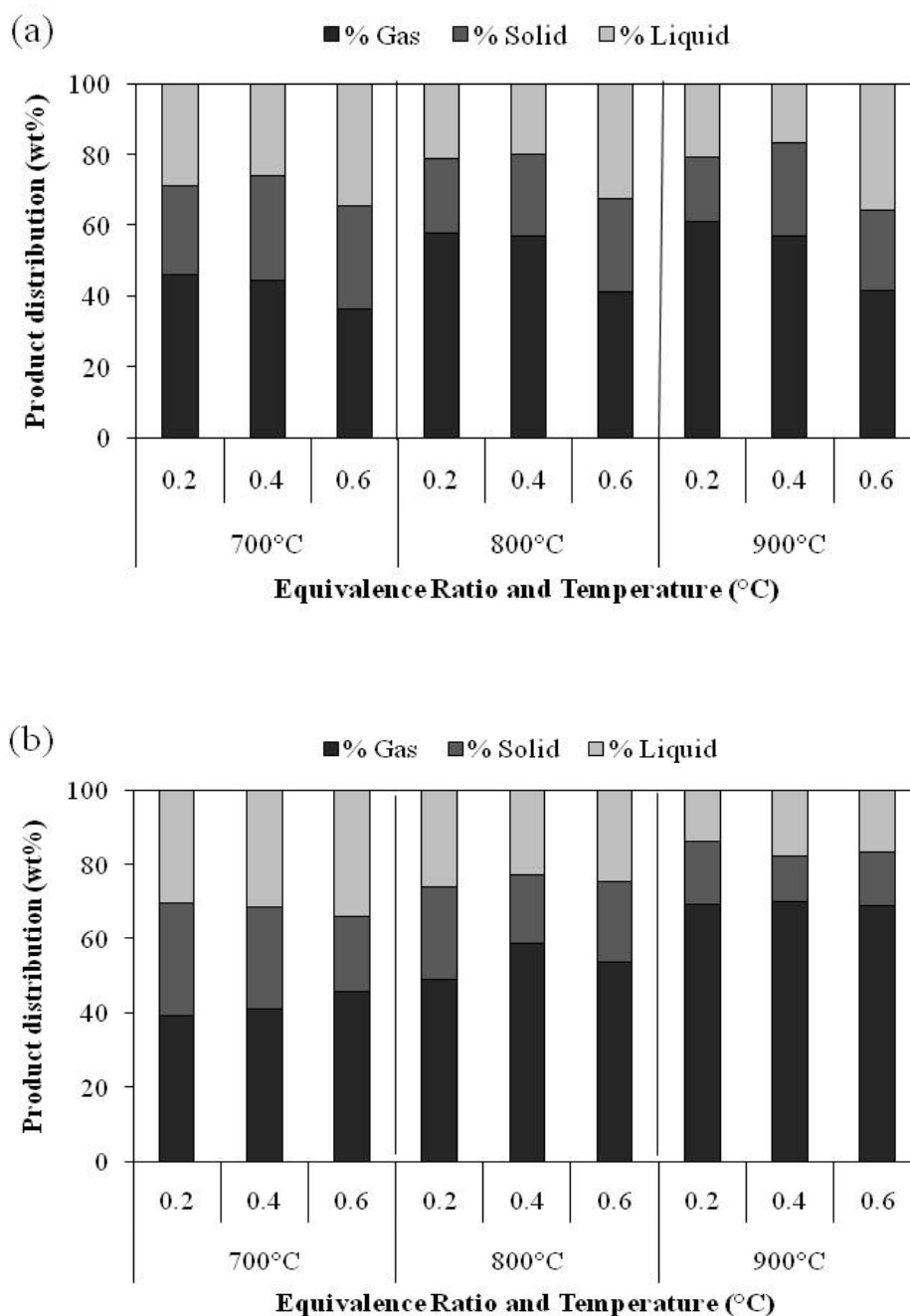
Figure 4.4 Product yields for (a) the ratio of pulp sludge mixed with black liquor of 50:50 (b) the ratio of pulp sludge mixed with black liquor of 40:60
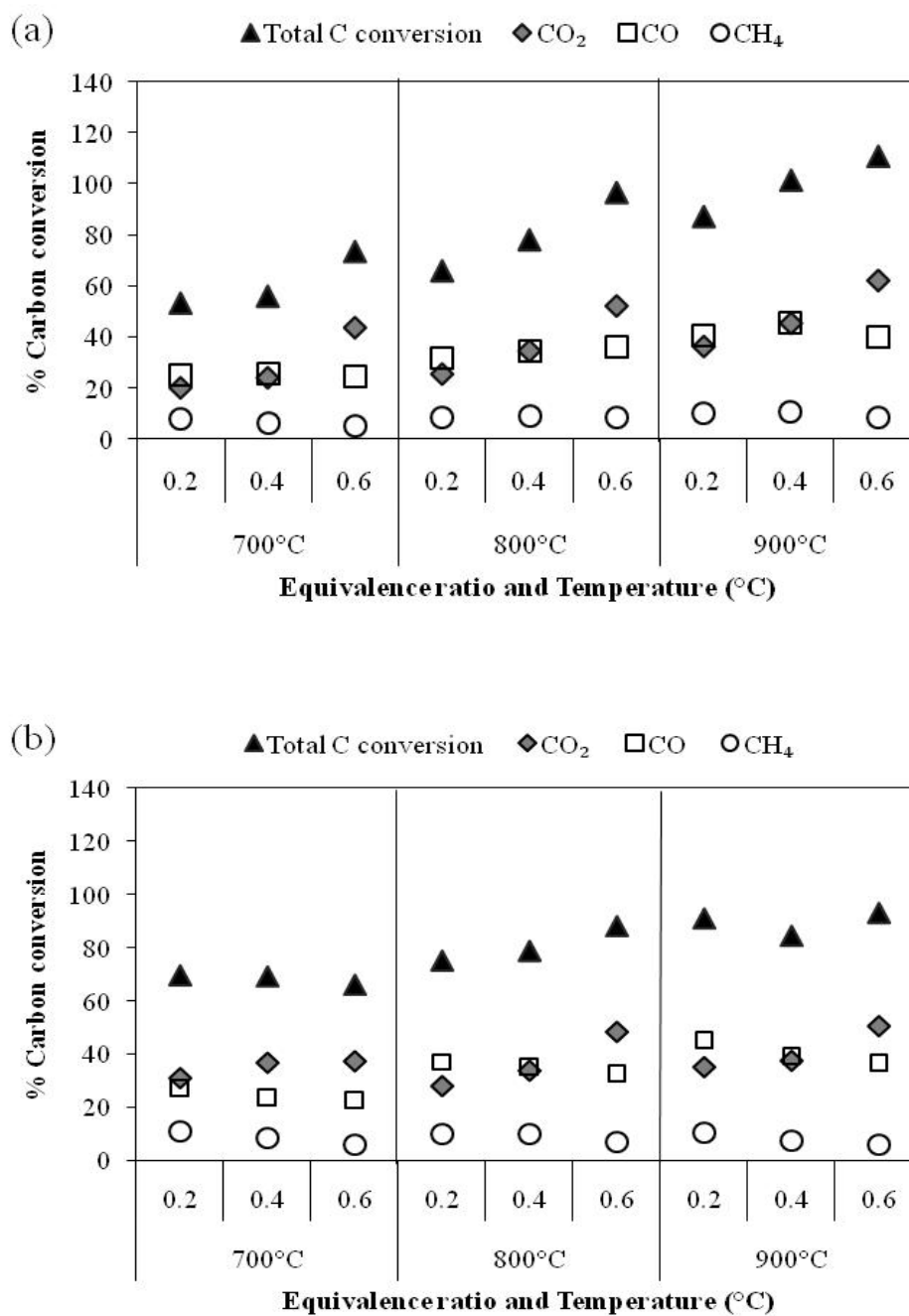
Figure 4.5 Carbon conversions for (a) the ratio of pulp sludge mixed with black liquor of 50:50 (b) the ratio of pulp sludge mixed with black liquor of 40:60

Figure 4.6 Hydrogen conversions for (a) the ratio of pulp sludge mixed with black liquor of 50:50 (b) the ratio of pulp sludge mixed with black liquor of 40:60
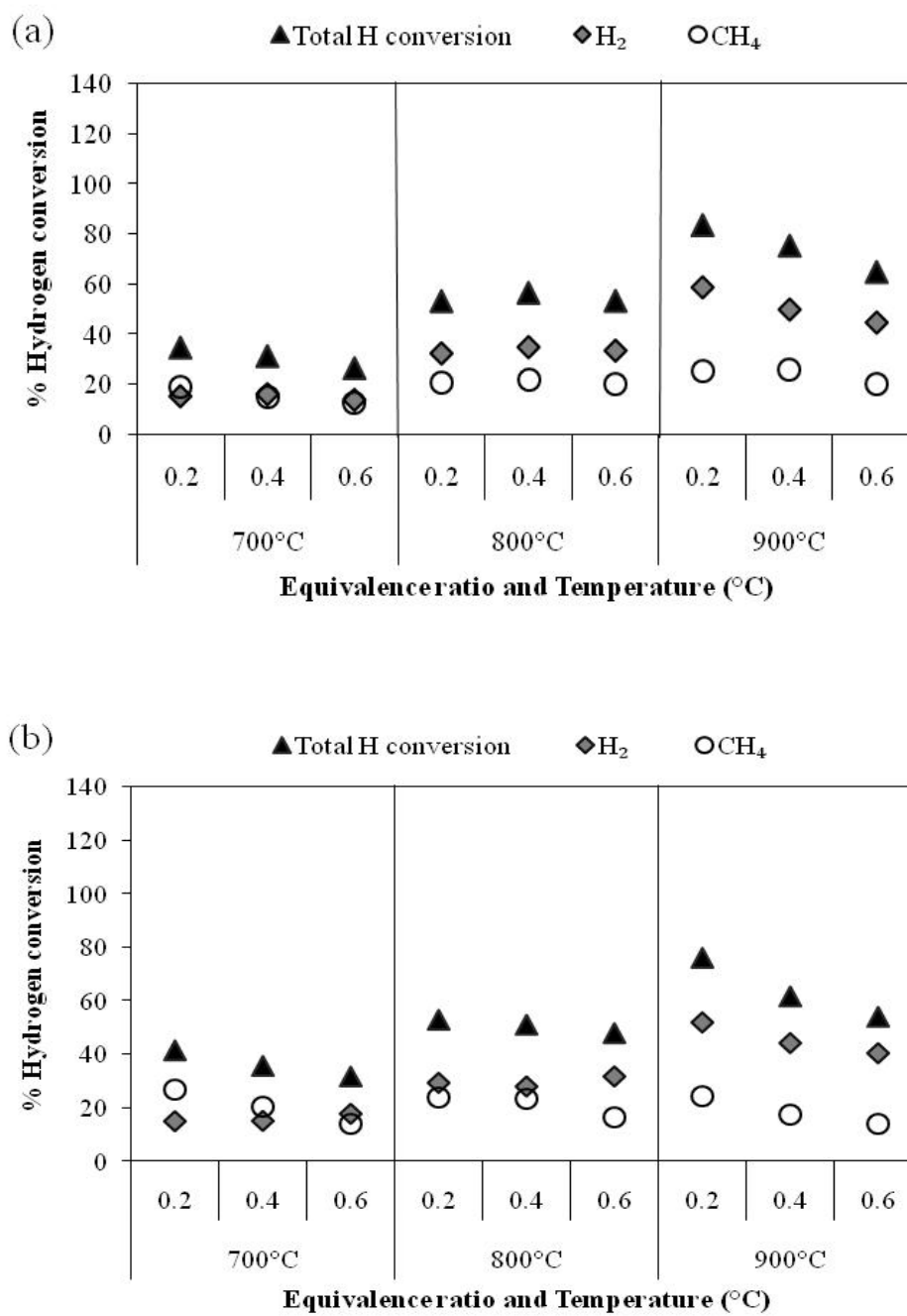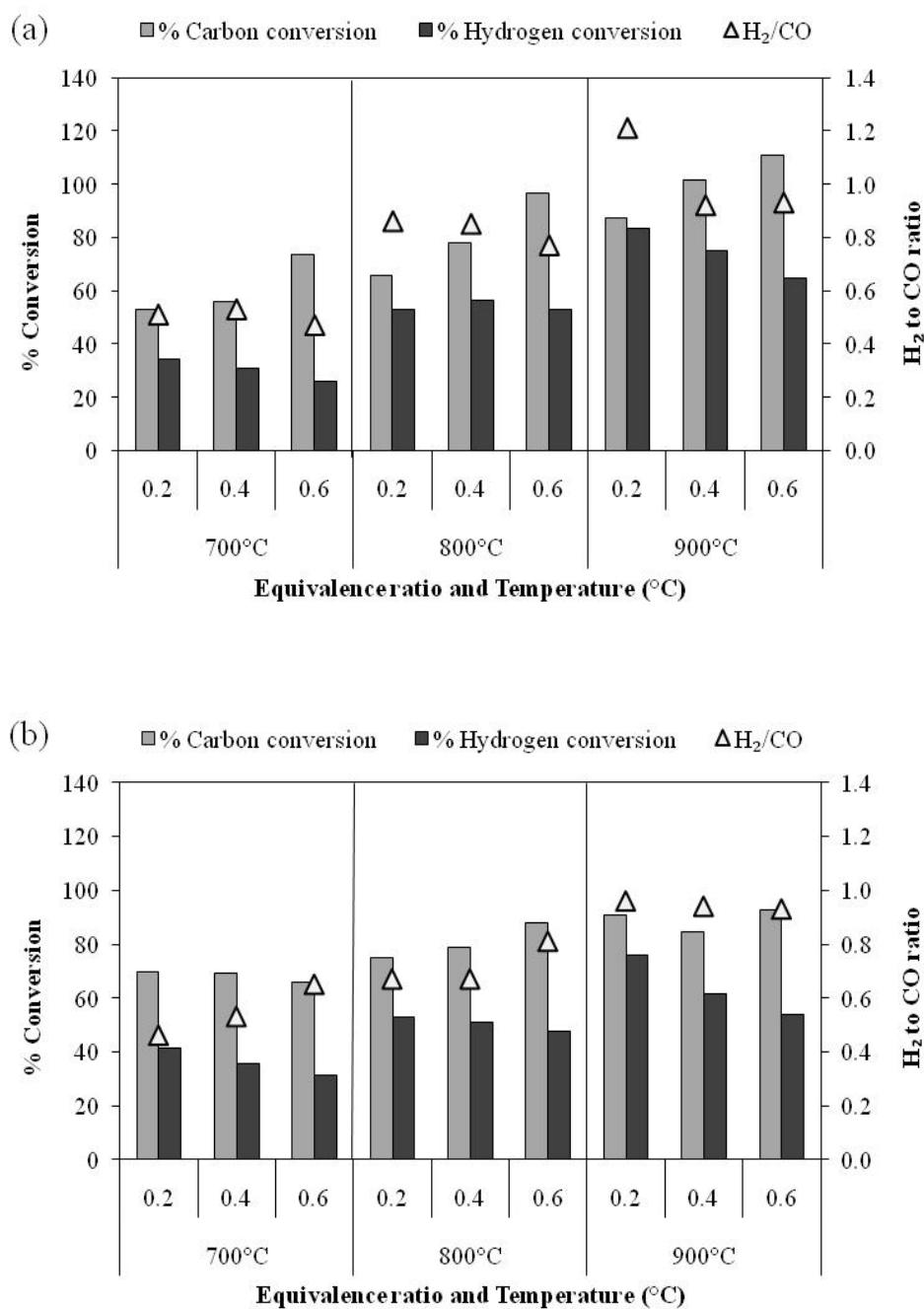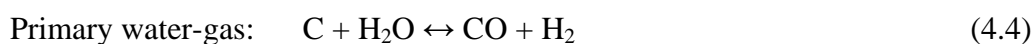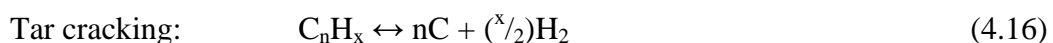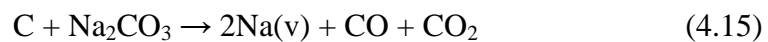
Figure 4.7 Conversions and H_2 to CO ratio of gas products (a) the ratio of pulp sludge mixed with black liquor of 50:50 (b) the ratio of pulp sludge mixed with black liquor of 40:60

