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นายธัชนันต์ สมานมูลย์

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GASIFICATION OF COTTON AND JATROPHA RESIDUE USING SUPERCRITICAL WATER

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ธัชนันต์ สมานบูลย์ : แก๊สซิฟิเคชันของฝ้ายและกากสบู่ดำด้วยน้ำเหนือวิกฤต (GASIFICATION OF COTTON AND JATROPHA RESIDUE USING SUPERCRITICAL WATER) อ.ที่ปรึกษาวิทยานิพนธ์ : รศ.ดร. ธวัชชัย ชรินพาณิชกุล, 80 หน้า

ชีวมวลคือหนึ่งในแหล่งพลังงานหมุนเวียนที่มีอยู่มากมาย มีชีวมวลประเภทต่างๆมากมายในประเทศไทย ซึ่งสำลียังไม่ได้มีการศึกษามากนัก โดยเศษสำลีประกอบด้วยเซลลูโลสปริมาณมาก ซึ่งน่าจะให้ปริมาณของผลิตภัณฑ์ที่เป็นก๊าซเชื้อเพลิงได้มาก กากสบู่ดำเป็นของเสียที่มีมากจากการสกัดเอาน้ำมันสบู่ดำ เพื่อใช้ในกระบวนการผลิตไบโอดีเซล กากสบู่ดำที่เหลือนี้มีความเป็นพิษ จึงไม่สามารถนำไปทำเป็นปุ๋ยได้ ดังนั้นชีวมวลทั้งสองจึงเหมาะสมที่จะนำมาใช้เป็นวัตถุดิบ น้ำเหนือวิกฤตมีความสามารถในการสกัดสารอินทรีย์เป็นอย่างดี ซึ่งสูงกว่าน้ำที่สภาวะปกติมาก จากคุณสมบัตินี้ทำให้น้ำเหนือวิกฤตทำปฏิกิริยา เปลี่ยนชีวมวลให้เป็นผลิตภัณฑ์ที่มีคุณค่าได้ ในงานวิจัยนี้ คณะผู้วิจัยได้ใช้น้ำเหนือวิฤตแก๊สซิฟิเคชัน ในการแก๊สซิไฟด์ไบโอแมสทั้งสองชนิด

ผงสำลีและกากสบู่ดำ ถูกแก๊สซิไฟล์ด้วยน้ำเหนือวิกฤตในเครื่องปฏิกรณ์แบบท่อไหล, ความยาวท่อ 12 เมตร, เพื่อผลิตก๊าซเชื้อเพลิง งานวิจัยนี้มุ่งเน้นที่จะศึกษาผลกระทบของความเข้มข้นของชีวมวลในช่วง 0.05 - 1.0 ร้อยละโดยน้ำหนัก, ผลกระทบของอุณหภูมิในช่วง 400 – 700 องศาเซลเซียส, ผลกระทบของขนาดชีวมวลในช่วงของ 45 – 150 ไมโครเมตร และ ผลกระทบของเรสสิเดนท์ไทม์ในช่วง 63 – 125 วินาที ต่อร้อยละผลได้ของก๊าซเชื้อเพลิงที่ผลิตได้ จากการศึกษาพบว่า ไฮโดรเจน, คาร์บอนไดออกไซด์, คาร์บอนมอนอกไซด์, มีเทน และ ปริมาณเล็กน้อยของ อีเทน และ เอทิลีน สามารถผลิตได้จากการกระบวนการแก๊สซิฟิเคชันนี้ ร้อยละผลได้ของไฮโดรเจนไม่ได้ขึ้นอยู่กับการเพิ่มขึ้นของความเข้มข้นของชีวมวลเพียงอย่างเดียว การเพิ่มอุณหภูมิและการเติมตัวเร่งปฏิกิริยาเป็นที่ต้องการสำหรับความเข้มข้นชีวมวลที่สูง แต่ยังคงขึ้นอยู่กับอุณหภูมิที่เพิ่มขึ้นด้วย การลดขนาดอนุภาคของชีวมวลช่วยส่งผลต่อการเพิ่มของผลิตภัณฑ์ก๊าซ ในขณะเดียวกันระยะเวลาที่ยาวขึ้นของเรสสิเดนท์ไทม์ทำให้เกิดผลในแนวทางเดียวกัน

ภาควิชา........วิศวกรรมเคมี..................ลายมือชื่อนิสิต ธัชนันท์ สมานบูลย์

สาขาวิชา.......วิศวกรรมเคมี..................ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์หลัก..........

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THACHANAN SAMANMULYA : GASIFICATION OF COTTON AND JATROPHA RESIDUE USING SUPERCRITICAL WATER. THESIS ADVISOR : ASSOC. PROF. TAWATCHAI CHARINPANITKUL, D.Eng., 80 pp.

Biomass is one of the most abundant renewable energy resources. Among various biomass materials available in Thailand, cotton has not been thoroughly investigated though they contain a large content of cellulose which would potentially provide high yield of fuel gas product. Jatropha residue is also an abundant waste generated from jatropha oil extraction in biodiesel production process. It is recognized that such toxic jatropha waste cannot be used as fertilizer. However, they can be a good candidate as biomass feedstock. Supercritical water has an excellent extracting capability which is superior to that of other solvents. These properties make supercritical water a very promising reaction medium for the conversion of biomass to value-added products. In this study we employ supercritical water for gasification of these two biomass material.

Powdery cotton and jatropha residue have been gasified by supercritical water in a tubular flow reactor with a length of 12 m, to produce fuel gas. The effects of biomass concentration in a range of 0.05-1.0 wt%, gasifying temperature in a range of 400 - 700°C, particle size of biomass feedstock in a range of 45 – 150 µm and residence time of 63-125 sec on yield of fuel gas were experimentally examined. It was found that hydrogen, carbon dioxide, carbon monoxide, methane and a small amount of ethane and ethylene could be produced from the gasification process. Yield of hydrogen product depends not only on the increasing biomass concentration of feedstock, but also the increase in the gasifying temperature. The decrease in average size of both raw materials would result in the increase in the gaseous products while the longer residence time would provide the same tendency.

Department : ....Chemical Engineering...... Student's signature....T. Samanmulya.....

Field of study : ..Chemical Engineering...... Advisor's signature....T. Charinpanitkul....

Academic year : ....2009...............

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CHAPTER I

INTRODUCTION

1.1 Background

Biomass is an organic substance that could be considered as natural source of energy. It refers to plant materials, animal wastes, forestry, agricultural, and urban wastes. Examples of agricultural residues and agro-industrial wastes are as follows:

- Rice husk and Straw from rice mills and rice fields
- Bagasse from sugar refineries
- Wood waste from Para wood and Eucalyptus forests and plantations
- Residue from palm oil extraction plants
- Cassava Rhizome from Tapioca starch factories
- Corncobs from corn
- Coconut shells and empty bunches from coconut oil and milk factories

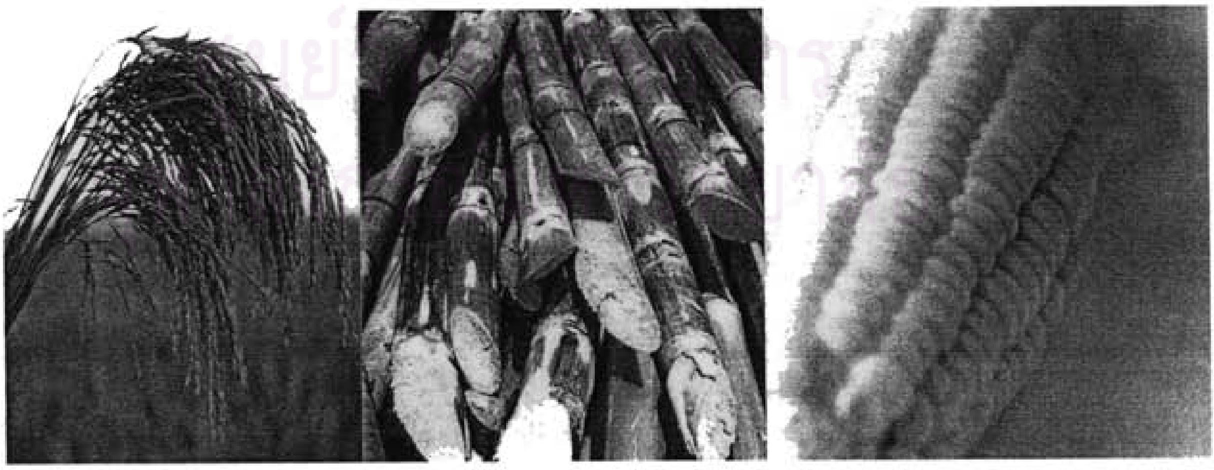

Figure 1.1 Rice – Sugar cane – Corn

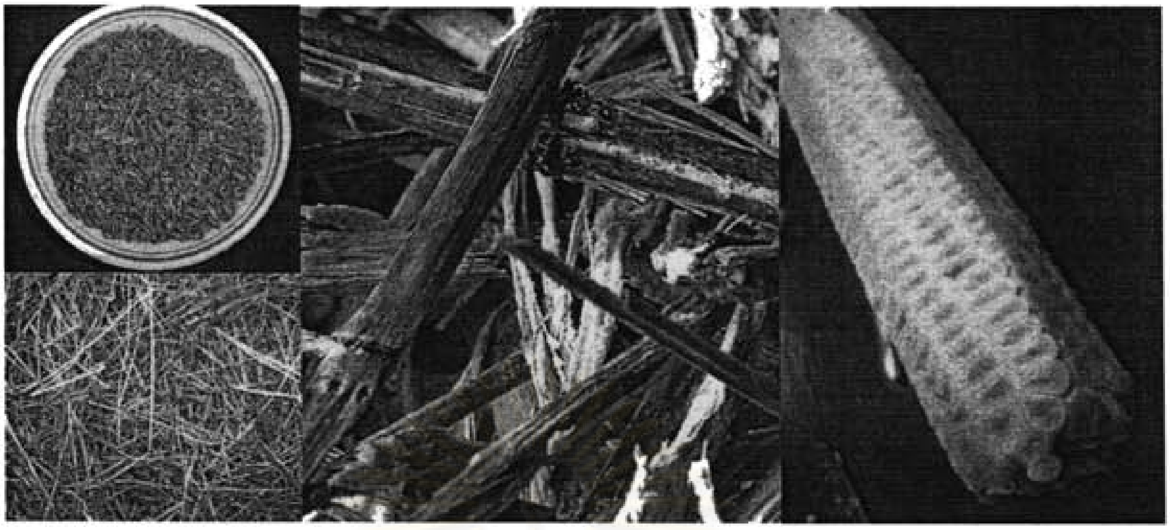

Figure 1.2 Rice husk and straw – Bagasse – Corncob

There are many kinds of biomass that are globally abundant. Biomass technology could handle those animal waste and agricultural residues for generating renewable energy. Biomass can be transformed into energy because in the photosynthesis process plants use CO_2 and water to convert solar energy into sugar and flour, and stock them in various parts of the tree. Biomass utilization is to use each or several of the above-mentioned biomass to produce steam and thermal energy or electricity.