On the effect of equivalence ratio on product yields of raw material ratio of 50:50, gas yields decreased with increasing equivalence ratio because more oxygen is available in the system. Thus, primary water-gas, secondary water-gas and water-gas shift reaction, equations (4.4), (4.5) and (4.6), reverse to produce less gas yield but more liquid yield at raising equivalence ratio. Moreover, hydrogen in raw material also reacts with oxygen fed to produce more liquid yield with combustion reaction, equation (4.9) and (4.10). The trend of solid yield is not notable. For the effect of equivalence ratio on product yields of pulp sludge mixed with black liquor of 40:60, gas yield and liquid yield increased when increasing equivalence ratio from 0.2 to 0.6. On the contrary, solid yield is less producing. Solid yield decreased when increased equivalence ratio because char cracking reaction, equation (4.11).

On the influence of raw material ratios on product yields, it was found that product yields improved when raw material ratio was changed from 50:50 to 40:60. At lower temperature, product yields of raw material ratio of 50:50 are very closed to 40:60. Thus, it can be concluded that raw material ratio have no influence on product yields at lower temperature. At higher temperature, the results indicated that product yields of raw material ratio at 50:50 are different from raw material ratio at 40:60. The data at 900°C indicated that gas yield of raw material ratio of 50:50 are lower than 40:60. Although sludge contains a lot of volatile matter than black liquor, black liquor contains Na and K like catalyst, and some lignin, multi-sugars and other organic matter being gasified easily (Jaffri and Zhang, 2008). Thus, raw materials ratio that contains more black liquor can converts to gaseous products than raw materials ratio that contains more sludge. Solid yield of raw material ratio of 50:50 is higher than 40:60 because it has more ash content. The trend of liquid yield is not clearly defined. From the results, products yields are correspond to raw material ratio, and raw material ratio of 40:60 suitable for equivalence ratio of 0.6 while raw material ratio of 50:50 proper for equivalence ratio of 0.2. The suitable equivalence ratio is selected from the ratio which produces the highest gas yield.

Boudouard: $\qquad$ $C + CO_2 \leftrightarrow 2CO$ $\qquad$ (4.3)

Primary water-gas: $\quad$ $C + H_2O \leftrightarrow CO + H_2$ $\qquad$ (4.4)

Secondary water-gas: $C + 2H_2O \leftrightarrow CO_2 + 2H_2$ (4.5)

Water-gas shift: $CO + H_2O \leftrightarrow CO_2 + H_2$ (4.6)

Methanation: $C + 2H_2 \leftrightarrow CH_4$ (4.7)

Combustion: $C + O_2 \rightarrow CO_2$ (4.8)

$4H + O_2 \rightarrow 2H_2O$ (4.9)

$C_nH_m + (^n/_2 + {}^m/_4)O_2 \rightarrow nCO_2 + {}^m/_2H_2O$ (4.10)

Char cracking: $Char \rightarrow CO + CO_2 + H_2 + solid\ residual$ (4.11)

$2C + Na_2SO_4 \rightarrow Na_2S + 2CO_2$ (4.12)

$4C + Na_2SO_4 \rightarrow Na_2S + 4CO$ (4.13)

$2C + Na_2CO_3 \rightarrow 2Na(v) + 3CO$ (4.14)

$C + Na_2CO_3 \rightarrow 2Na(v) + CO + CO_2$ (4.15)

Tar cracking: $C_nH_x \leftrightarrow nC + (^x/_2)H_2$ (4.16)

The gas compositions in this experiment were analyzed by online gas analyzer. Greater reaction temperature results in higher carbon and hydrogen conversions (Figure 4.5a, 4.5b, 4.6a, 4.6b, 4.7a and 4.7b).

At higher temperature, CO, CO_2 and H_2 formation increased due to Boudouard, primary water-gas and secondary water-gas reactions, equation (4.3), (4.4) and (4.5). These reactions are endothermic reactions, so the equilibrium forward to the right side at higher temperature. Moreover, water-gas shift, methanation reactions also reverse to form CO and H_2, equation (4.6) and (4.7). These reactions are exothermic reactions, thus the equilibrium reverse to the left side when temperature increased. These results

are in similar direction with reported of Wang and Kinoshita (1992) and Lapuerta et al. (2008). Wang and Kinoshita (1992) studied the effect of temperature on biomass gasification with steam and oxygen. In the reported indicated that increasing temperature from 700°C to 900°C results in carbon conversion efficiency increased due to polyatomic hydrocarbons convert into diatomic species such as CO and H_2. Lapuerta et al. (2008) observed that higher reaction temperature caused fuel production from biomass wastes increased. For synthesis gas ratio, the ratio between H_2 and CO also increased with temperature. The results indicated that at 900°C the ratio between H_2 to CO are very close to 1, so further applications of these gases to produce methanol and others synthesis fuels by Fischer-Tropsch reaction are possible. H_2 and CO are the major components of synthesis gas. These gases are basic building blocks of a number of others products such as chemicals and fertilizers (Gasification Technology Council, 2008). Fischer-Tropsch processes can be used to produce either a light synthetic crude oil (syncrude) and light olefin or heavy waxy hydrocarbons. Furthermore, the syncrude can be refined to environmentally friendly gasoline and diesel fuel (Knoef, 2005).

Different equivalence ratio has different effect on carbon conversion, hydrogen conversion and H_2/CO. From the results indicated that increasing equivalence ratio from 0.2 to 0.6 leads to higher carbon conversion and lower hydrogen conversion (Figure 4.7a and 4.7b). In these experiments, H_2 and CH_4 decreased, CO gradually decreased while CO_2 increased, equation (4.8) and (4.10). These results are in agreement with Xiao et al. (2007) who studied the effect of equivalence ratio on product yields distribution and gas compositions of air gasification of polypropylene plastic waste in fluidized bed gasifier. They reported that increasing equivalence ratio enhances partial combustion of various gaseous components which increase in CO_2. On the other hand, CO and H_2 decreased with raising equivalence ratio, and CH_4 also decrease gradually. The ratio between H_2 and CO is depends on carbon and hydrogen conversion. It depends on carbon conversion of CO and hydrogen conversion of H_2. Thus, the ratio between H_2 and CO of raw material ratio of 50:50 decreased with increasing equivalence ratio. In contrast, the ratio between H_2 and CO of pulp sludge mixed with black liquor of 40:60 increased when raising equivalence ratio.

From data indicated that changing raw material ratio from 50:50 to 40:60 results in lower carbon and hydrogen conversion. At lower temperature, carbon and

hydrogen conversions are not too difference, however carbon and hydrogen conversions are more difference at higher temperature. The data from ultimate analysis of pulp sludge and black liquor indicated that pulp sludge has percentage of carbon and hydrogen more than black liquor. From this reason, raw material ratio which have higher percentage of pulp sludge produce greater carbon and hydrogen conversion. For the effect of raw material ratio on the ratio between H_2 and CO, the results showed that the ratio between H_2 and CO of raw material ratio of 50:50 is higher than raw material ratio of 40:60. The condition showed that the highest ratio between H_2 and CO is raw material ratio of 50:50, 900°C and equivalence ratio of 0.2. This ratio is 1.21.

4.3.2 Effect of Ni-La-Mg/Al_2O_3 catalyst on product distribution

This research was studied the effect of Ni-La-Mg/Al_2O_3 catalyst on carbon conversion, hydrogen conversion, H_2/CO, product distribution and energy efficiency. The effects of catalytic cases were compared with non-catalytic cases. The conditions are feedstock of 50:50 and 40:60, temperature of 700 and 800°C, and equivalence ratio of 0.2, 0.4 and 0.6.

Addition of catalysts in biomass gasification is very common in order to reduce tar and use along with gasification temperature around 700-750°C (Martínez et al., 2003).

In this research, catalyst was mixed with raw materials at 20 wt.% before feeding into system. Ni was used as catalyst because of the metal availability and economic consideration (Djaidja et al., 2006). It is the most commonly used for steam reforming as well as alumina has work well for support Ni for steam reforming (Djaidja et al., 2006; Garcia et al.,2000; García et al., 2001; Martínez et al., 2002; Miyazawa et al., 2006; Li et al., 2009; Yung et al., 2009). Lantanum oxide was added as promoter for provided high conversions for reforming reactions and good resistance to deactivation by carbon decomposition. Magnesium oxide was also added as promoter for enhances steam adsorption capability and prevent catalyst sintering (Garcia et al., 2000).

Calcinations temperature leads to the catalyst activity of the derived catalyst (Wu and Williams, 2009). In this experiment, the catalyst was calcined at 850°C under air atmosphere and was reduced at 700°C for 2 hours. This experiment using a similar

method to Garcia et al. (2000) who also calcined Ni/MgO-Al$_2$O$_3$ and Ni/MgO-La$_2$O$_3$-Al$_2$O$_3$ catalysts at 850°C for 2 hours and reduced at 700°C for 2 hours.
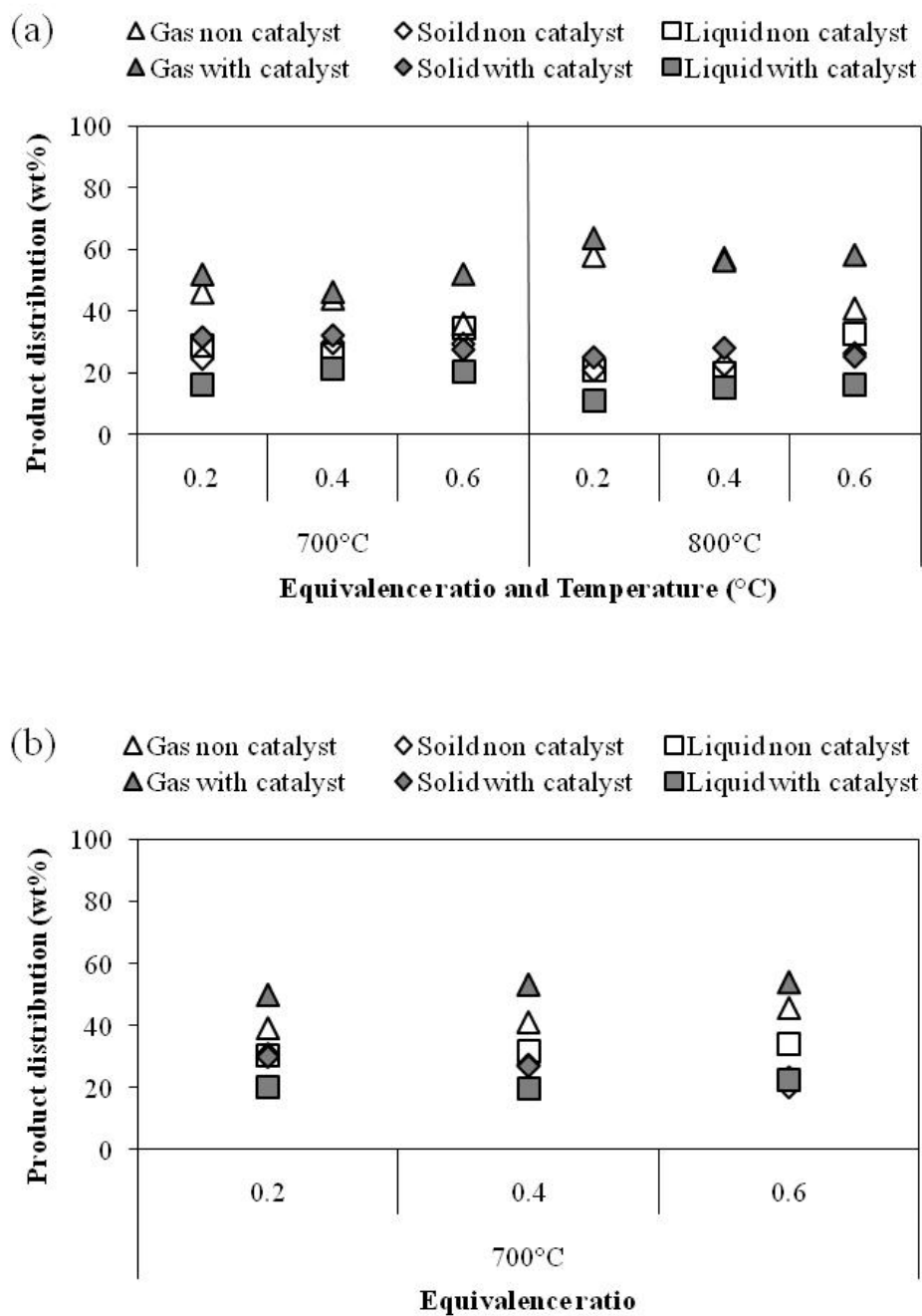
Figure 4.8 Product yields for (a) the ratio of pulp sludge mixed with black liquor of 50:50 with catalyst (b) the ratio of pulp sludge mixed with black liquor of 40:60 with catalyst
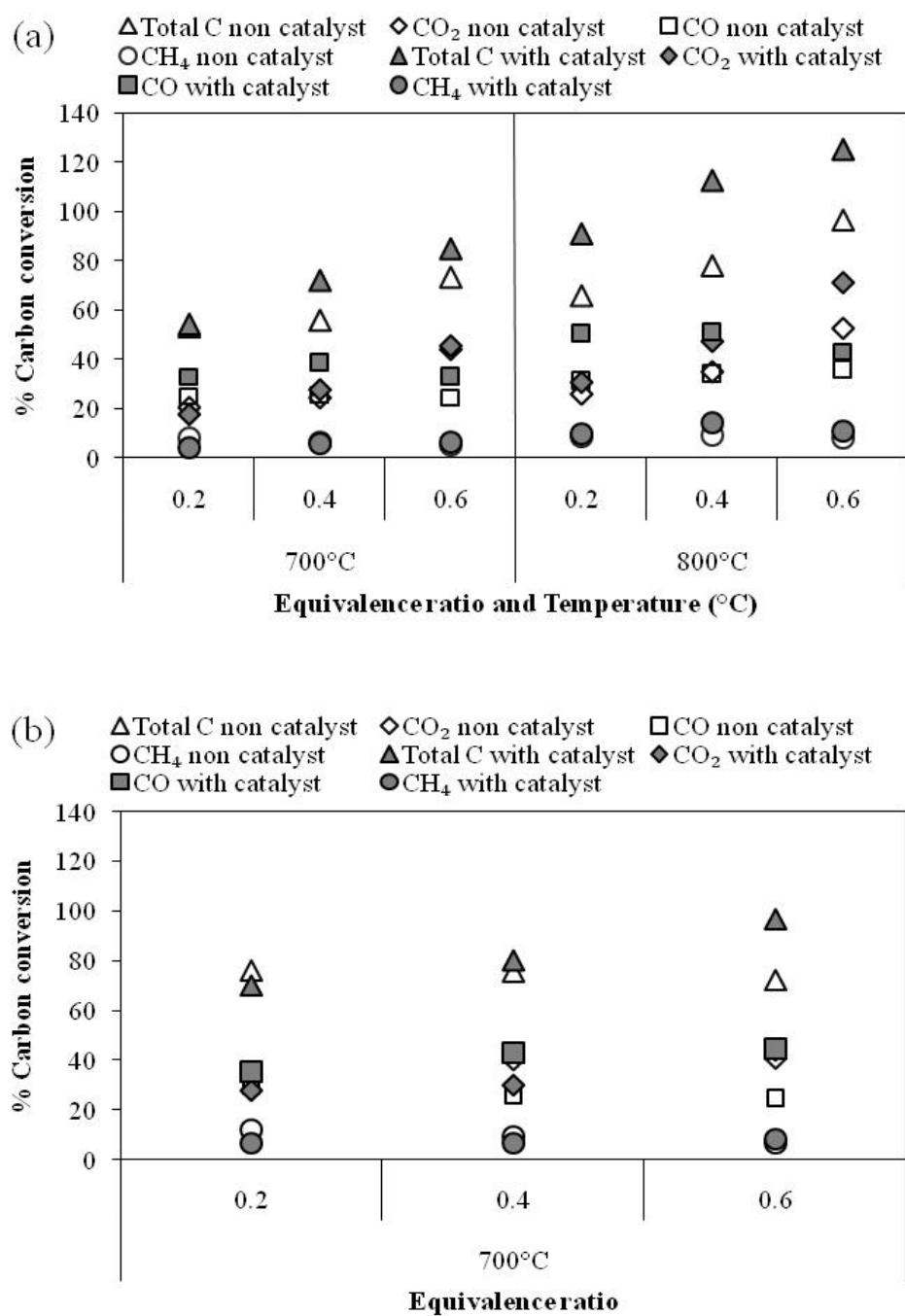
Figure 4.9 Carbon conversions for (a) the ratio of pulp sludge mixed with black liquor of 50:50 with catalyst (b) the ratio of pulp sludge mixed with black liquor of 40:60 with catalyst

Figure 4.10 Hydrogen conversions for (a) the ratio of pulp sludge mixed with black liquor of 50:50 with catalyst (b) the ratio of pulp sludge mixed with black liquor of 40:60 with catalyst
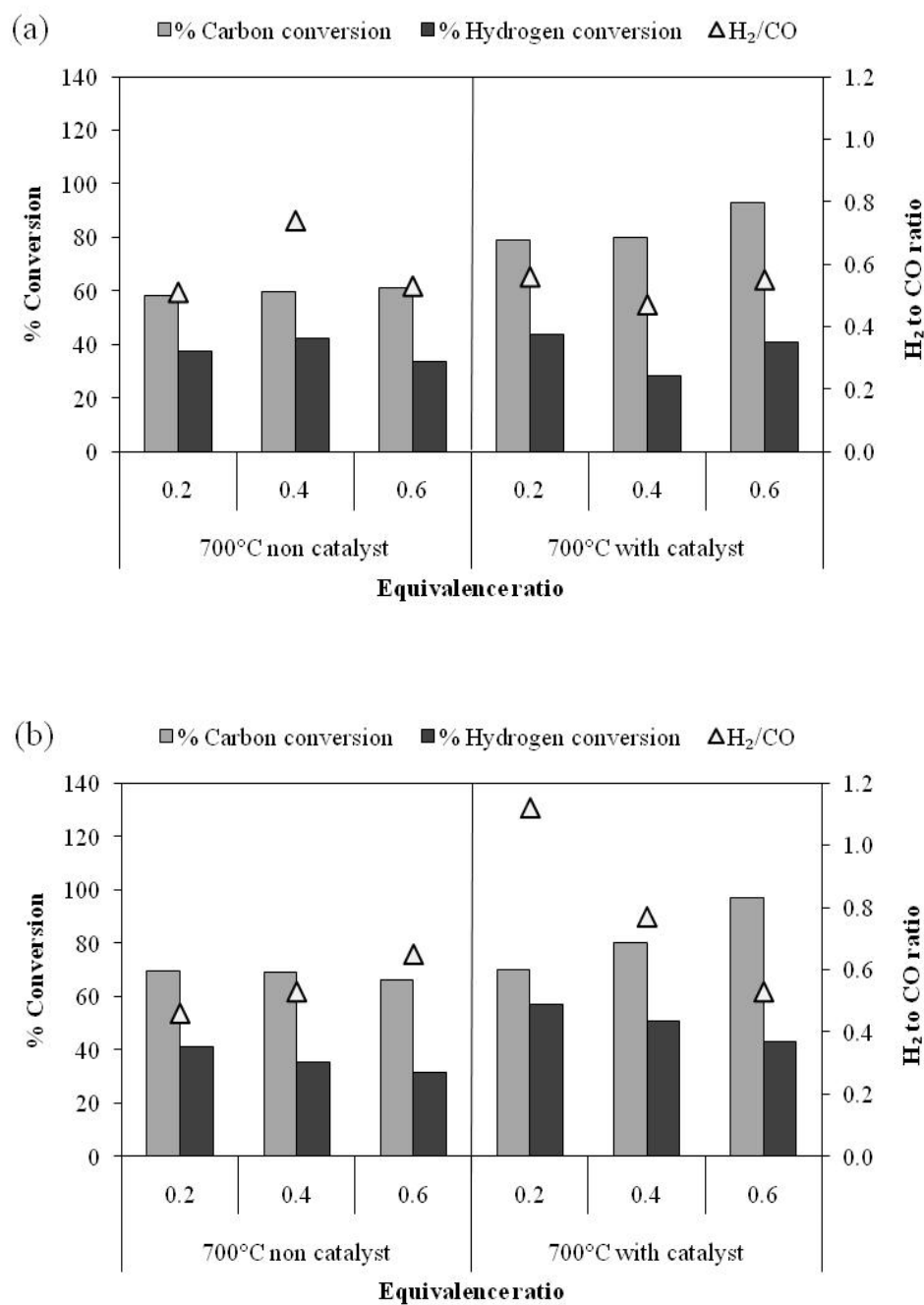
Figure 4.11 Conversions and H_2 to CO ratio of gas products (a) the ratio of pulp sludge mixed with black liquor of 50:50 with catalyst at 700°C (b) the ratio of pulp sludge mixed with black liquor of 40:60 at 700°C
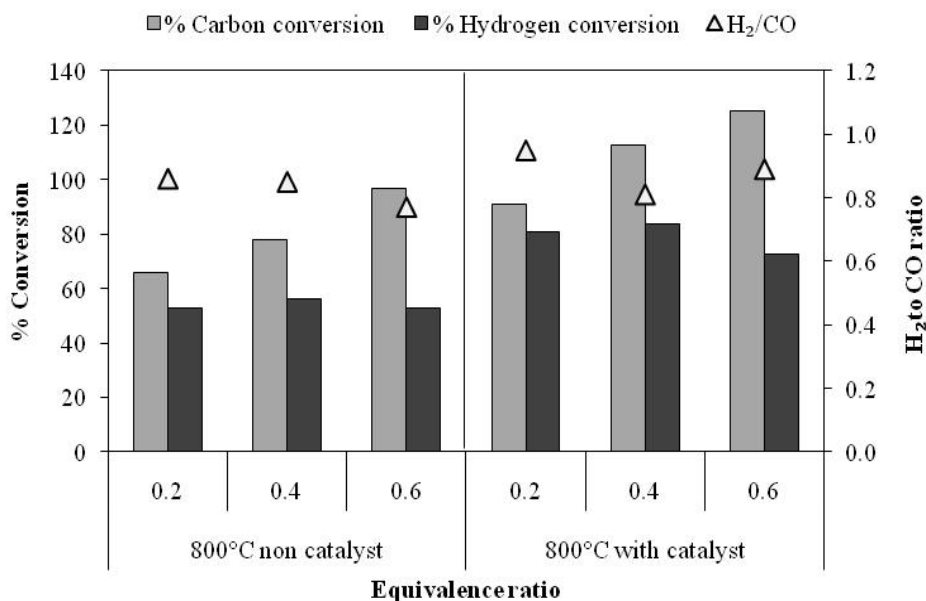
Figure 4.12 Conversions and H_2 to CO ratio of gas products of the ratio of pulp sludge mixed with black liquor of 50:50 with catalyst at 800°C