Biomass resources are also abundant in Thailand. Its utilization helps reduce the expensive fuel import. Its benefit also includes the environment conservation matter. With the appropriate technology, the biomass energy generation will not cause pollution and Green House Effect due to the CO_2 recycling process of the plant rotation. We also aim to develop the biomass projects to the extent that communities become economically stronger on participation.

Cotton is a natural fiber harvested from the cotton plant. Cotton is one of the oldest fibers under human cultivation, with traces of cotton over 7,000 years old recovered from archaeological sites. Cotton is also one of the most used natural fibers in existence today, with consumers from all classes and nations wearing and using cotton in a variety of applications. There are many parts of Thailand that grows cotton as follows:

Table 1.1 Cultivated place of cotton in Thailand (www.doae.go.th)

Central	Saraburi, Lopburi
East	Chantaburi, Srakaew
North-east	Nakhonratchasima, Ubonratchathani, Chaiyaphum, Udonthani, Loei, Nongbualamphu
North	Chiangmai, Lampang, Phrae, Nan, Uttaradit, Phayao, Phitsanulok, Sukhothai, Tak, Kamphaengphet, Uthaithani, Phetchabun, Nakhonsawan
West	Kanchanaburi, Ratchaburi, Phetchaburi

Figure 1.3 Cotton

Thailand exports textile products which produce from cotton. Then, cotton is the raw material that is significant for textile industry of Thailand. There are plenty waste of cotton from a process of textile production.

Cellulose is one of many polymers found in nature. Wood, paper, and cotton are contained cellulose. Cotton can be a good candidate as biomass feedstock. Because cotton contains cellulose more than 90% that it may give high yield of gas product.

Jatropha is resistant to drought and pests, and produces seeds containing up to 40% oil. When the seeds are crushed and processed, the resulting oil can be used in a standard diesel engine, while the residue can also be processed into biomass to power electricity plants. Jatropha is one of the best candidates for biodiesel production. Jatropha residue is expected to be produced by a large amount from Jatropha oil extraction process for biodiesel production. Anyway, jatropha residue cannot be produce food for feeding animal because it has a toxic. Then, it can be use for biomass feedstock.

Figure 1.4 Jatropha seed

The available energy production processes from biomass can be divided into two general categories: thermo-chemical and biological processes. Combustion, pyrolysis, liquefaction and gasification are the four thermo-chemical processes. Direct bio-photolysis, indirect bio-photolysis, biological water–gas shift reaction, photo-fermentation and dark-fermentation are the five biological processes.

One method for hydrogen production is the steam reforming of biomass. The major problem in gasification by steam reforming is the formation of tars and char as the biomass does not react directly with steam at atmosphere pressure. Thermo-chemical gasification of biomass is likely to be a cost-effective process to produce fuel gas. Gasification of biomass in supercritical water have many advantages such as high gasification efficiency, high molar fraction of hydrogen, and no need of a drying process for wet biomass as compared to other biomass conversion methods.

Supercritical water has some very usual properties, which are different from those of liquid or gas. Many organic compounds cannot be dissolved in normal water. But supercritical water behaves like an organic solvent. Organic materials can be dissolved in it. Supercritical water in particular has the ability to dissolve materials not normally soluble in liquid water or steam. These properties make supercritical water a very promising reaction medium for the conversion of biomass to value-added products.

Under supercritical conditions, for example, water at temperatures above 374 °C and pressures above 22.1 MPa behaves like a powerful solvent and has tunable properties depending on temperature and pressure. Under such harsh conditions, biomass gets rapidly decomposed by hydrolysis and the cleavage products of biomass dissolve in the supercritical water there by minimizing the tar and coke formation. From the previous studies, supercritical water gasification (SCWG) of biomass seems to be a promising technology in the future for the production of energy rich gases such as hydrogen, synthesis gas or synthesis gas (mixture of CO and H_2) and methane from the wet biomass. A schematic representation of application outlets of SCWG of biomass is shown in figure 1.5

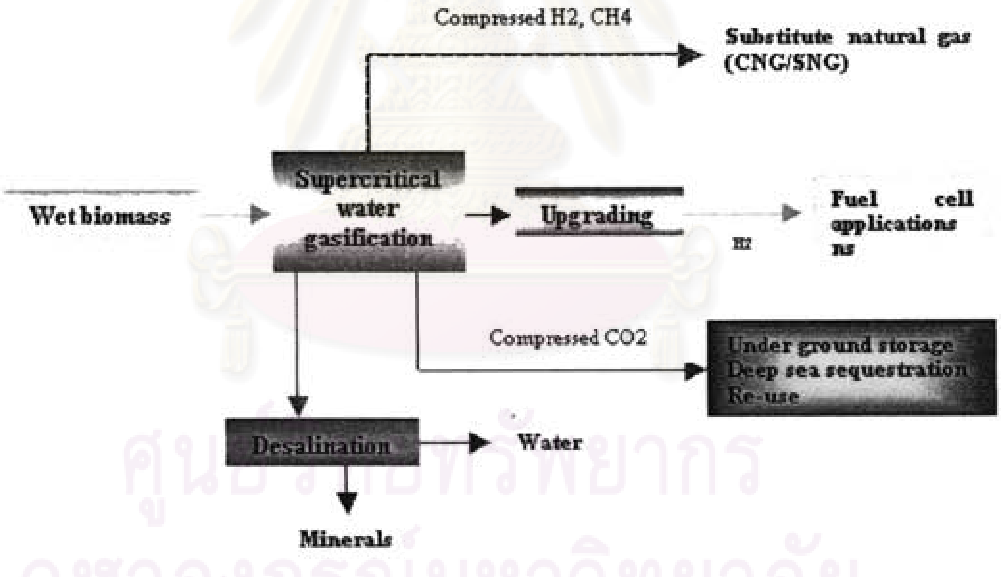

Figure 1.5 Application outlets of SCWG of biomass (Matsamura et al., 2005)

There are many parameters on biomass gasification. However, reactivity of cotton and jatropha residue has not been elucidated. This research is to investigate on the effect of concentration, temperature, particles size and residence time on gasification yield for cotton and jatropha residue. In this study we employ supercritical water gasification considering its advantage of producing tar free gas.

1.2 Objectives of the research

The objective of this research is to produce a fuel gas from biomass, which are cotton and jatropha seed residues by gasification in supercritical water. Investigation on effect of concentration, temperature, particles size and residence time upon gasification yield has been conducted experimentally. Analyses of gas compositions and amount of carbon in liquid product obtained from gasification were also carried out.

1.3 Scope of this research

1.3.1 Design condition for experimental.
    - Concentration range of 0.05 – 1.0 wt %
    - Temperature range of 400 – 700 °C
    - Particle size range of 45 – 150 μm.
    - Residence time range of 62 – 222 sec

1.3.2 Study the effect of concentration on biomass gasification.

1.3.3 Investigate optimum temperature of gasification which could give gas product with optimal hydrogen yield.

1.3.4 Study on the effect of particle size of feedstock on biomass gasification.

1.3.5 Determine variation of residence time that would give maximum gasification yield.

1.3.6 Analyze gas and liquid products obtained from gasification of each biomass using GC and TOC.

1.4 Expected benefit

The benefit to be expected from this research will be a knowledge of biomass gasification using supercritical water to treat a renewable and non-pollutant source. Understanding in hydrogen production by this way can be considered as a fundamental for utilization of a highly efficient clean and sustainable biomass resource to produce a fuel gas.

CHAPTER II

LITERATURE REVIEW

2.1 Hydrothermal gasification of biomass and organic wastes

Schmieder et al. (2000) produced hydrogen rich fuel gas from wet biomass and organic wastes. It can be efficiently gasified under hydrothermal conditions. They take carbohydrates, aromatic compounds, glycine (as a model compound for proteins) and real biomass in two tubular flow reactors and in two batch autoclaves. The model compounds glucose for cellulose, catechol and vanillin for lignin and glycine for proteins were used as aqueous solutions. Real biomass (wood as saw dust, straw) and wastes (sewage sludge and lignin) were treated in batch experiments by the addition of a certain amount of the material to the autoclaves. The first autoclaves designed for temperature of up to 700 °C and pressures of 1000 bar with an inner volume of 100 mL and is equipped with a magnetic stirrer for mixing. The educts were injected after heating of the water filled autoclave to the desired temperature. The second autoclave designed for temperature of up to 500 °C and pressures of 500 bar with inner diameter volume of 1000 mL. Mixing is achieved by a tumbling device. The educts were heated together with water to the desired temperature. The flow reactor was fabricated from Inconel 625 with a tube length of 55 mm, an outer diameter of 14.4 mm and an inner diameter of 8 mm. The reactant solution is fed into the reactor by a Bischoff 2250 HPLC pump. The feed is quickly heated to 600 °C with an electrical heater which is coiled around the entrance part of the reactor and maintained at this temperature by two additional heaters downstream of this entrance heater. That mean the reaction zone of the reactor has a length of 80 mm and diameter of 7.8 mm is placed at the entrance and the exit of the reactor. In this way, backmixing is suppressed and a fast heating of the feed flow at the reactor entrance and a fast quenching of the product flow at the reactor exit are guaranteed. The results are showed at different residence times, temperatures and pressures. At 600 °C and 250 bar all compounds are gasified completely with addition KOH or K_2CO_3. The main gas product is H_2 containing CO_2 and concentrations of CO, CH_4 and C_2–C_4 hydrocarbons are low in the product gas (<1, ~3 and <1 vol%, respectively). They used sawdust and straw as real biomass. The result shows temperature influence on gasification. Total organic carbon destruction efficiency was increased when increased temperature. At low temperature, soot and tar are formed. The experiments with glucose show that addition of KOH the carbon monoxide concentration in the product gas decreases. A similar influence is obtained in the experiments with vanillin where potassium carbonate was added instead of KOH. It can be concluded that the addition of alkali metals, probably as acid-base catalyst, increase the rate of the water gas shift reaction as following:

$$CO + H_2O \longrightarrow CO_2 + H_2$$

From this research, residence times and temperatures effect on gasification yield. At lower feed concentrations less than 0.2 M, residence times of about 30 seconds are required. At higher feed concentrations more than 0.6 M and constant potassium concentrations soot and tar formation appears. In addition of potassium decreases the carbon monoxide concentration and increases carbon dioxide and hydrogen in gas product. The addition of potassium carbonate or potassium hydroxide and temperatures more than 550 – 600 °C all of biomass is gasified completely.

2.2 Liquefaction of woody biomass in sub- and supercritical water

Qian et al. (2007) liquefied woody biomass in supercritical water at 280-420 °C in an autoclave with sodium carbonate as a catalyst. The main product of liquefaction is heavy oil. At reaction temperature 380 °C gives maximum yield. They analyzed the heavy oils at different reaction temperature by Fourier transform infrared spectroscopy (FTIR) and gas chromatography/mass spectrometry (GC/MS). The results indicate that the heavy oil is complex compound contain with hydrocarbon, aldehyde, ketone, hydroxybenzene and ester. The samples of silver birch were ground and screened, only the particle size smaller than 80 meshes were used in their studied. The reaction was carried out in a 500 ml stainless-steel autoclave with magnetic stirrer. The autoclave was heated with an external electrical furnace. In liquefaction process, a certain amount of raw material powder and distilled water were fed into the autoclave with the desired quantities of catalyst. After purging the residual air by hydrogen, the autoclave was charged with hydrogen at 8MPa then sealed and heated to the designed reaction temperature. The temperature was kept constant during the desired reaction time.

To investigate the effect of reaction temperature on the yield of the heavy oil, experimental were carried out with different temperatures. The yield of heavy oil strongly depends on the reaction temperature in the range of 280 – 420 °C. It can be seen that the heavy oil yield increases with increasing reaction temperature and then it is a rapid decrease with increasing reaction temperature. This is due to the competition of two reactions involved in the liquefaction which are hydrolysis and repolymerization. At the initial stage, biomass is decomposed and depolymerized to small compounds and these compounds may rearrange through condensation, cyclization and polymerization to form new compounds. The highest heavy oil yield of 53.3% was obtained at reaction temperature of 380 °C in their studied. When reaction temperature is higher or lower than this temperature, the yield of heavy oil decreases.

From this research, the experimental studied on direct liquefaction of silver birch in the liquid water with catalyst. Temperatures influence effect on yield of heavy oil from liquefaction. The yield of heavy oil has maximum in the range of temperature of 280 – 420 °C. Both yield and characteristics of heavy oil from woody biomass are dependent on the direct liquefaction conditions.

2.3 Gasification of biomass in supercritical water

Yoshida et al. (2004) gasified lignin, cellulose and their mixture in supercritical water at 673 K and 25 MPa with nickel as a catalyst. Efficiency of gasification is low, increases with the amount of the catalyst when lignin is contain in the feedstock. The tarry product from reaction between cellulose and lignin deactivated the nickel catalyst. Appropriate amount of catalyst gives high gasification efficiency when cellulose and lignin were mixed for the feedstock. They used sawdust and rice straw for the real biomass feedstock. These real biomass were gasified in the same condition.

From this research, components of each biomass effect on gasification efficiency. When lignin is contained in the feedstock, gasification yield is low. To help this problem, addition amount of nickel catalyst in feedstock increase yield of gas product. Nickel catalyst deactivate the tarry product from gasification.

D'Jesus et al. (2006) investigated with influence of pressure, temperature, residence time and alkali addition on the gasification of corn starch, clover grass and corn silage in supercritical water. Gasification yield was not changed by pressure. Increasing the temperature not improved the conversion of biomass. Longer residence time, yield of gasification was increased until a maximum was reached. Gas composition was changed by residence time and temperature. Alkali addition, Potassium influenced the gasification yield of corn starch, but did not influence the gasification yield of the potassium-containing natural products.

From this research, study influence of pressure, temperature, residence time and alkali addition on the gasification. Increasing in residence time improves the yield of gasification. If the residence time is longer than 9 min, gasification yield does not increase. Potassium addition, influence on gasification of model biomass but no effect in gasification yield of the potassium-containing natural products.

2.3.1 The effect of the nature of biomass

Yanik et al. (2007) gasified biomass feedstocks, including lignocellulosic material and the tannery wastes, in supercritical water. Gasification was produced in a batch autoclave at 500 °C. Gas composition and water soluble compounds from gasification were analyzed. The hydrogen yields are between 4.05 and 4.65 mol H_2/ kg. biomass have been obtained. The results showed that the yields and gas composition depend on the organic materials than cellulose and lignin in lignocellulosic material. The kind of lignin effected on gasification products.

From this research compare yield of gasification of eight different types of real biomass. Six of them are agricultural wastes and the others are leather wastes. The yield of gasification and composition of gas product depend on the gasification conditions and another composition of biomass, even it has high amount of cellulose plus hemicellulose.

2.3.2 A parametric study on biomass gasification

Lu et al. (2006) produced hydrogen from biomass gasification in supercritical water. Hydrogen production by biomass gasification in supercritical water is a promising technology for utilizing high moisture content biomass, but reactor plugging is a critical problem when feedstocks with high biomass content are gasified. The objective of this paper is to prevent the plugging problem by studying the effects of the various parameters on biomass gasification in supercritical water. These parameters include pressure, temperature, residence time, reactor geometrical configuration, reactor types, heating rate, reactor wall properties, biomass types, biomass particle size, catalysts and solution concentration. Biomass model compounds (glucose, cellulose) and real biomass are used in this work. All the biomasses have been successfully gasified and the product gas is composed of hydrogen, carbon dioxide, methane, carbon monoxide and a small amount of ethane and ethylene. The results show that the gas yield of biomass gasification in supercritical water is sensitive to some of the parameters and the ways of reducing reactor plugging are obtained.

From this research, there are many parameters on biomass gasification. The effect of pressure does not influence on biomass gasification too much. Gas product yield of each pressure values does not increase much from 17 to 30 MPa. Especially, Carbon gasification efficiency dose not improve when increasing pressure. It is shown that the parameters, such as carbon gasification efficiency and gasification efficiency, are not monotonic function of pressure.

The effect of temperature has significant influence on biomass gasification. Gas product yield was improved when temperature was increased. The reason might be high temperature promotes the free–radical reactions, which are necessary for gas formations.

The effect of residence time has influence on biomass gasification. The carbon gasification efficiency increase with increasing residence time and the unconverted TOC in liquid product decreases. It can believe that longer residence time is need to biomass gasification.

Higher concentration of biomass feedstock required higher temperature, high heating rate and catalyst. At low temperature and high concentration of biomass feedstock, there was plugging occur. Only increasing concentration of biomass feedstock does not improve the gas product yield.

The biomass feedstock with smaller particle size could provide the increased yield of hydrogen. The particle size has effected on biomass gasification. The carbon gasification efficiency was improved when conducted biomass gasification at a condition of smaller particle size.

2.3.3 Decomposition of cellulose and glucose

Minowa et al. (1998) studied the composition of cellulose and glucose in hot-compressed water under catalyst-free conditions. Cellulose is a major component of woody biomass that was reacted in hot-compressed water under catalyst-free conditions at different reaction temperatures in a range of 200 - 300 °C. Decomposition of cellulose started at around 200 °C. The amount of decomposed cellulose increased with reaction temperature until 240 °C. In water soluble product, the sugars were obtained between 200 – 220 °C. The result suggests that the first reaction step might be hydrolysis:

Cellulose → (Hydrolysis) → Sugar

→ (Secondary decomposition)

→ non-sugar products (1)

The cellulose decomposed quickly from 240 to 270 °C, and the formation of oil, char and gases stared. The results suggest that water soluble products and oil are intermediates for char formation:

Water soluble products → (decomposition) → oil + char + gases (2)

Oil → (decomposed) → char + gases (3)

Combining Eqs. (1) and (3) we get

Cellulose → sugar → non-sugar products → oil + char + gases (4)

A simplified reaction scheme is proposed, in which char-like residue are produced from cellulose through water soluble products and oil, as intermediates.

CHAPTER III

FUNDAMENTAL THEORY

3.1 Biomass

Biomass, as a renewable energy source, refers to living and recently dead biological material that can be used as fuel or for industrial production. For commonly, biomass refers to plant matter grown to generate electricity or produce for example trash such as dead trees and branches, yard clippings and wood chips biofuel, and it also includes plant or animal matter used for production of fibers, chemicals or heat. Biomass may also include biodegradable wastes that can be burnt as fuel. It excludes organic material which has been transformed by geological processes into substances such as coal or petroleum.

Biomass can be grown from numerous types of plants, including miscanthus, switchgrass, hemp, corn, poplar, willow, sorghum, sugarcane, and a variety of tree species, ranging from eucalyptus to oil palm (palm oil). The particular plant used is usually not important to the end products, but it does affect the processing of the raw material. Production of biomass is a growing industry as interest in sustainable fuel sources is growing. Although fossil fuels have their origin in ancient biomass, they are not considered biomass by the generally accepted definition because they contain carbon that has been "out" of the carbon cycle for a very long time. Their combustion therefore disturbs the carbon dioxide content in the atmosphere.

Biomass is part of the carbon cycle. Carbon from the atmosphere is converted into biological matter by photosynthesis. On death or combustion the carbon goes back into the atmosphere as carbon dioxide (CO_2). This happens over a relatively short timescale and plant matter used as a fuel can be constantly replaced by planting for new growth. Therefore a reasonably stable level of atmospheric carbon results from its use as a fuel. It is accepted that the amount of carbon stored in dry wood is approximately 50% by weight.

Though biomass is a renewable fuel, its use can still contribute to global warming. This happens when the natural carbon equilibrium is disturbed; for example by deforestation or urbanization of green sites. When biomass is used as a fuel, as a replacement for fossil fuels, it still puts the same amount of CO_2 into the atmosphere. However, when biomass is used for energy production it is widely considered carbon neutral, or a net reducer of greenhouse gases because of the offset of methane that would have otherwise entered the atmosphere. The carbon in biomass material, which makes up approximately fifty percent of its dry-matter content, is already part of the atmospheric carbon cycle. Biomass absorbs CO_2 from the atmosphere during its growing lifetime, after which its carbon reverts to the atmosphere as a mixture of CO_2 and methane (CH_4), depending on the ultimate fate of the biomass material. CH_4 converts to CO_2 in the atmosphere, completing the cycle.

Energy produced from feces residues displaces the production of an equivalent amount of energy from fossil fuels, leaving the fossil carbon in storage. It also shifts the composition of the recycled carbon emissions associated with the disposal of the biomass residues from a mixture of CO_2 and CH_4, to almost exclusively CO_2. In the absence of energy production applications, biomass residue carbon would be recycled to the atmosphere through some combination of rotting (biodegradation) and open burning. Rotting produces a mixture of up to fifty percent CH_4, while open burning produces five to ten percent CH_4. Controlled combustion in a power plant converts virtually all of the carbon in the biomass to CO_2. Because CH_4 is a much stronger greenhouse gas than CO_2, shifting CH_4 emissions to CO_2 by converting biomass residues to energy significantly reduces the greenhouse warming potential of the recycled carbon associated with other fates or disposal of the biomass residues.