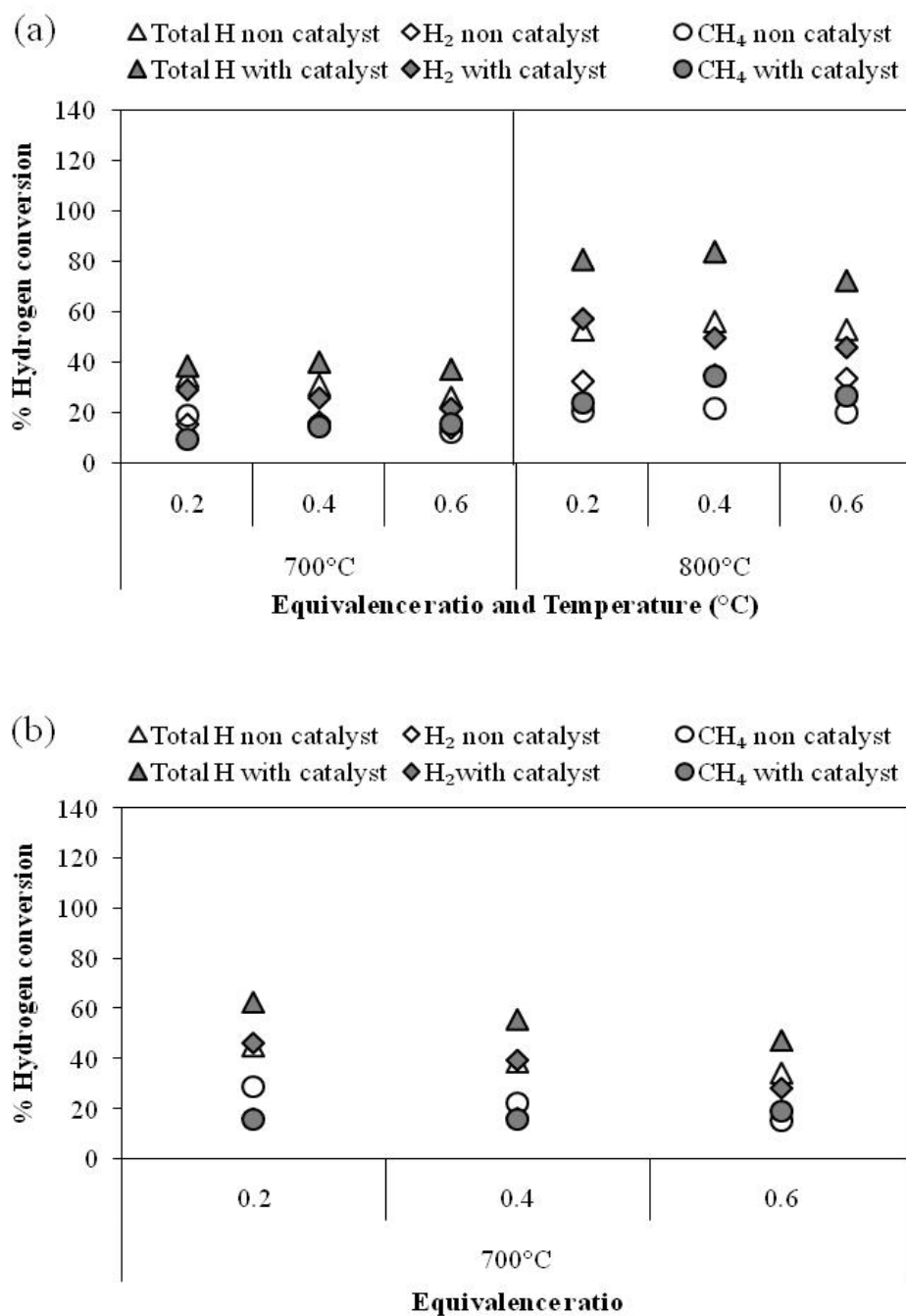Addition of catalyst enhances gas yield for approximately 10 wt.%. This catalyst helps reduce a lot of liquid yields while solid yields are relatively stable (Figure 4.8a and 4.8b). The results are likely due to water-gas shift reaction, equation (4.6). As expected, products yields were improved at 800°C more than that of 700°C. Li et al. (2009) who studied the product yields from steam and catalytic gasification of saw dust at 750-850°C also reported that adding catalyst causes gas yield increased markedly, and gas yield increased from 1.88 to 2.40 Nm^3/kg with raising temperature from 750 to 850°C. For effect of this catalyst on equivalence ratio, the percentage of product yields in each equivalence ratio are close to each others. Thus, it can be concluded that the effects of this catalyst are not relative with equivalence ratio. When compare addition of catalyst to raw material ratio of 50:50 with raw material of 40:60 at same temperature and equivalence ratio, it was found that catalyst can improves gas yield of raw material ratio of 40:60 more than raw material ratio of 50:50. These results indicated that Ni catalyst can be reducing tar and converts to useful gases such as CO and H_2 (Miyazawa et al., 2006).

Steam reforming: $\qquad CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad\qquad$ (4.17)

CO$_2$ reforming: CH$_4$ +CO$_2$ ↔ 2CO + 2H$_2$ (4.18)
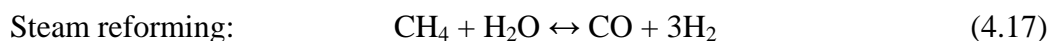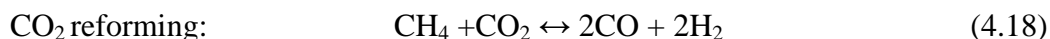
Table 4.7 Effect of catalyst on product distribution of raw material ratio of 50:50 (non catalytic cases compare with catalytic cases at same conditions)

Temperature	700°C			800°C		
Equivalence Ratio	0.2	0.4	0.6	0.2	0.4	0.6
Gas yield (wt.%)	↑ 5.69	↑ 1.94	↑ 15.84	↑ 5.78	↓ 0.82	↑ 17.22
Solid yield (wt.%)	↑ 7.00	↑ 2.65	↓ 1.69	↑ 4.14	↑ 5.45	↓ 0.96
Liquid yield (wt.%)	↓ 12.69	↓ 4.58	↓ 14.15	↓ 9.91	↓ 4.63	↓ 16.26

*<u>Remark</u>:   ↑ is conversion increase

↓ is conversion decrease

Table 4.8 Effect of catalyst on product distribution of raw material ratio of 40:60 (non catalytic cases compare with catalytic cases at same conditions)

Temperature	700°C		
Equivalence Ratio	0.2	0.4	0.6
Gas yield (wt.%)	↑ 10.85	↑ 12.16	↑ 8.32
Solid yield (wt.%)	↓ 0.54	↓ 0.22	↑ 3.15
Liquid yield (wt.%)	↓ 10.31	↓ 11.94	↓ 11.47

*<u>Remark</u>:   ↑ is conversion increase

↓ is conversion decrease

Adding Ni-La-Mg/Al$_2$O$_3$ catalyst causes carbon and hydrogen conversion increased especially for CO and H$_2$ conversions while CO$_2$ conversion decreased (Figure 4.9a, 4.9b, 4.10a and 4.10b). This can be explained by water-gas shift, steam reforming and CO$_2$ reforming reactions, equation (4.6), (4.17) and (4.18). CH$_4$ also decreased because magnesium in catalyst contribute to high methane conversion to CO and H$_2$ (Yung et al., 2009). From this reason, the ratio between H$_2$ and CO also approved as well (Figure 4.11a, 4.11b and 4.12). It should be noted that catalytic process can improve gas quality and tar removal.

Table 4.9 Effect of catalyst on gas compositions of raw material ratio of 50:50 (non catalytic cases compare with catalytic cases at same conditions)

Temperature	700°C			800°C		
Equivalence Ratio	0.2	0.4	0.6	0.2	0.4	0.6
% C conversion	↑ 1.45	↑ 17.80	↑ 12.65	↑ 27.45	↑ 37.70	↑ 31.14
% C conversion as CO_2	↓ 2.84	↑ 3.68	↑ 1.71	↑ 5.36	↑ 13.57	↑ 20.36
% C conversion as CO	↑ 8.59	↑ 14.35	↑ 9.40	↑ 20.72	↑ 18.24	↑ 7.61
% C conversion as CH_4	↓ 4.30	↓ 0.23	↑ 1.54	↑ 1.37	↑ 5.89	↑ 3.17
% H conversion	↑ 4.66	↑ 10.04	↑ 12.27	↑ 30.36	↑ 30.14	↑ 21.10
% H conversion as H_2	↑ 14.97	↑ 10.60	↑ 8.57	↑ 27.11	↑ 16.05	↑ 13.51
% H conversion as CH_4	↓ 10.31	↓ 0.56	↑ 3.69	↑ 3.25	↑ 14.09	↑ 7.59
H_2/CO	↑ 0.23	↑ 0.03	↑ 0.08	↑ 0.09	↓ 0.04	↑ 0.12

*<u>Remark</u>: ↑ is conversion increase

↓ is conversion decrease

Table 4.10 Effect of catalyst on gas compositions of raw material ratio of 40:60 (non catalytic cases compare with catalytic cases at same conditions)

Temperature	700°C		
Equivalence Ratio	0.2	0.4	0.6
% C conversion	↓ 6.08	↑ 4.60	↑ 24.72
% C conversion as CO_2	↓ 5.87	↓ 9.98	↑ 3.36
% C conversion as CO	↑ 5.28	↑ 17.30	↑ 19.79
% C conversion as CH_4	↓ 5.49	↓ 2.72	↑ 1.57
% H conversion	↑ 17.28	↑ 16.77	↑ 12.76
% H conversion as H_2	↑ 30.27	↑ 23.20	↑ 9.04
% H conversion as CH_4	↓ 12.99	↓ 6.43	↑ 3.72
H_2/CO	↑ 0.66	↑ 0.24	↓ 0.12

*<u>Remark</u>: ↑ is conversion increase

↓ is conversion decrease

4.3.3 Energy efficiency

In these experiments, the results showed that temperature, equivalence ratio and raw material ratio have effect on lower heating value and cold gas efficiency (Figure 4.13-4.14). Moreover, addition of catalyst also has effect on energy efficiency. From Figures 4.13a, 4.13b, 4.14a and 4.14b, it was found that the results have the similar trend in both the ratio of pulp sludge mixed with black liquor of 50:50 and 40:60.

The LHV of gas products can be calculated by eqs.4.19 (Atong et al., 2009):

$$\text{LHV (MJ/m}^3) = (0.126 \times CO) + (0.108 \times H_2) + (0.358 \times CH_4) \tag{4.19}$$

Where CO, H_2 and CH_4 are volume (molar) percentage of these gas species, respectively.

Higher temperature enhances heating value of gas products. Heating value of gas products depend on the kind of gaseous components and the quantity of gas yield. Heating value of gas products is increased when CO, H_2, CH_4 and gas yield increased and especially on greater portion of CH_4 because of its high heating value.

Heating value of gas products decreased with greater equivalence ratio. Increasing equivalence ratio more O_2 fed leads to larger CO_2 production which does not contribute to heating value of product gas. Others gas products which have high heating value such as CO, H_2 and CH_4 are reduced.

For the effect of raw material ratio, it was found that lower heating value is not observed the difference on data of raw material ratio of 50:50 and 40:60. Lower heating value ranges of non catalytic cases are 3.37-5.91 MJ/m^3. These low to medium heating value ranges indicated that produced gas can be used in industrial processes for power production such as gas and steam turbine.

For catalytic conditions, lower heating value increased around 0.5-2.0 MJ/m^3 (Table 4.11 and 4.12). Increasing temperature results in heating values increased more than equivalence ratio and raw material ratio (Figure 4.14a and 4.14b). It can be concluded that temperature has significant effect on lower heating value of gas products. Lower heating value catalytic cases are 3.78-6.73 MJ/m^3.
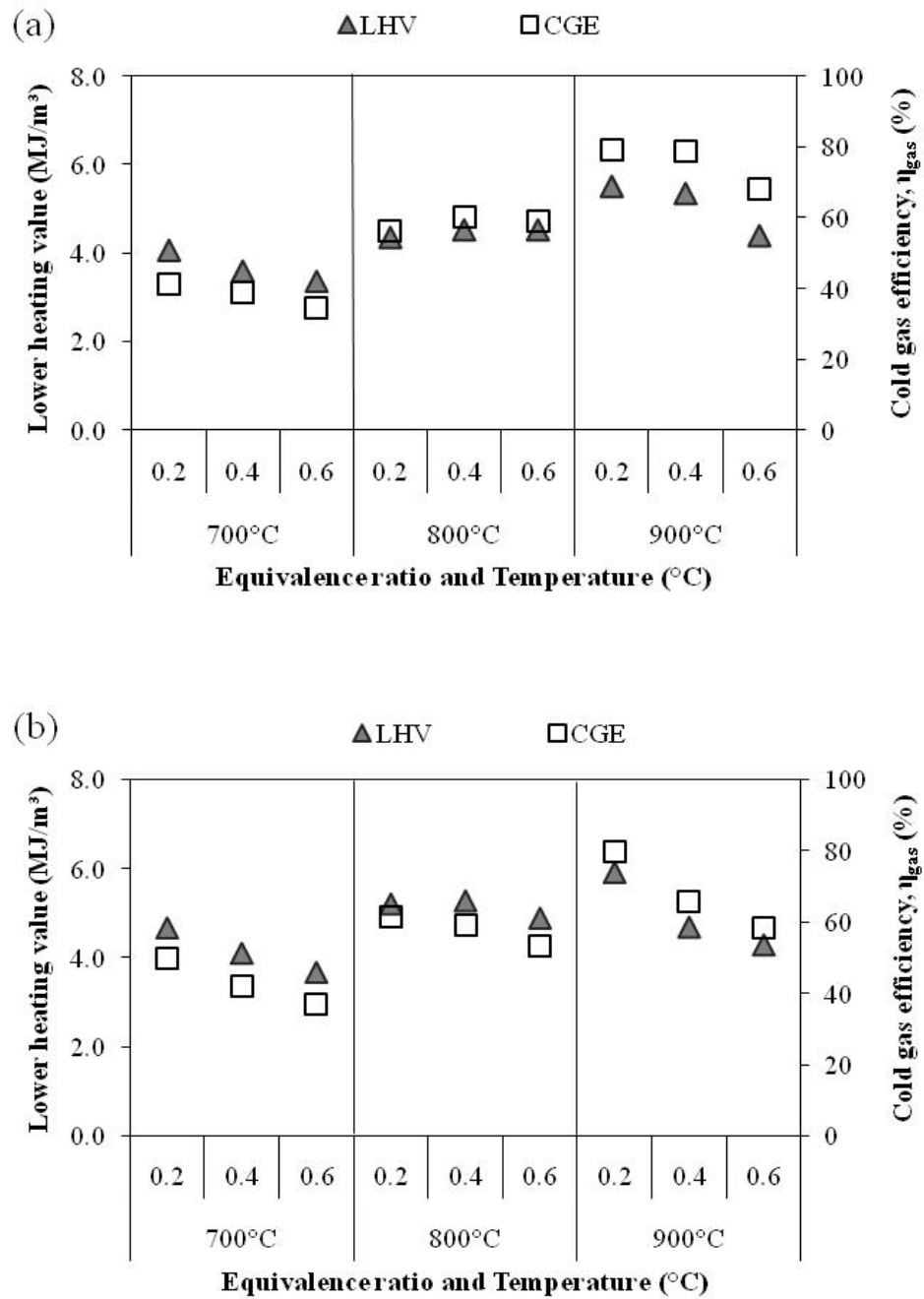
Figure 4.13 Energy efficiency of non catalytic cases (a) the ratio of pulp sludge mixed with black liquor of 50:50 (b) the ratio of pulp sludge mixed with black liquor of 40:60
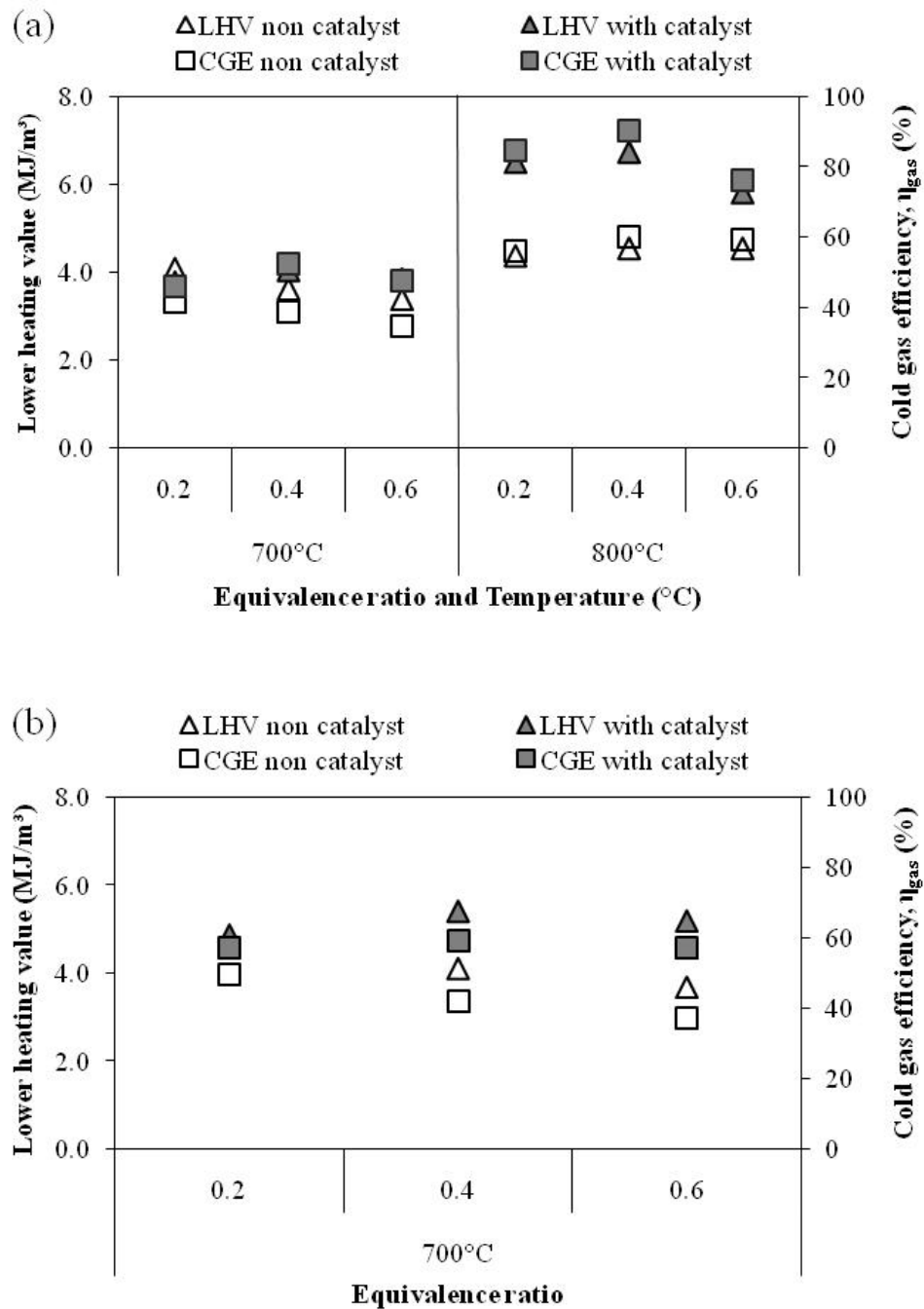
Figure 4.14 Energy efficiency of non catalytic and catalytic cases (a) the ratio of pulp sludge mixed with black liquor of 50:50 (b) the ratio of pulp sludge mixed with black liquor of 40:60

Table 4.11 Effect of catalyst on energy efficiency of raw material ratio of 50:50 (non catalytic cases compare with catalytic cases at same conditions)

Temperature	700°C			800°C		
Equivalence Ratio	0.2	0.4	0.6	0.2	0.4	0.6
Lower Heating Value (MJ/m^3)	↓ 0.29	↑ 0.45	↑ 0.48	↑ 2.14	↑ 2.20	↑ 1.28
Cold gas efficiency, η_{gas} (%)	↑ 4.62	↑13.80	↑12.91	↑28.56	↑30.13	↑17.06

*Remark: ↑ is conversion increase

             ↓ is conversion decrease

Table 4.12 Effect of catalyst on energy efficiency of raw material ratio of 40:60 (non catalytic cases compare with catalytic cases at same conditions)

Temperature	700°C		
Equivalence Ratio	0.2	0.4	0.6
Lower Heating Value (MJ/m^3)	↑ 0.21	↑ 1.32	↑ 1.53
Cold gas efficiency, η_{gas} (%)	↑ 7.57	↑ 17.19	↑ 20.06

*Remark: ↑ is conversion increase

             ↓ is conversion decrease

Cold gas efficiency defined as the ratio of total lower heating value (LHV) of product gas to the LHV of raw material fed. Thus, the results of cold gas efficiency depend on LHV of gas products.

Cold gas efficiency (η_{gas}) is defined as follows:

$$\eta_{gas}\left(\%\right) = \frac{LHV_{gas} \times Y_{gas}}{LHV_{raw\ material}} \times 100\%$$ (4.20)

Where Y_{gas} is yield of product gas per kilogram of fed raw material (Nm^3/kg) and LHV $_{raw\ material}$ may be measured by bomb calorimeter (Atong et al., 2009).

Greater temperature results in increasing energy efficiency due to promote the gasification reactions by Boudouard, primary water-gas and secondary water-gas reactions, equation (4.3), (4.4) and (4.5) (Kumar et al., 2009 and Wang et al., 2007). These results are similar to Kumar et al. (2009), who studied the effect of gasification temperature on steam-air fluidized bed gasification of distillers grains. They also reported that greater temperature with increasing energy efficiency because more heat energy supplied to the gasification system. At equivalence ratio of 0.6, cold gas efficiency decreased due to heating value of produced gas reduced. From the figures showed that equivalence ratio might be a little effect on energy efficiency and the effect of raw material ratio on cold gas efficiency is not remarkable. Generally, the data suggest that good energy efficiency may be achieved at temperature around 800°C and 900°C.

Cold gas efficiency ranges of catalytic cases were 46.02-90.13% while those obtained from non-catalytic trials were 34.63-79.13%. It can be concluded that addition of catalyst results in energy efficiency improvement. These results indicated that addition of catalyst contribute to improve energy efficiency in gasification process.

4.4 The qualification analysis of char from co-gasification process

Moisture content, volatile matter, fixed carbon and ash content of char from co-gasification process was analyzed by using proximate analysis. The results were shown in Figure 4.15a and 4.15b.
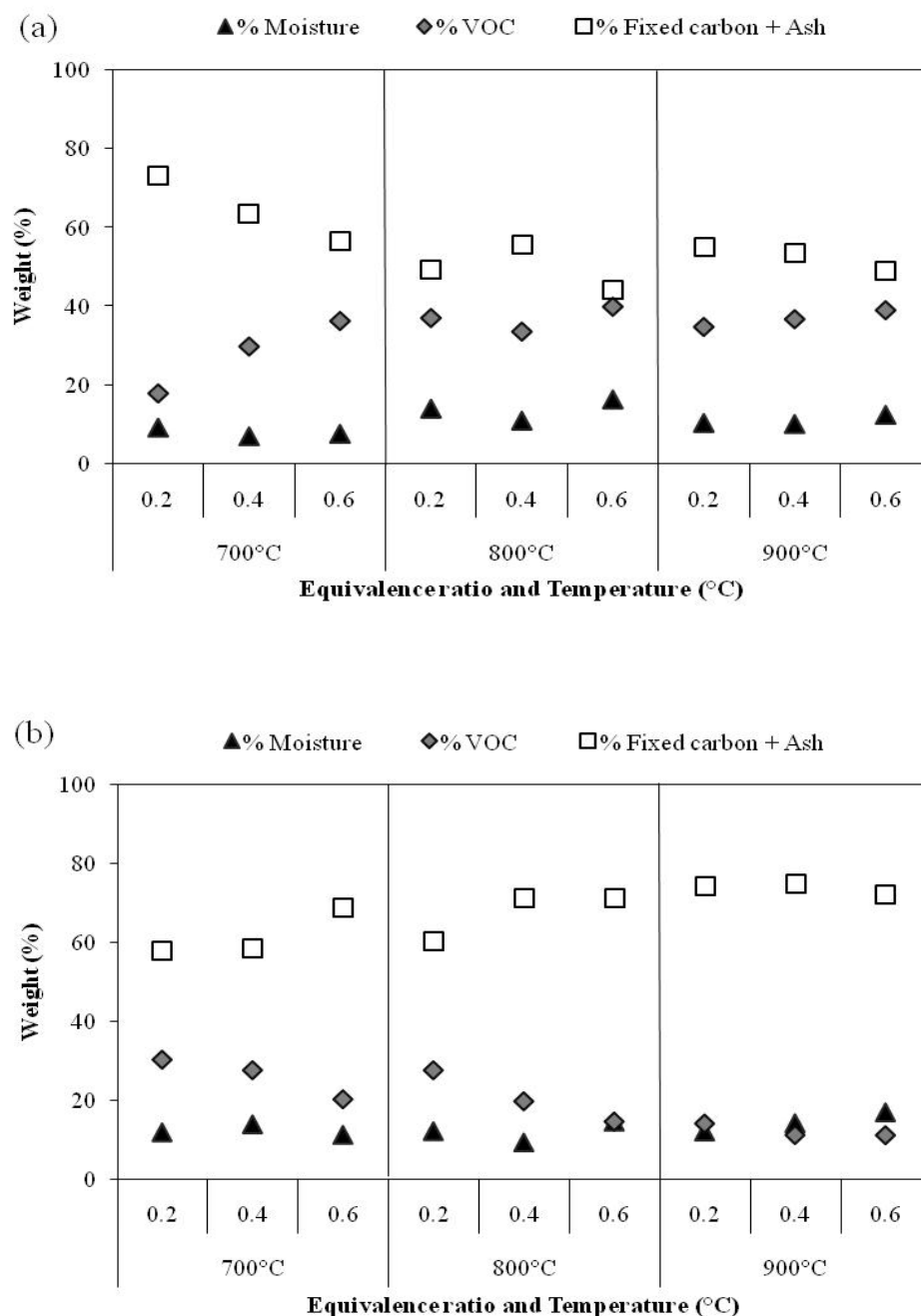
Figure 4.15 Proximate analysis of char from the process (a) the ratio of pulp sludge mixed with black liquor of 50:50 (b) the ratio of pulp sludge mixed with black liquor of 40:60

From the results of proximate analysis of char, it was found that moisture content and volatile matter were reduced with increasing temperature and equivalence ratio because they changed into gaseous products. Fixed carbon cannot detected by this method because sodium residue in black liquor. When insert oxygen into system sodium might be interacted with oxygen to form sodium oxide (NaO) at high temperature, and increased weights of char. From the result of high fixed carbon + ash content, it was indicated that this material mainly consists of inorganic materials. From the results of increasing of fixed carbon+ ash value, it was indicated that char residue mainly consists of sodium content which can be reused as chemicals via chemical recovery process.

The results of ultimate analysis (Figure 4.16a and 4.16b), it was found that higher temperature results in carbon in char residues reduced. Raising equivalence ratio causes carbon in char residues decreased. Changing of raw material ratio from 50:50 to 40:60 also contribute to decrease carbon in char residues. For others element such as hydrogen, nitrogen and sulfur, these elemental compositions are relatively small change with temperature, equivalence ratio and raw material ratio.