The existing commercial biomass power generating industry in the United States, which consists of approximately 1,700 MW (megawatts) of operating capacity actively supplying power to the grid, produces about 0.5 percent of the U.S. electricity supply. This level of biomass power generation avoids approximately 11 million tons per year of CO_2 emissions from fossil fuel combustion. It also avoids approximately two million tons per year of CH_4 emissions from the biomass residues that, in the absence of energy production, would otherwise be disposed of by burial (in landfills, in disposal piles, or by the plowing under of agricultural residues), by spreading, and by open burning. The avoided CH_4 emissions associated with biomass energy production have a greenhouse warming potential that is more than 20 times greater than that of the avoided fossil-fuel CO_2 emissions. Biomass power production is at least five times more effective in reducing greenhouse gas emissions than any other greenhouse-gas-neutral power-production technology, such as other renewable and nuclear.

Currently, the New Hope Power Partnership is the largest biomass power plant in North America. The 140 MWH facility uses sugar cane fiber (bagasse) and recycled urban wood as fuel to generate enough power for its large milling and refining operations as well as to supply renewable electricity for nearly 60,000 homes. The facility reduces dependence on oil by more than one million barrels per year, and by recycling sugar cane and wood waste, preserves landfill space in urban communities in Florida.

The amount of biomass available is usually not as great as stated in the example above. Many times, especially in Europe where large agricultural developments are not usual, the cost for transporting the biomass overcomes its actual value and therefore the gathering ground has to be limited to a certain small area. This fact leads to only small possible power outputs around 1 MW_{el}. To make an economic operation possible those power plants have to be equipped with the ORC technology, a cycle similar to the water steam power process just with an organic working medium. Such small power plants can be found in Europe.

Despite harvesting, biomass crops may sequester carbon. So for example soil organic carbon has been observed to be greater in switchgrass stands than in cultivated cropland soil, especially at depths below 12 inches. The grass sequesters the carbon in its increased root biomass. But the perennial grass may need to be allowed to grow for several years before increases are measurable.

3.2 Cellulose

Cellulose is an organic compound with the formula $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundred to over ten thousand $\beta(1\rightarrow4)$ linked D-glucose units. Cellulose is the structural component of the primary cell wall of green plants, many forms of algae and the oomycetes. Some species of bacteria secrete it to form biofilms. Cellulose is the most common organic compound on Earth. About 33 percent of all plant matter is cellulose (the cellulose content of cotton is 90 percent and that of wood is 50 percent).

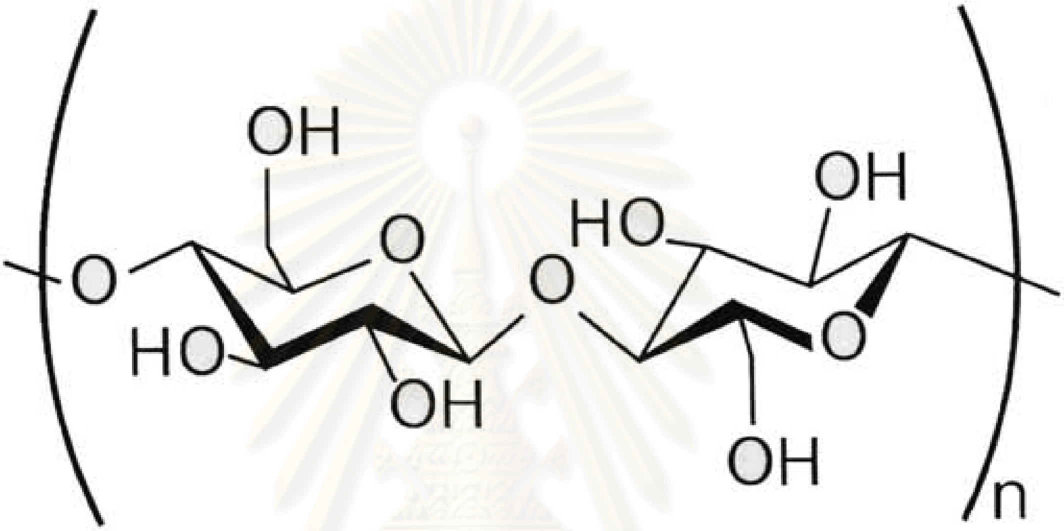

Figure 3.1 Cellulose structure

Cellulose is found in plants as micro fibrils (2-20 nm diameter and 100 – 40,000 nm long). These form the structurally strong frame work in the cell walls. Cellulose is mostly prepared from wood pulp. Cellulose is also produced in a highly hydrated form by some bacteria.

For industrial use, cellulose is mainly obtained from wood pulp and cotton. It is mainly used to produce cardboard and paper; to a smaller extent it is converted into a wide variety of derivative products such as cellophane and rayon. Converting cellulose from energy crops into biofuels such as cellulosic ethanol is under investigation as an alternative fuel source. Some animals, particularly ruminants and termites, can digest cellulose with the help of symbiotic micro-organisms that live in their guts. Cellulose is not digestible by humans and is often referred to as 'dietary fiber' or 'roughage', acting as a hydrophilic bulking agent for feces.

3.3 Supercritical water

Supercritical water is water at temperature and pressure above a critical point. Under these conditions water becomes a fluid. In the supercritical area there is one state of fluid and it has gas-like and liquid-like properties. Through, normal water has three situations, which are solid, liquid and gas. When water is in critical point, it becomes a fluid with unique properties that can be used to dissolve organic compounds. From figure 3.2 critical point of water is 22.1 MPa and 374 °C.

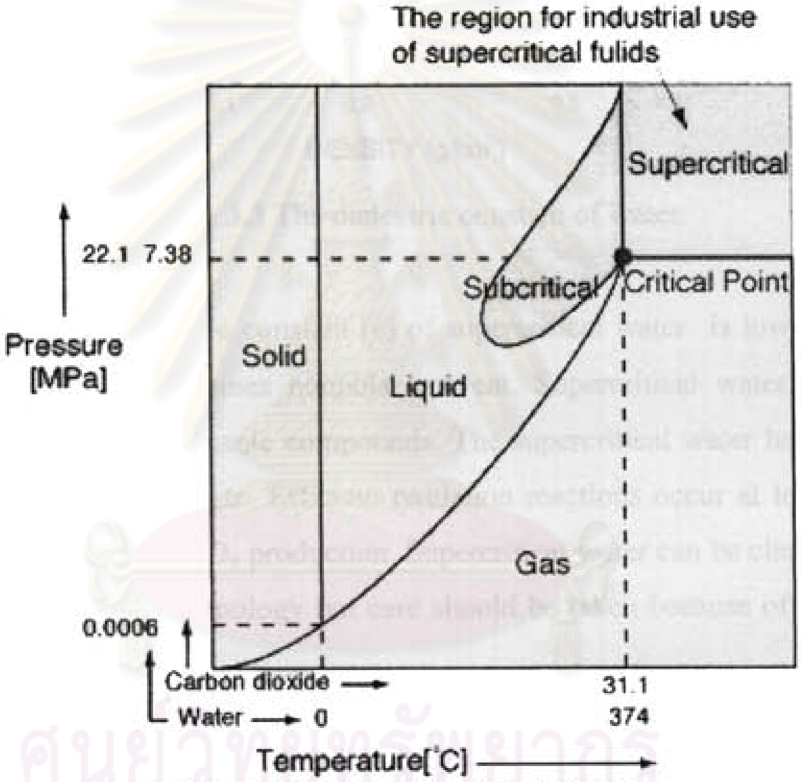

Figure 3.2 Phase diagram of fluids

Figure 3.3 shows the temperature/pressure dependency of the dielectric constant ε of water. The dielectric constant of supercritical water is in the range of from 2 to 30, which is similar to the range from a nonpolar solvent such as hexane (with a dielectric constant of about 1.8) to a polar solvent such as a methanol (with a dielectric constant of 32.6). In other words, with supercritical water it becomes possible to dissolve organic substances that do not dissolve in water under atmospheric conditions.

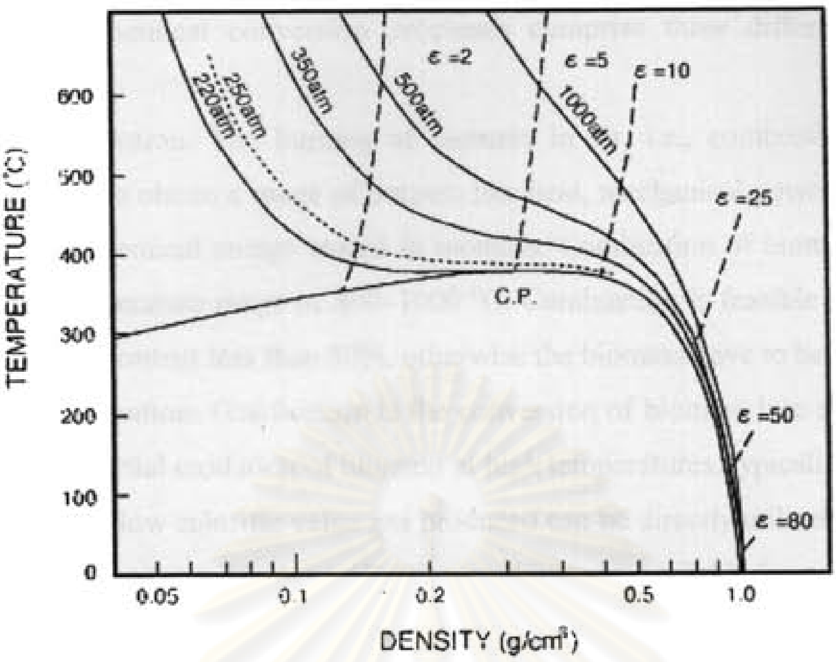

Figure 3.3 The dielectric constant of water

In other case, dielectric constant (ε) of supercritical water is lower than normal water, that make water becomes nonpolar solvent. Supercritical water is a nonpolar solvent that can be mixed organic compounds. The supercritical water has been used in decomposition of organic waste. Efficient oxidation reactions occur at low temperature (400-650 °C) with reduced NO_x production. Supercritical water can be classified as green chemistry or as a Clean Technology but care should be taken because of high pressures and temperatures.

3.4 Biomass conversion technologies

Biomass can be converted into useful forms of energy products using a number of different processes. Factors that influence the choice of process are the type and quantity of biomass feedstock. Different routes for biomass conversion into hydrogen rich gas are: (Saxena et al., 2007)

(i) Thermo-chemical conversion.
(ii) Bio-chemical/biological conversion.
(iii) Mechanical extraction.