Carbon in the raw material can be gasified and changed to gaseous products by Boudouard, primary water-gas, secondary water-gas and combustion reactions, equation (4.3), (4.4), (4.5) and (4.8). These results occurred with raising temperature and equivalence ratio. It can be explained that increasing temperature and equivalence ratio results in carbon in char residues reduced. Moreover, carbon in chars may also react with Na_2SO_4 and Na_2CO_3 (equation (4.12), (4.13), (4.14) and (4.15)) and change to gaseous products at greater temperature. These processes contribute to loss of carbon and inorganic matter in this material. Due to the results of gas yield and carbon conversion of two raw material ratios, carbon of raw material ratio of 50:50 is lower than 40:60.

The results of carbon in char residues of raw material ratio of 50:50 at 700°C, it was indicated that increasing equivalence ratio results in higher carbon in char residues. It may also come from the carbon in carbonate form, so carbon changed to gaseous products decreased when rising equivalence ratio.

Sulfur in char residues is approximately 2 wt.%. The sulfur content can be converted to Na_2S that used as chemical in pulping process by retain the sulfur in

condensed phase, with reduction to Na_2S after gasification step (Backman et al., 1993).
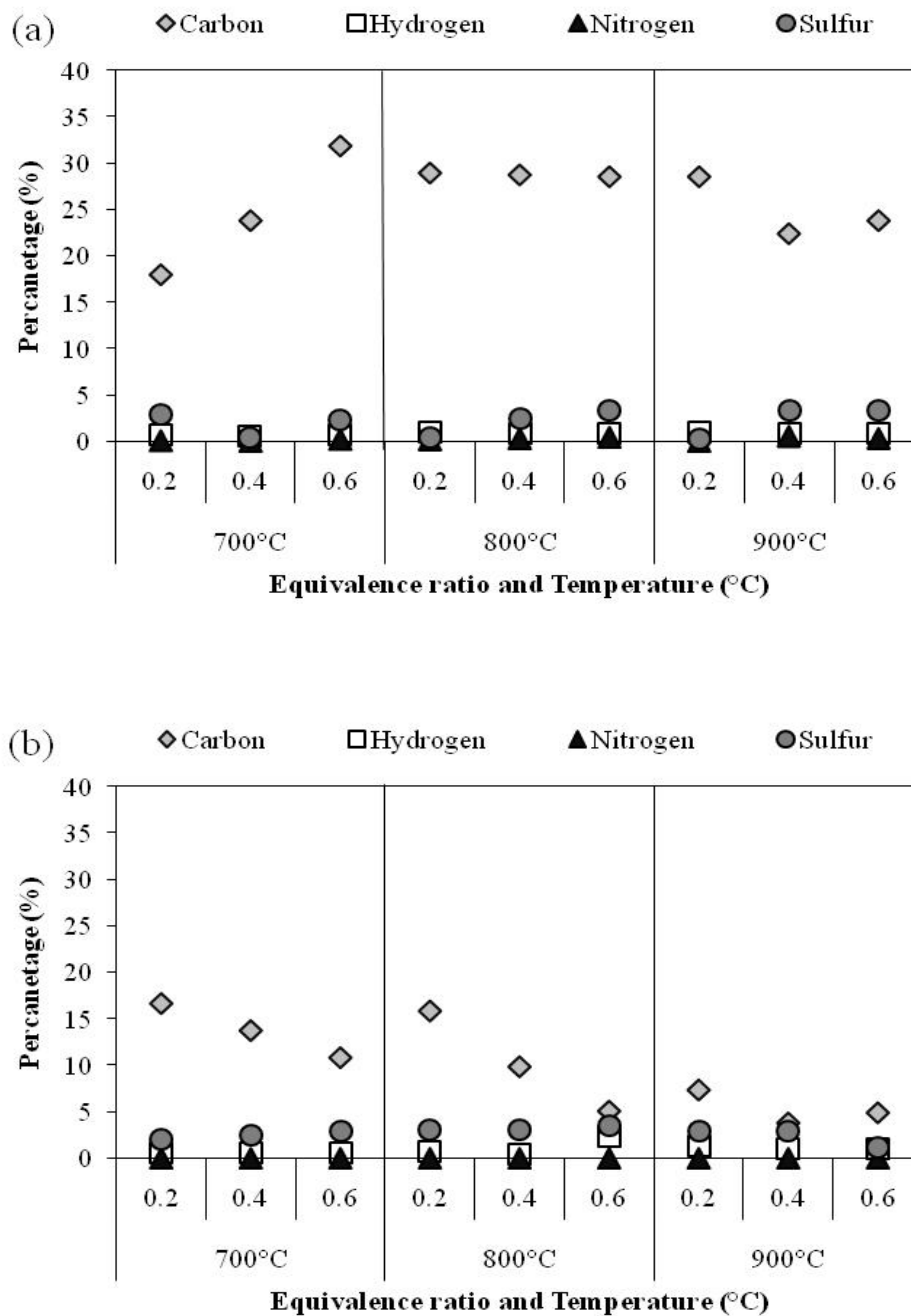
Figure 4.16 Ultimate analysis of char from the process (a) the ratio of pulp sludge mixed with black liquor of 50:50 (b) the ratio of pulp sludge mixed with black liquor of 40:60
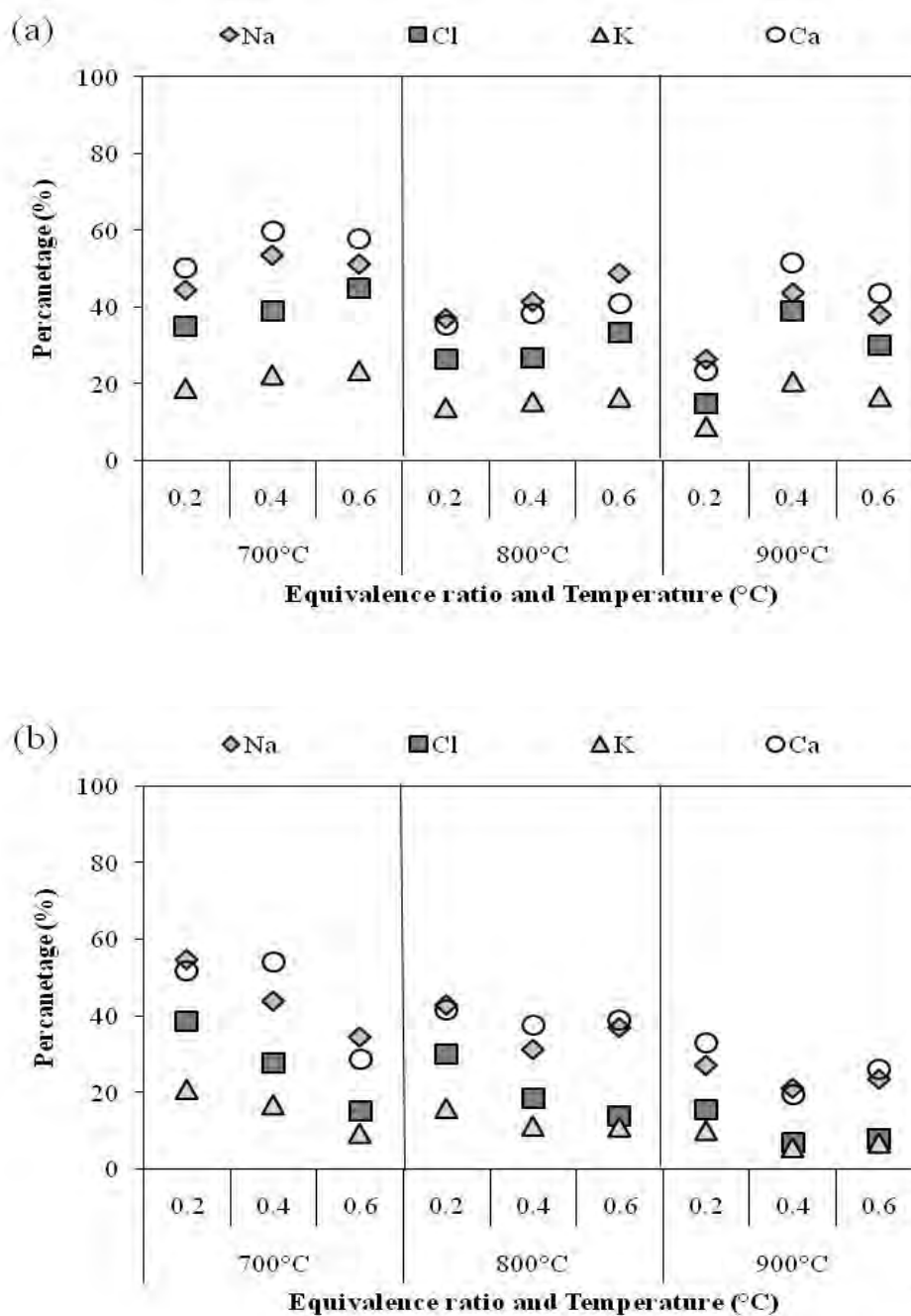
Figure 4.17 Elemental analysis of char from the process (a) the ratio of pulp sludge mixed with black liquor of 50:50 (b) the ratio of pulp sludge mixed with black liquor of 40:60

The elemental analysis of char from the process was analyzed by using X-ray fluorescence technique. The results showed in Figure 4.17. The results found that sodium in char were around 40-50 wt.% when compared with sodium in raw material fed. Thus, this process can recover sodium to use as chemicals around 50 wt.%. Changes of sodium content in char residues are relatively small with temperature, equivalence ratio and raw material ratio. Increasing black liquor in raw material causes sodium content in char residues increased. As sodium content in black liquor is higher than pulp sludge. Sodium content in char residues are similar in each operating condition because carbonate reactions during co-gasification process. Carbonate reduction is more rapidly at higher temperature and producing sodium and potassium vapor (Sricharoenchaikul et al., 2003). Thus sodium and potassium decreased with increasing temperature. Moreover, the rate of sodium vaporization during gasification is sensitive to temperature, so sodium losses would be increased at higher temperature (Backman et al., 1993).

It can be concluded that the optimal condition was was temperature of 900°C, ER of 0.2 and raw material ratio of 40:60 because it produce highest gas yield and energy efficiency. Addition of Ni-La-Mg/Al$_2$O$_3$ catalyst, improvement of the gasification performance may be achieved, especially at 800°C.

CHAPTER V
CONCLUSION AND RECOMMENDATION

In this research, co-gasification of pulp sludge mixed with black liquor was performed to study the effect of temperature, equivalence ratio and ratio of pulp sludge mixed with black liquor of 50:50 and 60:40 on products distribution and energy efficiency. In addition, $Ni-La-Mg/Al_2O_3$ catalyst was prepared by co-impregnation method and mixed with raw material before fed into system to study its effect on thermochemical conversion reaction. The following is a conclusion and recommendation from this research.

5.1 Conclusion

The pulp sludge mixed with black liquor has great potential to be used as raw material for fuel gases production as it contains high volatile matter, low ash content and high carbon content with proper heating value. Temperature, equivalence ratio and ratio of pulp sludge to black liquor have significant influence on product distribution and energy efficiency. Gas production especially synthesis gas (CO and H_2) was improved and higher energy efficiency was obtained with increasing temperature and decreasing equivalence ratio for raw material ratio of 50:50, while it increased with increasing temperature and rising equivalence ratio for raw material ratio of 40:60.

The results of non-catalytic cases indicated that the optimal condition was temperature of 900°C, ER of 0.2 and raw material ratio of 40:60 with gas yield of 69.18%, H_2 to CO ratio of 0.96, lower heating value of 5.91 MJ/m^3 and cold gas efficiency of 79.55%. Since synthesis gas ratio at 800°C and 900°C are close to 1, so they can be further applied to produce methanol and others synthesis fuels by Fischer-Tropsch reactions. For catalytic cases, it was found that $Ni-La-Mg/Al_2O_3$ catalyst can improve the percentage of carbon and hydrogen conversion, especially at 800°C. The ratio between H_2 and CO, lower heating value and cold gas efficiency increased when catalyst was added. Furthermore, higher gas yield with decreased solid and liquid yields were achieved. Lower heating value ranges of catalytic cases were 3.78-6.73 MJ/m^3 and cold gas efficiency ranges were 46.02-90.13% while those obtained from non catalytic trials were 3.37-5.51 MJ/m^3 and 34.63-79.13%, respectively. From

these results, co-gasification of pulp sludge mixed with black liquor can be considers as a novel method to convert pulp sludge and black liquor into fuel products and also alternative option for wastes management in pulp and paper industry.

5.2 Recommendation

From the results of this research, many problems occurred during the operation, thus some recommendations for further studies can be proposed.

1. In this research, synthesis gas production from co-gasification of pulp sludge mixed with black liquor should be have a further studied to produce fuel gases that suitable for use as renewable energy in the future, and can enhance the economic value of pulp and paper industry.

2. Raw material ratios should be considered about their characteristics and quantities for apply to use in pulp and paper industry.

3. Energy efficiency in this work should be considered as the economical feasibility in the further studied.

4. This suggested that further studied about alkali recovery may be required for utilized in the pulp and paper industry.

5. This process should be considered about economical aspects when addition of catalyst.

6. The system should have secondary reactor for collect catalyst in order to regeneration and reuse for develop economically valuable and sustainable energy conversion process.