Thermo-chemical conversion processes comprise three different processes as described below:

(i) Combustion: The burning of biomass in air, i.e., combustion is worldwide adopted process to obtain a range of outputs like heat, mechanical power or electricity by converting the chemical energy stored in biomass. Combustion of biomass produces hot gases in the temperature range of 800–1000 °C. Combustion is feasible only for biomass having moisture content less than 50%, otherwise the biomass have to be pre-dried

(ii) Gasification: Gasification is the conversion of biomass into a combustible gas mixture by the partial oxidation of biomass at high temperatures, typically in the range of 800–900 °C. The low calorific value gas produced can be directly utilized as a fuel for gas turbines and gas engines. Many gasification methods are available for producing fuel gas. Based on throughput, cost, complexity and efficiency issues, circulated fluidized bed gasifiers are suitable for large-scale fuel gas production.

(iii) Pyrolysis: Pyrolysis is conversion of biomass to liquid, solid and gaseous fractions by heating the biomass in the absence of air at around 500 °C temperature. In addition to gaseous product, pyrolysis produces a liquid product called bio-oil, which is the basis of several processes for the development of the various energy fuels and chemicals. Pyrolysis reaction is an endothermic reaction as mentioned below:

$$\text{Biomass+ Energy} \longrightarrow \text{Bio oil +Char + Gas.}$$

3.5 Biomass Gasification

Gasification is the conversion of biomass into a combustible gas mixture by the partial oxidation of biomass at high temperatures, typically in the range of 800–900 °C. The process performs partial oxidation to convert carbonaceous feed stock into gaseous energy carrier consisting of permanent, non-condensable gas mixture (CO, CO_2, CH_4, H_2 and H_2O). In an ideal gasification process biomass is converted completely to CO and H_2 although in practice some CO_2, water and other hydrocarbons including methane are formed. Most simple biomass gasifiers produce approximately equal proportions of CO and hydrogen.

The main reaction steps in biomass gasification are: (Kersten et al., 2003)

- Heating and pyrolysis of the biomass whereby converting biomass into gas, char and primary tar.

- Cracking of primary tar to gases and secondary and tertiary tars.

- Cracking of secondary and tertiary tars.

- Heterogeneous gasification reactions of the char formed during pyrolysis and homogeneous gas phase reactions.

- Combustion of char formed during pyrolysis and oxidation of combustible gases.

In a gasification processes, the solid fuels are completely converted (except the ashes in the feed) to gaseous products having different compositions. Because of the production of cleaner gaseous fuel as well as almost complete conversion of biomass, the gasification process for converting biomass into energy is becoming an attractive option. The char produced from the fast pyrolysis of biomass is highly reactive and can be gasified with gasifying agents such as steam, CO_2, oxygen and H_2 to gaseous fuels. Recently, there is a lot of interest in utilizing the pyrolysis derived char for steam gasification to produce gaseous fuel. The oxidation reaction involved is mentioned below:

$$C + O_2 \longrightarrow CO_2 \tag{1}$$

$$2(-2CH_2) + 3O_2 \longrightarrow 2H_2O + 2CO_2 \tag{2}$$

Meng et al. (2006) The gasification reactions of organic materials are also mentioned as follows:

$$C + H_2O \longrightarrow CO + H_2 \tag{3}$$

$$C + CO_2 \longrightarrow 2CO \tag{4}$$

$$(-2CH_2) + H_2O \longrightarrow CO + 2H_2 \tag{5}$$

$$(-2CH_2) + CO_2 \longrightarrow 2CO + H_2 \tag{6}$$

(i) Air gasification: Air gasification is most widely used technology as single product is formed at high efficiency and with out requiring oxygen. A low heating value gas is produced containing up to 60% N_2 having a typical heating value of 4–6 MJ/Nm^3 with byproducts such as water, CO_2, hydrocarbons, tar, and nitrogen gas. The reactor temperature of 900–1100 °C was achieved.

(ii) Oxygen gasification: Yields a better quality gas of heating value of 10–15 MJ/Nm^3. In this process relatively a temperature of 1000–1400 °C is achieved. But it requires an O_2 supply with simultaneous problem of cost and safety.

(iii) Steam gasification: Biomass steam gasification results in the conversion of carbonaceous material to permanent gases (H_2, CO, CO_2, CH_4 and light hydrocarbons), char and tar. To avoid corrosion problems, poisoning of catalysts and to improve the overall efficiency of the gasification process, tar components needs to be minimized. (Adhikari et al., 2006)

3.6 The reaction rate constant

In the chemical reactions considered in the following, it takes as the basis of calculation a species A, which is one of the reactants that is disappearing as a result of the reaction. The limiting reactant is usually chosen as basis of calculation. The rate of disappearance of A, $-r_A$, depends on temperature and composition. For many reaction it can be written as the product of a *reaction rate constant* k and a function of the concentrations (activities) of the various species involved in the reaction. The relation between reaction rate and concentration is shown in equation (3.1)

$$-\boldsymbol{r}_{\mathbf{A}} = [\boldsymbol{k}_{\mathbf{A}}\,(\mathbf{T})]\ [\ \mathbf{fn}\ \mathbf{C}_{\mathbf{A}}, \mathbf{C}_{\mathbf{B}}, \ldots\ ] \tag{3.1}$$

The algebraic equation that relates $-r_A$ to the species concentrations is called the kinetic expression or rate law. The specific rate of reaction, k_A, like the reaction rate $-r_A$, is always referred to a particular species in the reactions and normally should be subscripted with respect to that species. However, for reactions in which the stoichiometric coefficient is 1 for all species involved in the reaction.

The reaction rate constant k is not truly a constant, but is merely independent of the concentrations of the species involved in the reaction. The quantity k is also referred to as the **specific reaction rate (constant)**. It is almost always strongly dependent on temperature. In gas-phase reactions, it depends on the catalyst and may be a function of total pressure. In liquid systems it can also be a function of total pressure, and in addition can depend on other parameters, such as ionic strength and choice of solvent. Those other variables normally exhibit much less effect on the specific reaction rate than does temperature, so for the purposes of material presented here it will be assumed that k_A depends only on temperature. This assumption is valid in most laboratory and industrial reactions and seems to work quite well.

It was the great Swedish chemist Arrhenius who first suggested that the temperature dependence of specific reaction rate, k_A, could be correlated by an equation of type.

$$k_A(T) = Ae^{-(E/RT)} \tag{3.2}$$

where A = pre-exponential factor or frequency factor
E = activation energy, J/mol or cal/mol
R = gas constant = 8.314 J/mol · K = 1.987 cal/mol · K
T = absolute temperature, K

Equation (3.2) is known as the Arrhenius equation, has been verified empirically to give the temperature behavior of most reaction rate constants within experimental accuracy over fairly large temperature ranges.

The activation energy *E* has been equated with a minimum energy that must be possessed by reacting molecules before the reaction will occur. From the kinetic theory of gases, the factor $e^{-(E/RT)}$ gives the fraction of the collisions between molecules that together have this minimum energy *E*. Although this might be an acceptable elementary explanation, some suggest that *E* is nothing more than an empirical parameter correlating the specific reaction rate to temperature. The activation energy is determined experimentally by carrying out the reaction at several different temperatures. After taking the natural logarithum of Equation (3.2), it can be seen that a plot of ln k_A versus 1/T should be a straight line whose slope is proportional to the activation energy.

CHAPTER IV

EXPERIMENTAL

4.1 Feedstock

Cotton and Jatropha residue were ground with a vibration ball mill into cotton powder and jatropha residue powder that are used in all experiments. Appearance of cotton powder and jatropha residue powder are show in figure 4.1. Both of them were classified and chose particle size smaller than 150 μm. for using.

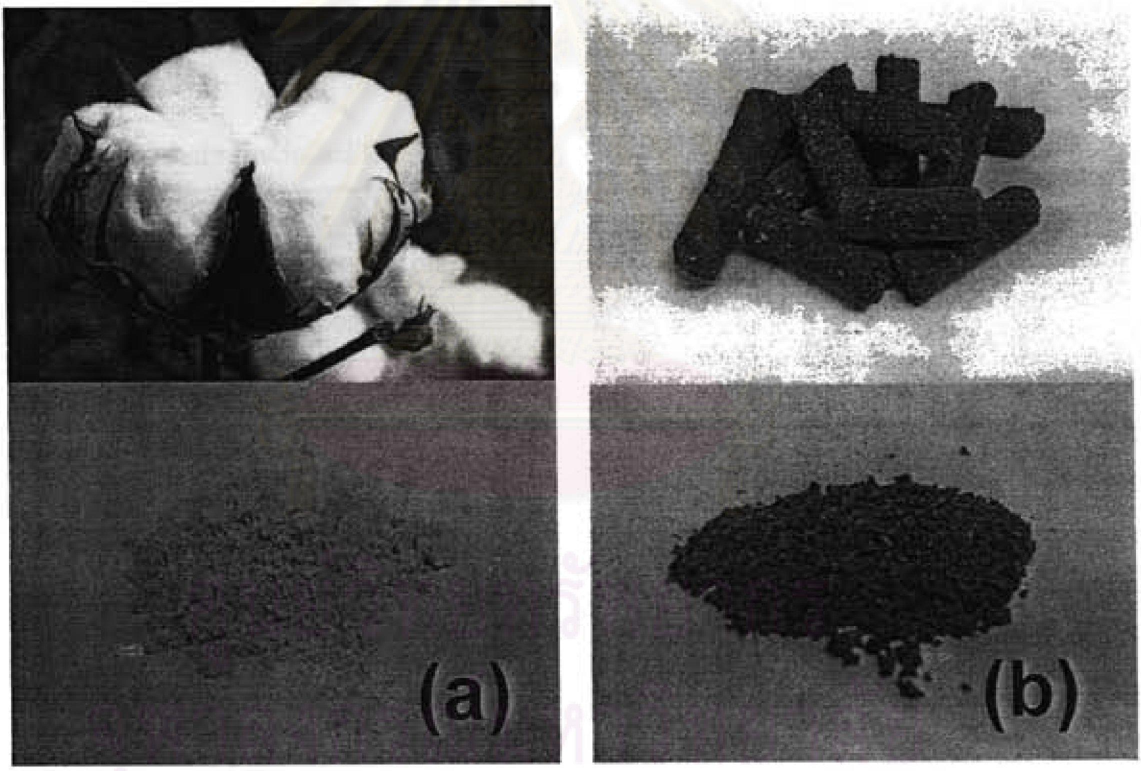

Figure 4.1 Image of biomass powder: (a) Cotton and (b) Jatropha residues

4.2 Raw material characterization

4.2.1 Elemental compositions

Table 4.1 and 4.2 are shown the elemental composition of cotton powder and jatropha residue powder. Element Analyzer (Perkin Elmer PE2400 SeriesII) has been used for analyzing chemical elements containing in cotton and jatropha seed residues.

Table 4.1 Chemical elements analysis of cotton powder

Elemental composition	wt%
C	39.5
H	5.9
N	0
Others (included O)	54.6

Table 4.2 Chemical elements analysis of jatropha residue powder

Elemental composition	wt%
C	41.6
H	6.6
N	2.5
Others (included O)	49.3

4.2.2 Particle size distribution

Figure 4.2- 4.6 show the particle size distribution of cotton powder and jatropha residue powder, which are ground into smaller than 150, 90 and 45 μm by vibration ball mill and measured by Master sizer 2000.

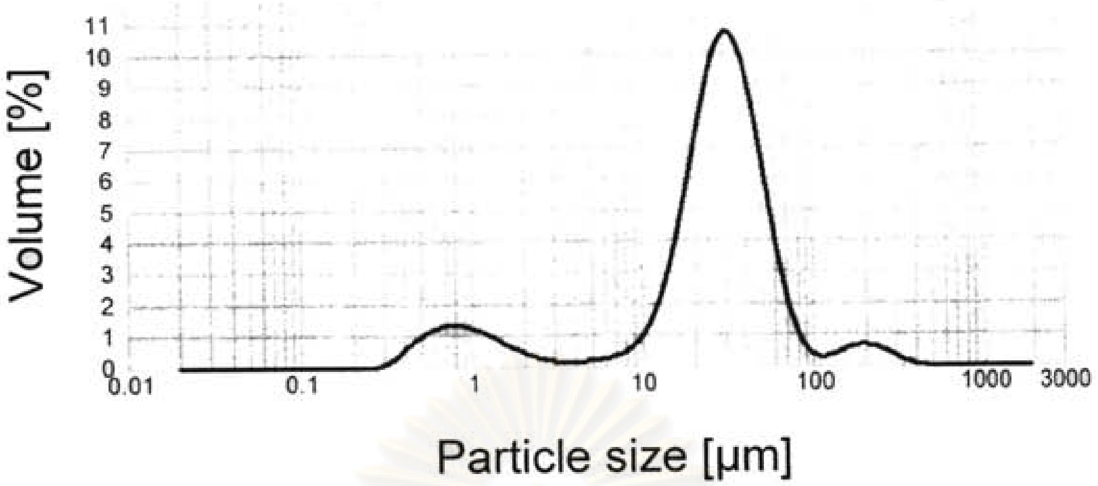

Figure 4.2 Particle size distribution of cotton powder, smaller than 45 μm.

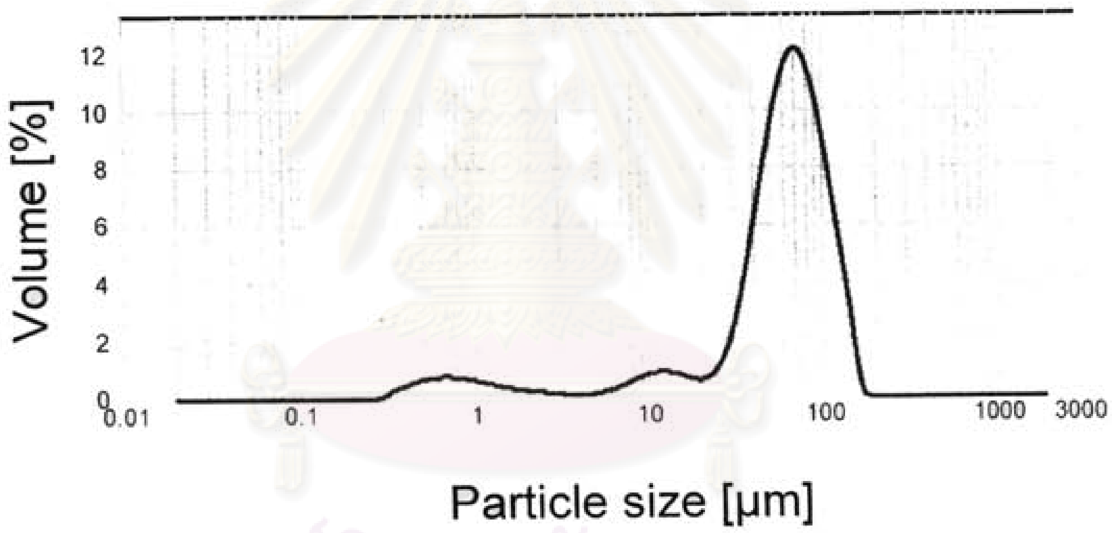

Figure 4.3 Particle size distribution of cotton powder, smaller than 90 μm.

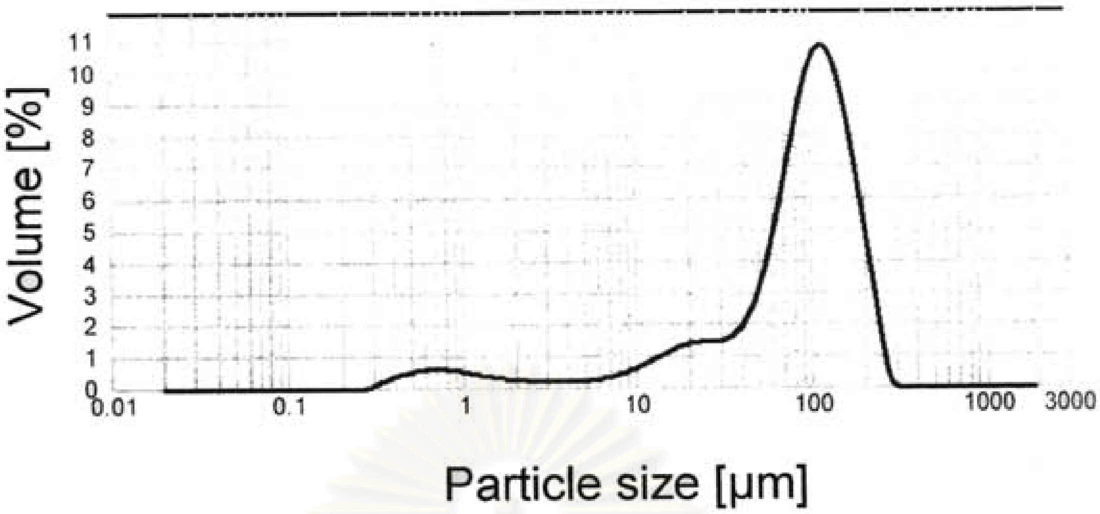

Figure 4.4 Particle size distribution of cotton powder, smaller than 150 µm.

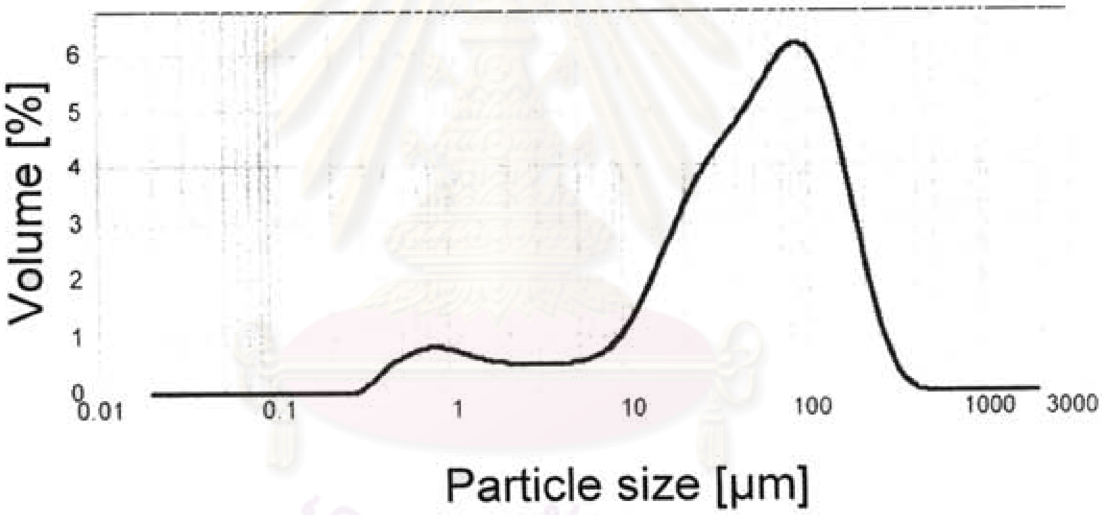

Figure 4.5 Particle size distribution of jatropha residue powder, smaller than 90 µm.

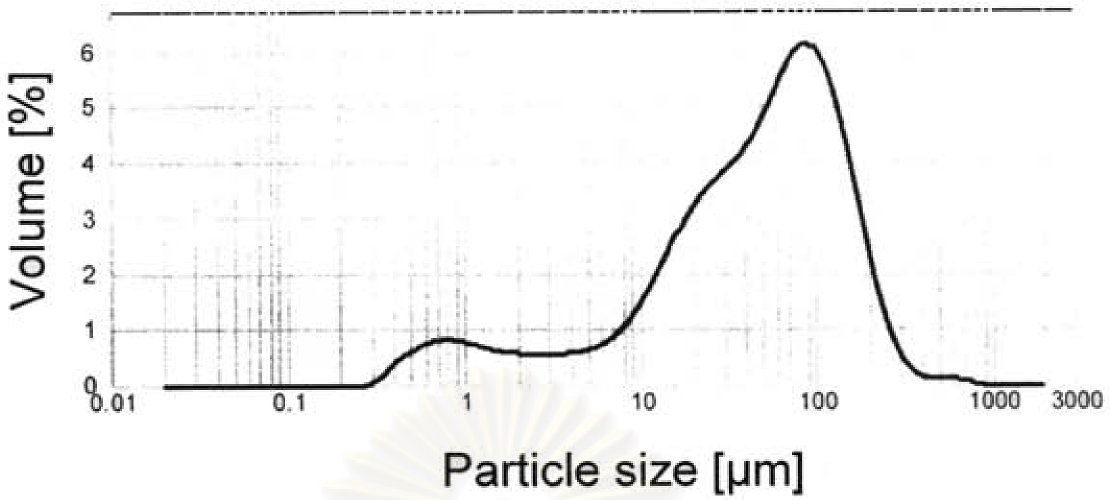

Figure 4.6 Particle size distribution of jatropha residue powder, smaller than 150 µm.

Table 4.3 shows the average particle size in each range.

Table 4.3 Average particle size in each range of particle size

Range of sieve size (µm)	Average particle size of cotton powder (µm)	Average particle size of jatropha powder (µm)
< 45	29	-
< 90	63	51
< 150	95	51.6

4.2.3 USDA method

This method use for determine the amount of hemi-cellulose or cell wall, lignin and cellulose in the raw materials. The step of USDA method shows in appendix A. Table 4.4 shows the components of the rubber wood powder (dry weight basis) determined by the USDA's method.

Table 4.4 Overall analysis of biomass components

Contents [wt%]	Cotton powder	Jatropha powder
Hemi-cellulose	-	50
Lignin	-	12.3
Cellulose	96.7	37.1
Ash	3.3	1.1

4.3 Biomass gasification

4.3.1 Tubular flow reactor

Both of biomass feedstocks were gasified using tubular flow reactor at thermal engineering laboratory of Hiroshima University, Japan.