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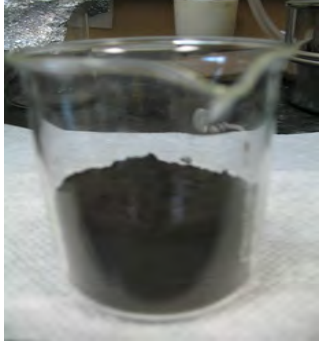
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APPENDICES

APPENDIX A

Table A-1 Pictures of materials used in this experiment

Material	Picture
Black liquor	
Dewatered sludge	
Alumina, Al_2O_3 (bed)	
Ni-La-Mg/Al_2O_3 (catalyst)	

Material	Picture
Nitrogen refrigerated liquid 99.99%	
Oxygen 99.5% (purified oxygen)	
Hydrogen gas 99.99%	
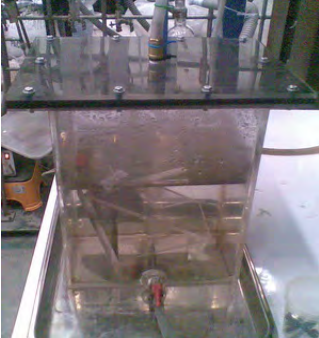
Table A-2 Pictures of equipments that used in this experiment

Equipment	Picture
Fine Grinder	
Grinder	
Sieve (aperture size 2.0 mm, 10 mesh, and aperture size 150 micron, 100 mesh)	
Feeder	

Equipment	Picture
Rotameters	
Pressure gauge	
Gas pre-heater	
Temperature controller	

Equipment	Picture
Electrical furnace	
Stainless Tube	
Cyclone and collector	
Chiller	

Equipment	Picture
Condensers and collectors	
Gas washer	
Gas flow meter	
Analyzer	
Stop-watch	

Equipment	Picture
A scale (2 and 4 decimal places)	
Oven	
High temperature furnace	

APPENDIX B

The sample calculation of carbon and hydrogen convert to gaseous products (% conversion). The conditions are temperature of 700°C, equivalence ratio of 0.4, and ratio of pulp sludge mixed with black liquor of 50:50.

Percent carbon conversion

Carbon in raw materials	=	32.755 %
Moisture in raw materials	=	25.00 %
Feed raw materials into system	=	5 g/min
Raw material fed into system	=	5 g/min × (1-0.25)
	=	3.75 g/min
So, carbon fed into system	=	3.75 g/min × 0.32755
	=	1.2283 g/min
	=	1.2283 g/min ÷ 12
	=	0.1024 mol/min

Carbon conversion of CO_2

Volume of CO_2	=	12.68 %
Outlet gases flow rate	=	4.78 l/min
So, volume of CO_2	=	4.78 l/min × 0.1268
	=	0.6061 l/min
Mole of C in CO_2 in gases	=	0.6061 ÷ 24.45
	=	0.02479 mol
Thus, % carbon conversion of CO_2	=	(0.02479 ÷ 0.1024) × 100
	=	24.22 %

Carbon conversion of CO

Volume of CO	=	13.32 %
Outlet gases flow rate	=	4.78 l/min
So, volume of CO	=	4.78 l/min × 0.1332
	=	0.6367 l/min

Mole of C in CO in gases	=	0.6367 ÷ 24.45
	=	0.02605 mol
Thus, % carbon conversion of CO	=	(0.02605 ÷ 0.1024) × 100
	=	25.45 %

Carbon conversion of CH_4

Volume of CH_4	=	3.25 %
Outlet gases flow rate	=	4.78 l/min
So, volume of CH_4	=	4.78 l/min × 0.0325
	=	0.1554 l/min

Mole of C in CH_4 in gases	=	0.1554 ÷ 24.45
	=	0.00635 mol
Thus, % carbon conversion of CH_4	=	(0.00635 ÷ 0.1024) × 100
	=	6.20 %

Percent hydrogen conversion

Hydrogen in raw materials	=	4.565 %
Moisture in raw materials	=	25.00 %
Feed raw materials into system	=	5 g/min
Raw material fed into system	=	5 g/min × (1-0.25)
	=	3.75 g/min
So, hydrogen fed into system	=	3.75 g/min × 0.04565
	=	0.1712 g/min
	=	0.1712 g/min ÷ 1
	=	0.1712 mol/min

Hydrogen conversion of H_2

Volume of H_2	=	7.03 %
Outlet gases flow rate	=	4.78 l/min
So, volume of H_2	=	4.78 l/min × 0.0703
	=	0.3360 l/min
Mole of H in H_2 in gases	=	(0.3360 ÷ 24.45) × 2
	=	0.02750 mol
Thus, % hydrogen conversion of H_2 =		(0.02750 ÷ 0.1712) × 100
	=	16.06 %

Hydrogen conversion of CH_4

Volume of CH_4	=	3.25 %
Outlet gases flow rate	=	4.78 l/min
So, volume of CH_4	=	4.78 l/min $\times$ 0.0325
	=	0.1554 l/min
Mole of H in CH_4 in gases	=	$(0.1554 \div 24.45) \times 4$
	=	0.02541 mol
Thus, % hydrogen conversion of CH_4 =		$(0.02541 \div 0.1712) \times 100$
	=	14.84 %

APPENDIX C

Table C-1 Co-gasification of pulp sludge mixed with black liquor (50:50) at various temperature and equivalence ratio

Temperature (°C)	700			800			900		
Equivalence Ratio	0.2	0.4	0.6	0.2	0.4	0.6	0.2	0.4	0.6
N_2 feed rate (l/min)	2.51	2.01	1.51	2.25	1.75	1.25	1.57	1.07	0.57
O_2 feed rate (l/min)	0.50	1.00	1.50	0.50	1.00	1.50	0.50	1.00	1.50
Gas outlet flow rate (l/min)	4.53	4.78	4.58	5.74	5.90	5.81	6.41	6.56	6.89
% C conversion of CO_2	20.25	24.22	43.83	25.68	34.75	52.34	36.44	45.54	62.28
% C conversion of CO	24.93	25.45	24.46	31.55	34.34	36.06	40.37	45.26	40.18
% C conversion of CH_4	7.96	6.20	5.13	8.64	8.98	8.22	10.38	10.63	8.39
% Total C conversion	53.14	55.87	73.42	65.87	78.07	96.62	87.19	101.43	110.85
% H conversion of H_2	15.27	16.06	13.79	32.28	34.78	33.39	58.54	49.71	44.54
% H conversion of CH_4	19.04	14.84	12.27	20.66	21.47	19.65	24.84	25.42	20.07
% Total H conversion	34.31	30.90	26.06	52.94	56.25	53.04	83.38	75.13	64.61

Table C-1 (cont.) Co-gasification of pulp sludge mixed with black liquor (50:50) at various temperature and equivalence ratio

Temperature (°C)	700			800			900		
Equivalence Ratio	**0.2**	**0.4**	**0.6**	**0.2**	**0.4**	**0.6**	**0.2**	**0.4**	**0.6**
H_2/CO	0.51	0.53	0.47	0.86	0.85	0.77	1.21	0.92	0.93
Higher Heating Value (MJ/m^3)	16.15	15.27	15.01	14.87	14.76	14.55	14.14	14.37	14.10
Lower Heating Value (MJ/m^3)	4.07	3.60	3.37	4.36	4.53	4.53	5.51	5.35	4.40
Solid yield (wt%)	24.77	29.75	29.46	21.08	22.82	26.41	18.09	26.63	22.56
Liquid yield (wt%)	29.05	26.06	34.43	21.01	20.06	32.61	20.75	16.60	35.89
Gas yield (wt%)*	46.18	44.18	36.11	57.90	57.12	40.98	61.16	56.77	41.54
Cold gas efficiency, η_{gas} (%)	41.40	38.64	34.63	56.05	60.00	58.98	79.13	78.62	67.91

* by difference

Table C-2 Co-gasification of pulp sludge mixed with black liquor (40:60) at various temperature and equivalence ratio

Temperature (°C)	700			800			900		
Equivalence Ratio	0.2	0.4	0.6	0.2	0.4	0.6	0.2	0.4	0.6
N_2 feed rate (l/min)	2.75	2.29	1.83	2.51	2.05	1.59	1.81	1.35	0.89
O_2 feed rate (l/min)	0.46	0.92	1.38	0.46	0.92	0.46	0.46	0.92	1.38
Gas outlet flow rate (l/min)	4.35	4.19	4.15	4.83	4.58	4.47	5.50	5.74	5.57
% C conversion of CO_2	31.04	36.79	37.35	28.06	33.84	48.38	35.17	37.54	50.53
% C conversion of CO	27.33	23.70	22.82	37.05	35.12	32.75	45.41	39.43	36.62
% C conversion of CH_4	11.20	8.67	5.87	9.97	9.77	6.86	10.26	7.40	5.77
% Total C conversion	69.57	69.16	66.04	75.08	78.73	87.99	90.84	84.37	92.92
% H conversion of H_2	14.78	14.94	17.57	29.17	27.80	31.56	51.77	44.05	40.24
% H conversion of CH_4	26.51	20.53	13.90	23.60	23.14	16.23	24.30	17.51	13.67
% Total H conversion	41.29	35.47	31.47	52.77	50.94	47.79	76.07	61.56	53.91

Table C-2 (cont.) Co-gasification of pulp sludge mixed with black liquor (40:60) at various temperature and equivalence ratio

Temperature (°C)	700			800			900		
Equivalence Ratio	**0.2**	**0.4**	**0.6**	**0.2**	**0.4**	**0.6**	**0.2**	**0.4**	**0.6**
H_2/CO	0.46	0.53	0.65	0.67	0.67	0.81	0.96	0.94	0.93
Higher Heating Value (MJ/m^3)	17.26	16.57	15.13	15.22	15.31	14.29	14.21	13.86	13.57
Lower Heating Value (MJ/m^3)	4.66	4.09	3.66	5.20	5.27	4.88	5.91	4.68	4.28
Solid yield (wt%)	30.60	27.26	20.23	24.99	18.66	21.78	17.04	12.47	14.34
Liquid yield (wt%)	30.28	31.67	34.13	26.19	22.78	24.56	13.78	17.70	16.85
Gas yield (wt%)*	39.12	41.07	45.64	48.82	58.56	53.66	69.18	69.83	68.81
Cold gas efficiency,η_{gas} (%)	49.57	41.97	37.07	61.39	58.94	53.30	79.55	65.56	58.35

* by difference

Table C-3 Co-gasification of pulp sludge mixed with black liquor (50:50) with Ni-La-Mg/Al$_2$O$_3$ catalyst at various temperature and equivalence ratio

Temperature (°C)	700°C with catalyst			800°C with catalyst		
Equivalence Ratio	**0.2**	**0.4**	**0.6**	**0.2**	**0.4**	**0.6**
N$_2$ feed rate (l/min)	2.51	2.01	1.51	2.25	1.75	1.25
O$_2$ feed rate (l/min)	0.50	1.00	1.50	0.50	1.00	1.50
Gas outlet flow rate (l/min)	5.43	5.77	5.51	5.80	5.97	5.83
% C conversion of CO$_2$	17.63	27.59	45.39	30.60	47.19	70.99
% C conversion of CO	32.81	38.58	33.06	50.53	51.05	43.02
% C conversion of CH$_4$	4.02	5.98	6.54	9.88	14.37	11.13
% C conversion	54.46	72.15	84.99	91.01	112.61	125.14
% H conversion of H$_2$	28.99	25.78	21.64	57.12	49.49	45.77
% H conversion of CH$_4$	9.60	14.30	15.63	23.62	34.37	26.61
% H conversion	38.59	40.08	37.27	80.74	83.86	72.38

Table C-3 (cont.) Co-gasification of pulp sludge mixed with black liquor (50:50) with Ni-La-Mg/Al$_2$O$_3$ catalyst at various temperature and equivalence ratio

Temperature (°C)	700°C with catalyst			800°C with catalyst		
Equivalence Ratio	**0.2**	**0.4**	**0.6**	**0.2**	**0.4**	**0.6**
H$_2$/CO	0.74	0.56	0.55	0.95	0.81	0.89
Higher Heating Value (MJ/m^3)	13.43	14.13	14.68	13.94	15.03	14.66
Lower Heating Value (MJ/m^3)	3.78	4.05	3.85	6.50	6.73	5.81
Solid yield (wt%)	31.77	32.40	27.77	25.22	28.27	25.45
Liquid yield (wt%)	16.36	21.48	20.28	11.10	15.43	16.35
Gas yield (wt%)*	51.87	46.12	51.95	63.68	56.30	58.20
Cold gas efficiency,ηgas (%)	46.02	52.44	47.54	84.61	90.13	76.04

*by difference

Table C-4 Co-gasification of pulp sludge mixed with black liquor (40:60) with Ni-La-Mg/Al$_2$O$_3$ catalyst at various equivalence ratio

Temperature (°C)	700°C with catalyst		
Equivalence Ratio	**0.2**	**0.4**	**0.6**
N$_2$ feed rate (l/min)	2.75	2.29	1.83
O$_2$ feed rate (l/min)	0.46	0.92	1.38
Gas outlet flow rate (l/min)	4.80	4.47	4.50
% C conversion of CO$_2$	25.67	27.65	40.42
% C conversion of CO	32.17	39.93	40.95
% C conversion of CH$_4$	6.18	6.18	7.31
% C conversion	64.02	73.76	88.68
% H conversion of H$_2$	42.49	36.20	25.84
% H conversion of CH$_4$	14.62	14.62	17.31
% H conversion	57.11	50.82	43.15

Table C-4 (cont.) Co-gasification of pulp sludge mixed with black liquor (40:60) with Ni-La-Mg/Al$_2$O$_3$ catalyst at various equivalence ratio

Temperature (°C)	700°C with catalyst		
Equivalence Ratio	**0.2**	**0.4**	**0.6**
H$_2$/CO	1.12	0.77	0.53
Higher Heating Value (MJ/m^3)	13.67	13.77	14.48
Lower Heating Value (MJ/m^3)	4.87	5.41	5.19
Solid yield (wt%)	30.06	27.04	23.38
Liquid yield (wt%)	19.97	19.73	22.66
Gas yield (wt%)*	49.97	53.23	53.96
Cold gas efficiency,ηgas (%)	57.14	59.16	57.13

*by difference

APPENDIX D

Calculation of catalyst loading

Molecular weight of $Ni(NO_3)_2.6H_2O$ = 290.8100; Ni = 58.71

Molecular weight of $La_2(NO_3)_2.6H_2O$ = 433.0108; La = 138.91

Molecular weight of $Mg(NO_3)_2.6H_2O$ = 256.3120; Mg = 24.305

One experiment use raw material 150 g and addition of catalyst 20 wt% , so addition

of catalyst (20/100)*150 = 30 g per experiment

Use α-Al_2O_3 = 100% = 30 g

10% Ni loading on Al_2O_3 support = (10/100)*30 = 3 g

Ni 58.71 g in $Ni(NO_3)_2.6H_2O$ 290.81 g

Ni 3.00 g in $Ni(NO_3)_2.6H_2O$ 14.86 g

So, add $Ni(NO_3)_2.6H_2O$ = 14.86 g

5% La loading on Al_2O_3 support = (5/100)*30 = 1.5 g

La 138.91 g in $La_2(NO_3)_2.6H_2O$ 433.01 g

La 1.5 g in $La_2(NO_3)_2.6H_2O$ 4.68 g

So, add $La_2(NO_3)_2.6H_2O$ = 4.68 g

5% Mg loading on Al_2O_3 support = (5/100)*30 = 1.5 g

Mg 24.31 g in $Mg(NO_3)_2.6H_2O$ 256.31 g

Mg 1.5 g in $Mg(NO_3)_2.6H_2O$ 15.82 g

So, add $Mg(NO_3)_2.6H_2O$ = 15.82 g

APPENDIX E
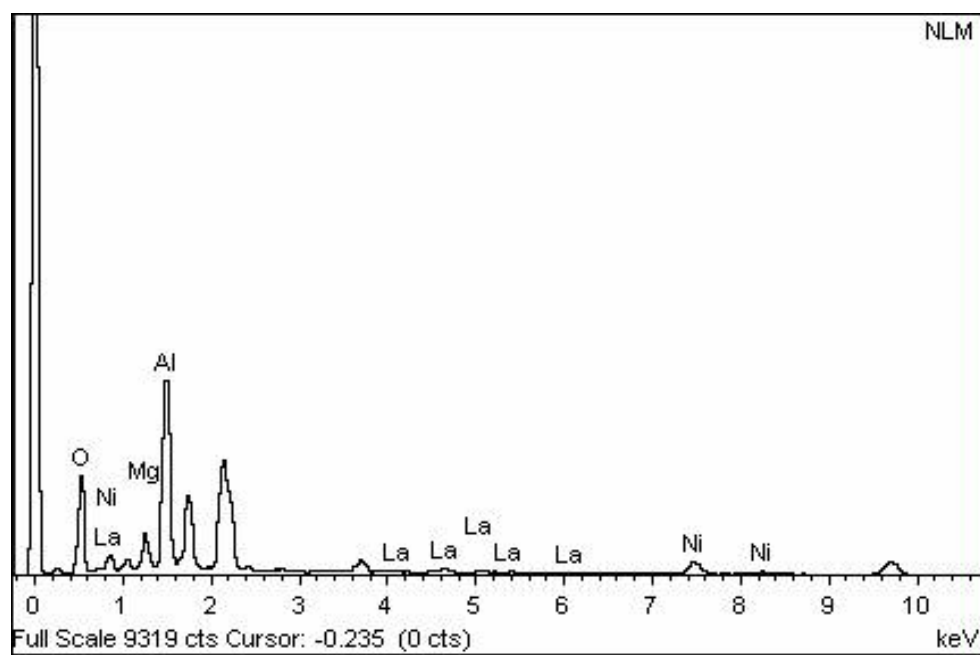
Figure E-1 Energy dispersive X-ray spectroscopy (EDX) analysis of the catalyst.

APPENDIX F

Table F-1 Proximate analysis of char from co-gasification process (% by weight) in various temperature, equivalence ratio and raw material ratio.

Char from process	Temp. (°C)	ER	% Moisture	% VOC	% Fixed Carbon + % Ash
Raw mat. ratio 50:50	700°C	0.2	9.12	17.96	72.92
		0.4	6.91	29.74	63.36
		0.6	7.53	36.14	56.33
	800°C	0.2	13.91	36.89	49.21
		0.4	10.88	33.46	55.65
		0.6	16.24	39.72	44.04
	900°C	0.2	10.29	34.64	55.07
		0.4	10.02	36.59	53.39
		0.6	12.34	38.84	48.82
Raw mat. ratio 40:60	700°C	0.2	11.79	30.29	57.92
		0.4	13.85	27.60	58.55
		0.6	11.13	20.18	68.69
	800°C	0.2	12.09	27.59	60.32
		0.4	9.19	19.68	71.14
		0.6	14.50	14.49	71.00
	900°C	0.2	11.97	13.98	74.04
		0.4	14.14	11.05	74.81
		0.6	16.93	11.01	72.06

APPENDIX G

Table G-1 Ultimate analysis of char from co-gasification process (% by weight) in various temperature, equivalence ratio and raw material ratio.

Char from process	Temp. (°C)	ER	Carbon	Hydrogen	Nitrogen	Sulfur
Raw mat. ratio 50:50	700°C	0.2	18.00	0.70	0.08	2.90
		0.4	23.80	0.52	0.00	0.36
		0.6	31.80	0.74	0.22	2.33
	800°C	0.2	28.90	0.98	0.17	0.36
		0.4	28.70	0.90	0.30	2.52
		0.6	28.50	0.82	0.44	3.40
	900°C	0.2	28.50	0.93	0.00	0.30
		0.4	22.40	0.80	0.54	3.37
		0.6	23.80	0.79	0.32	3.39
Raw mat. ratio 40:60	700°C	0.2	16.60	0.52	0.00	2.04
		0.4	13.70	0.60	0.00	2.46
		0.6	10.80	0.58	0.00	2.89
	800°C	0.2	15.80	0.72	0.00	3.04
		0.4	9.83	0.36	0.00	3.01
		0.6	5.08	2.31	0.00	3.48
	900°C	0.2	7.34	1.28	0.00	2.89
		0.4	3.81	1.04	0.00	2.93
		0.6	4.90	1.01	0.00	1.09

APPENDIX H

Table H-1 Elemental analysis of raw material

Raw material	Black liquor	Sludge
Elem. Compo. (wt.%)		
O	43.83	72.14
Na	25.84	0.29
Mg	0.07	0.68
Al	0.02	4.77
Si	0.25	12.24
P	0.04	0.64
S	5.56	1.20
Cl	3.77	0.43
K	20.23	0.31
Ca	0.26	7.07
Ti	-	0.13
Zn	-	0.10
Br	0.03	-
Rb	0.10	-
Sr	-	0.01
Zr	-	0.01
Mo	0.01	-
Ba	-	-

Table H-2 Elemental analysis of char from co-gasification process of pulp sludge mixed with black liquor (50:50) in various temperature, equivalence ratio and raw material ratio.

Temp.	700°C			800°C			900°C		
ER	0.2	0.4	0.6	0.2	0.4	0.6	0.2	0.4	0.6
Elem. Compo. (wt.%)									
O	39.08	41.01	43.00	45.76	41.54	45.14	50.47	42.23	41.32
Na	23.37	23.46	22.67	22.87	23.65	24.11	18.94	21.38	21.94
Mg	0.48	0.40	0.40	0.40	0.35	0.39	0.33	0.41	0.42
Al	3.37	2.75	2.70	2.38	2.58	2.45	2.16	2.70	2.74
Si	9.80	8.74	6.82	7.80	8.62	7.42	7.23	8.45	9.15
P	0.50	0.50	0.47	0.39	0.47	0.42	0.32	0.46	0.47
S	5.02	5.14	5.17	4.78	7.15	5.22	8.98	6.10	6.32
Cl	2.97	2.75	3.19	2.63	2.46	2.64	1.72	3.07	2.80
K	7.78	7.68	8.14	6.66	6.86	6.35	4.97	7.91	7.56
Ca	7.42	7.35	7.21	6.16	6.15	5.70	4.74	7.07	7.08
Ti	0.13	0.13	0.14	0.10	0.13	0.10	0.09	0.14	0.12
Zn	-	-	-	-	-	-	-	-	-
Br	0.01	0.01	0.02	0.02	-	0.01	-	0.01	-
Rb	0.03	0.04	0.03	0.03	0.01	0.02	0.01	0.03	0.04
Sr	0.01	0.02	0.01	0.01	-	0.01	-	0.01	0.01
Zr	0.02	0.02	0.01	0.02	0.01	0.01	0.00	0.01	0.02
Mo	-	0.01	0.01	-	0.02	0.01	0.04	0.01	-
Ba	-	-	-	-	-	-	-	-	-

Table H-3 Elemental analysis of char from co-gasification process of pulp sludge mixed with black liquor (40:60) in various temperature, equivalence ratio and raw material ratio.

Temp.	700°C			800°C			900°C		
ER	0.2	0.4	0.6	0.2	0.4	0.6	0.2	0.4	0.6
Elem. Compo. (wt.%)									
O	39.91	42.83	47.21	41.77	40.59	41.99	43.39	44.15	43.61
Na	27.93	25.14	26.68	26.81	26.19	26.53	24.89	26.55	25.66
Mg	0.35	0.35	0.33	0.35	0.43	0.45	0.35	0.41	0.43
Al	2.36	2.42	2.11	2.28	2.66	2.79	2.50	2.63	2.57
Si	6.54	7.29	6.66	6.57	8.08	8.21	7.31	8.16	8.46
P	0.39	0.37	0.35	0.36	0.40	0.39	0.36	0.37	0.36
S	5.87	5.45	4.71	6.00	5.63	6.42	5.44	6.02	6.06
Cl	3.06	2.46	1.84	2.91	2.41	1.55	2.20	1.36	1.36
K	8.37	7.59	5.73	7.84	7.46	6.25	7.32	5.61	5.93
Ca	5.05	5.90	4.23	4.94	5.99	5.30	5.79	4.61	5.39
Ti	0.08	0.12	0.08	0.09	0.10	0.08	0.11	0.08	0.10
Zn	-	-	-	-	-	-	0.21	-	-
Br	0.02	0.02	-	0.09	-	-	-	0.01	-
Rb	0.04	0.03	0.03	0.04	0.03	0.03	0.03	0.02	0.02
Sr	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01
Zr	0.01	0.02	0.01	0.01	0.02	0.01	0.01	0.01	0.01
Mo	-	0.00	0.00	-	0.01	0.01	0.01	0.01	0.01
Ba	-	-	-	-	-	-	0.06	-	-

APPENDIX I

Table I-1 Elemental analysis of char from co-gasification process of pulp sludge mixed with black liquor (50:50) in various temperature, equivalence ratio and raw material ratio (calculate from raw material fed (g))

Temp.	700°C			800°C			900°C		
ER	0.2	0.4	0.6	0.2	0.4	0.6	0.2	0.4	0.6
Elem. Compo. (wt.%)									
Na	44.29	53.41	51.10	36.89	41.29	48.72	26.21	43.56	37.88
Cl	35.03	38.96	44.75	26.41	26.73	33.20	14.82	38.93	30.09
K	18.76	22.25	23.35	13.67	15.24	16.33	8.75	20.51	16.61
Ca	50.08	59.59	57.87	35.39	38.24	41.02	23.36	51.30	43.53

Table I-2 Elemental analysis of char from co-gasification process of pulp sludge mixed with black liquor (40:60) in various temperature, equivalence ratio and raw material ratio (calculate from raw material fed (g))

Temp.	700°C			800°C			900°C		
ER	0.2	0.4	0.6	0.2	0.4	0.6	0.2	0.4	0.6
Elem. Compo. (wt.%)									
Na	54.72	43.87	34.55	42.89	31.29	36.99	27.15	21.20	23.56
Cl	38.53	27.60	15.32	29.93	18.51	13.89	15.43	6.98	8.03
K	20.89	16.88	9.45	15.98	11.35	11.10	10.17	5.71	6.94
Ca	51.86	53.97	28.72	41.43	37.51	38.74	33.11	19.29	25.94

APPENDIX J

Paper Publications (Conference Articles)

1) Chanattapa Sirinawin, Duangduen Atong and Viboon Sricharoenchaikul. Fuel Gases from Co-Gasification of Pulp Sludge Mixed with Black Liquor. 2010. The Sixth Thailand Materials Science and Technology Conference August 26-27, 2010, Bangkok, Thailand.

2) Chanattapa Sirinawin, Duangduen Atong, Sildara Thassanaprichayanont and Viboon Sricharoenchaikul. Fuel Products from Catalytic Co-Gasification of Pulp Sludge Mixed with Black Liquor in Fixed Bed Reactor. 2011. International Conference on Solid Waste 2011 Moving Towards Sustainable Resource Management May 2-6, 2011, Hong Kong Special Administrative Region, China.

BIOGRAPHY

Miss Chanattapa Sirinawin was born on September 13, 1986 in Bangkok, Thailand. She obtained her B.Sc. Degree in Environmental technology from the Faculty of Environmental and Resource Studies of Mahidol University in 2007. She pursued her Master's degree studies at the International Postgraduate Programs in Environmental Management, Inter-Department of Environment Management, Chulalongkorn University, Bangkok, Thailand since May 2008. She finished her Master's of Science Degree in Environmental Management in May 2011.