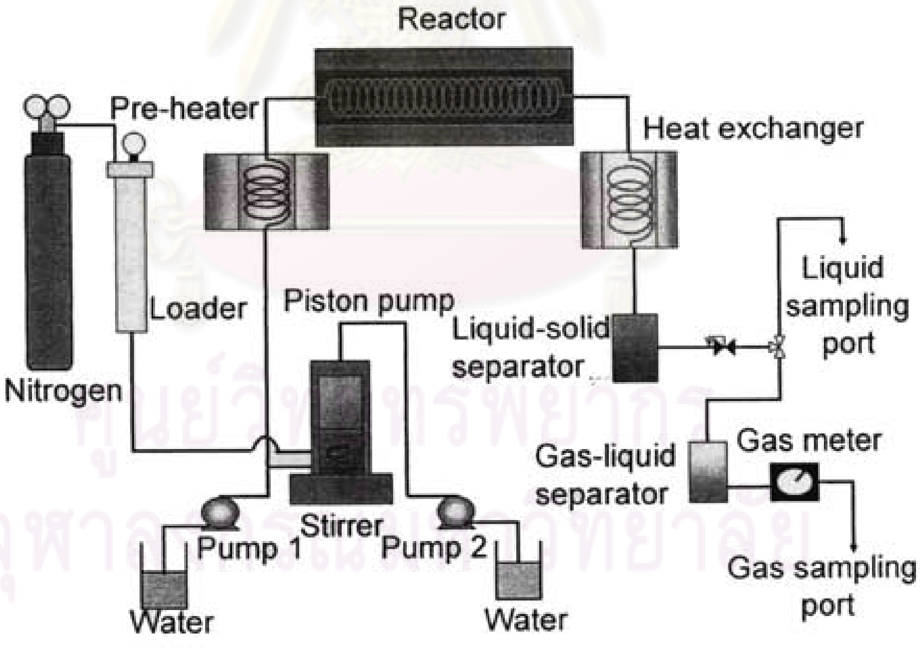

Figure 4.7 Experimental apparatus

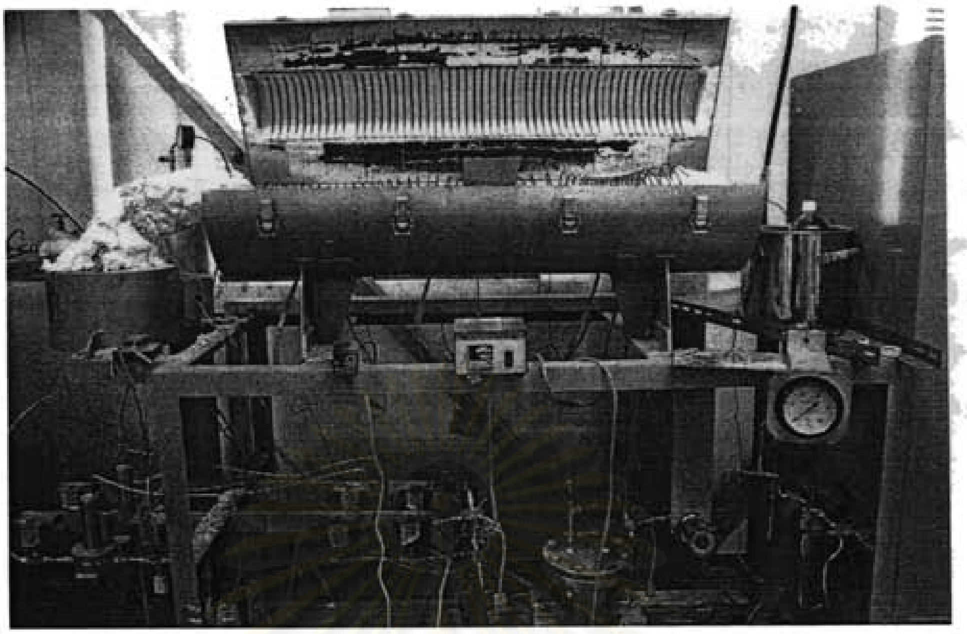

Figure 4.8 Experimental equipment

All gasification has been performed in a tubular flow reactor, shown in figure 4.7 and 4.8. An investigation of the influence of temperature and concentration on the gasification of cotton powder was conducted with an aim to improve the gasification yield of hydrogen. The tubular flow reactor had the inner diameter of 2.17 mm and the length of 12 m. Cotton or jatropha residue powder suspension was fed into the reactor by a piston pump (Toyokoatu Co., designed for using), shown in figure 4.9.

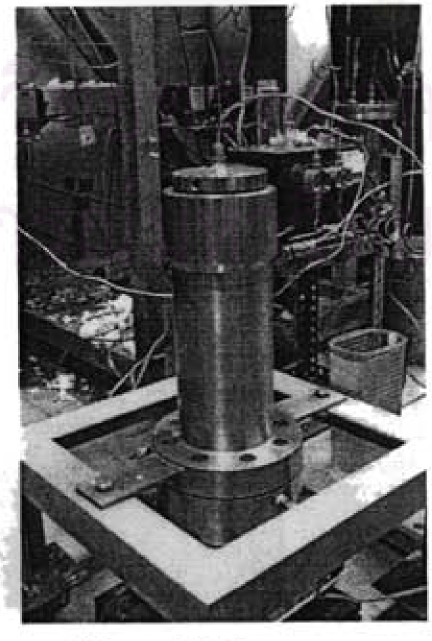

Figure 4.9 Piston pump

Except otherwise stated, the reactor temperature and pressure were 500°C and 25 MPa, respectively. The reactor was cooled down by the cooler before solid remaining was separated from suspension by the solid-liquid separator. Meanwhile, the exit gas flow was separated by the liquid-gas separator. The gas generation rate was measured by the gas meter (W-NK0.5A, Shinagawa Co.), shown in figure 4.10. The gas and liquid samples were analyzed with gas chromatograph (GC-14B, Shimadzu), shown in figure 4.11 and TOC (TOC-V_{CPH}, Shimadzu), shown in figure 4.12, respectively. In this work, the reaction temperature was varied from 400 to 700 °C and residence time in the range 80 – 222 s.

Figure 4.10 Gas meter

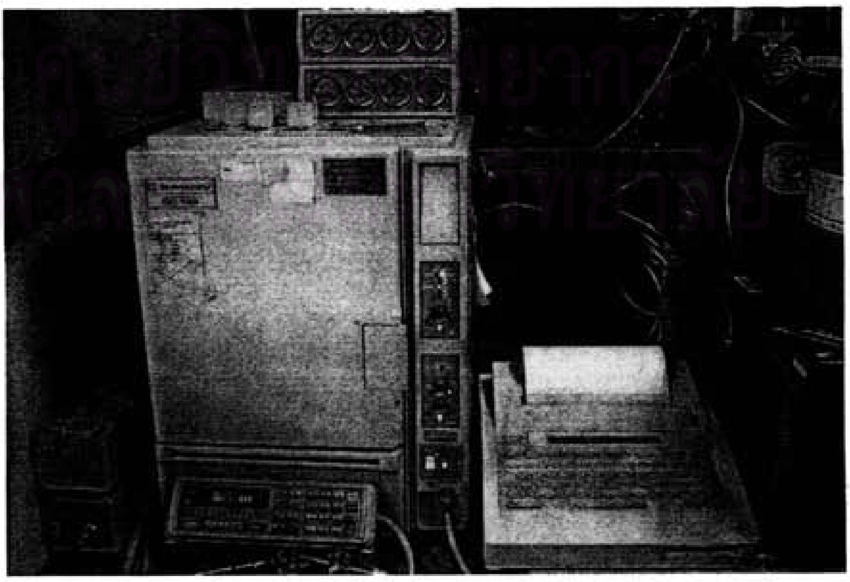

Figure 4.11 Gas chromatography

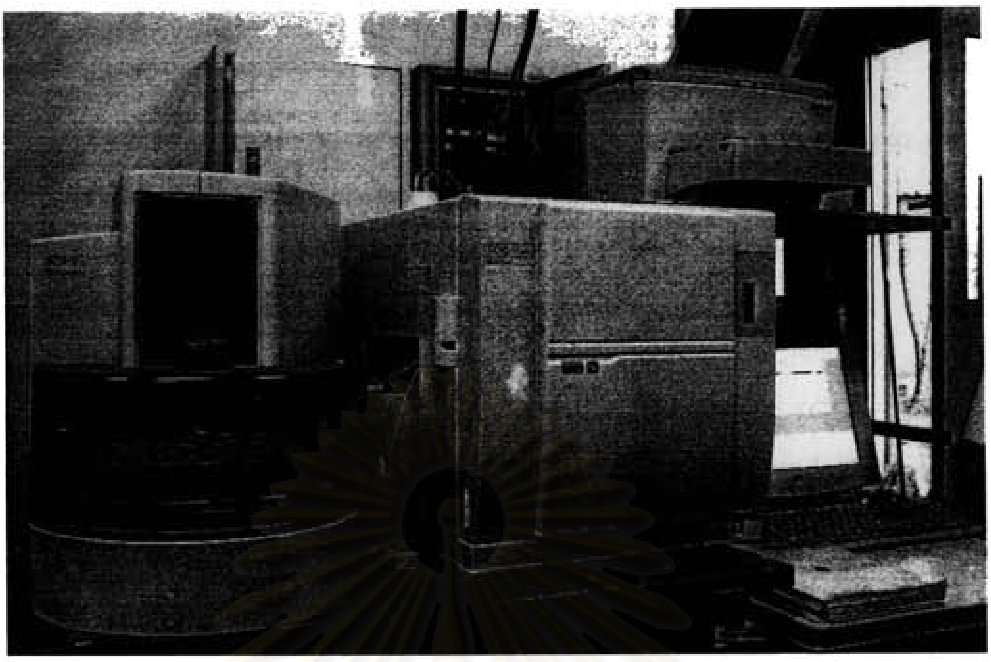

Figure 4.12 TOC analyzer

4.4 Collecting gas sample

First, we prepared 0.1 mol/L of Hydrochloric acid. In this case, Hydrochloric acid 6 mol/L (purchased from Sigma Aldrich) was diluted to 0.1 mol/L by deionized water (< 1 µs/cm; Organo water deionizer model BB-5A). The line of gas sampling port is U-shape. It is designed for collecting the gas samples under Hydrochloric acid solution as shown in figure 4.13. The idea is protection gas leakage Because Hydrocarbon gas can not dissolve in acid.

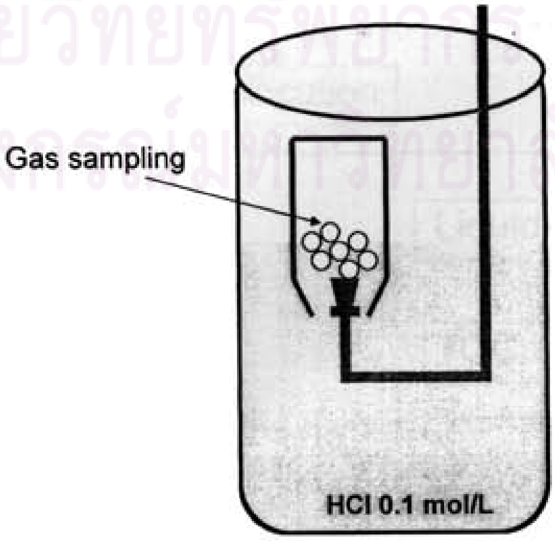

Figure 4.13 Gas sampling collection apparatus

4.5 Product analysis

The gasification products from biomass gasification are divided into gas product and liquid product. The step of product analysis is shown in figure 4.14.

4.5.1 Gas product

The gas product was analyzed with gas chromatography (GC). There are two types of gas sample analysis. First, carbon analysis was measured using helium as a carrier gas. Carbon dioxide and carbon monoxide were detected by GC-TCD (GC with a thermal conductivity detector) and methane, ethane and ethylene were detected by GC-FID (GC with a flame ionization detector). Second, hydrogen analysis was measured using nitrogen as a carrier gas. Hydrogen was detected by GC-TCD.

4.5.2 Liquid product

The liquid product was also analyzed by a Total Organic Carbon analyzer or TOC analyzer for measuring the amounts of carbon content in liquid product (non-purgeable organic carbon or NPOC) and the gas product that was dissolved in liquid (inorganic carbon or IC).

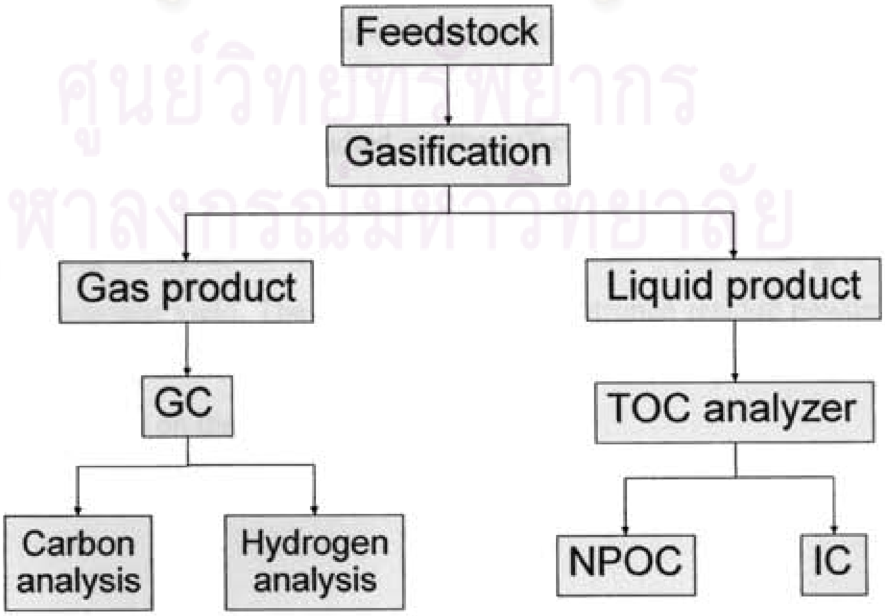

Figure 4.14 Scheme of step followed in product analysis

4.6 Experimental condition

4.6.1 The effect of concentration of biomass on gasification

Cotton powder and jatropha residue powder were varies concentrations in a range of 0.05 – 1.0 wt% for gasification. To check the reaction order in each concentration of both biomass feedstock and the gas product yield should be same. In this studied assumed the reaction of cotton powder and jatropha residue in gasification is the first order reaction. The cotton powder and jatropha residue powder were used in this studied that were classified into smaller than 150 μm. Table 4.5 shows the concentration conditions of biomass gasification.

Table 4.5 Concentration conditions of biomass gasification

	Cotton	Jatropha residue
Concentration (wt %)	0.1, 0.2, 0.3, 0.5 and 1.0	0.05, 0.1, 0.2 and 0.3
Temperature (°C)	500 °C	500 °C
Water flow rate (mL./min.)	2.0	2.0
Residence time (s)	119	119
Reactor length (m)	12	12
Pressure (MPa)	25	25

4.6.2 The effect of temperature on biomass gasification

In this studied, first will studied on the effect of temperature on gasification of cotton powder and jatropha residue powder. By varies temperature in a range of 400 – 700 °C for finding the optimum temperature of gasification which could give gas product with optimal hydrogen yield. The cotton powder and jatropha residue powder were used in this studied that were classified into smaller than 150 μm. Table 4.6 shows the conditions for studied on the effect of temperature .

Table 4.6 Temperature conditions of biomass gasification

	Cotton	Jatropha residue
Concentration (wt %)	1.0	0.1
Temperature (°C)	400, 500, 600 and 700	400, 500, 600 and 700
Water flow rate (mL./min.)	2.0	2.0
Residence time (s)	222, 119, 94 and 80	222, 119, 94 and 80
Reactor length (m)	12	12
Pressure (MPa)	25	25

4.6.3 The effect of particle size of biomass on gasification

In this studied, the cotton powder and jatropha residue powder were ground and classified into smaller than 150 μm, smaller than 90 μm. and smaller than 45 μm. The idea is, when the cotton powder and jatropha residue powder were crushed in to smaller size the surface area was increased compared with the bigger size. The smaller size may give high yield of gas product. Table 4.6 shows the conditions of the difference of particle size of biomass gasification.

Table 4.6 conditions of difference particle size on biomass gasification

	Cotton	Jatropha residue
Concentration (wt %)	1.0	0.1
Temperature (°C)	600	600
Water flow rate (mL./min.)	2.0	2.0
Residence time (s)	94	94
Reactor length (m)	12	12
Pressure (MPa)	25	25
Particle size (μm.)	45, 90 and 150	90 and 150

4.6.4 The effect of residence time on biomass gasification

The varies of residence time is depend on temperature and water flow rate. That mean, residence was changed when temperature or water flow rate was changed. Then temperature was fixed and varies only on water flow rate. The water flow rate that used in this studied is 1.5, 2 and 3 mL/min. They made the residence time changed to 125, 94 and 63 second, respectively. The idea is, studying the effect of residence time on biomass gasification and longer residence time may give high yield of gas product. Table 4.7 shows conditions of difference residence time of biomass gasification.

Table 4.7 conditions of difference residence time on biomass gasification

	Cotton	Jatropha residue
Concentration (wt %)	1.0	0.1
Temperature (°C)	600	600
Water flow rate (mL./min.)	1.5, 2.0 and 3.0	1.5, 2.0 and 3.0
Residence time (s)	125, 94 and 63	125, 94 and 63
Reactor length (m)	12	12
Pressure (MPa)	25	25
Particle size (μm.)	45	90

CHAPTER V

RESULTS AND DISCUSSIONS

Referring to many experimental results reported in other previous works, this research has set its aim to study effect of concentration on biomass gasification. Investigate optimum temperature of gasification which could give gas product with optimal hydrogen yield. Determine variation of residence time that would give maximum gasification yield. The effect of particle size of feedstock on biomass gasification were thoroughly investigated and then reported and discussed in this chapter.

In this studied, the gas products, which were identified and quantified, were Hydrogen, carbon monoxide, carbon dioxide, methane with a small amount of ethylene and ethane.

5.1 The study of operating parameters on cotton gasification

5.1.1 The effect of concentration

The effect of solution concentration on gasification of cotton powder was examined in the reason of finding suitable value of cotton concentration that gives high fraction of hydrogen. From literature review, Guo et al., (2005) studied the effect of solution concentration on biomass gasification. It found that higher concentration cannot improve gasification efficiency. Schmieder et al., (1999) said at higher feed concentrations (constant potassium concentrations) soot and tar formation appears. Then, we chose to vary the feedstock concentrations in a range of 0.05 – 1.0 wt%. To study only solution concentration, we have to specify reaction temperature and pressure. Then we conducted with fixed temperature at 500 °C and pressure at 25 MPa as shown in table 4.5. The result is shown in figure 5.1. It is shown that the concentration of feedstock has essential effect on biomass gasification. For the gas product, the fraction of Hydrogen and carbon dioxide of low concentration feedstock gasification are higher than those of high concentration feedstock gasification. While the fraction of methane, ethylene, ethane and carbon monoxide of higher concentration feedstock are higher than the lower concentration feedstock. But the carbon gasification efficiency of low concentration feedstock is not much different compared with high concentration feedstock. The reason might be the temperature is not high enough in the entrance region of reactor and biomass gasification is an endothermic reaction. Then at low temperature, biomass is gasified with the formation of char and tar which are difficult to decompose in supercritical water (Lu et al., 2005). The effect of biomass concentration on carbon gasification efficiency is shown in figure 5.2. The total organic carbon (TOC) was increased with increasing cotton concentration. That mean, an increasing in concentration of feedstock leads to amount of carbon in liquid product. We regard the carbon gasification efficiency = (the total carbon in the product gas)/(the total carbon in the dry feedstock).

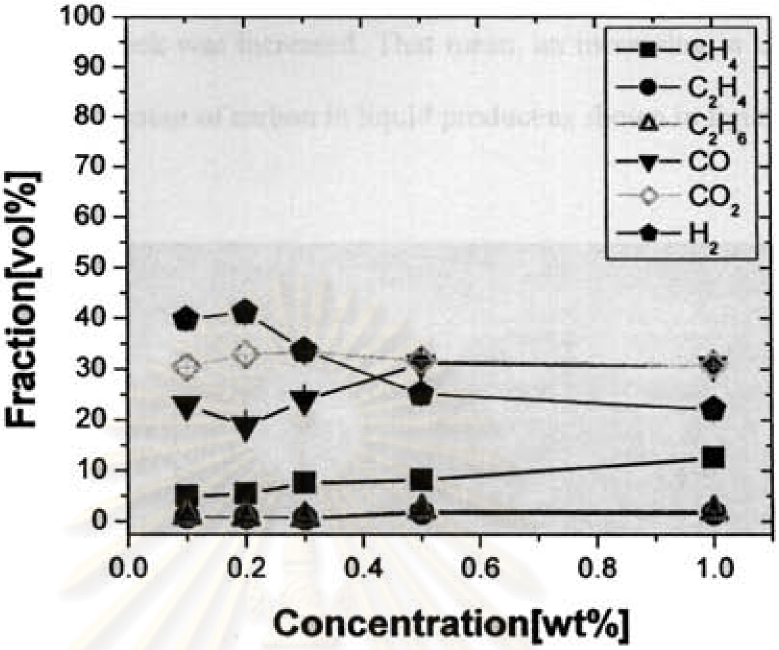

Figure 5.1 Gas products of each concentration of cotton.

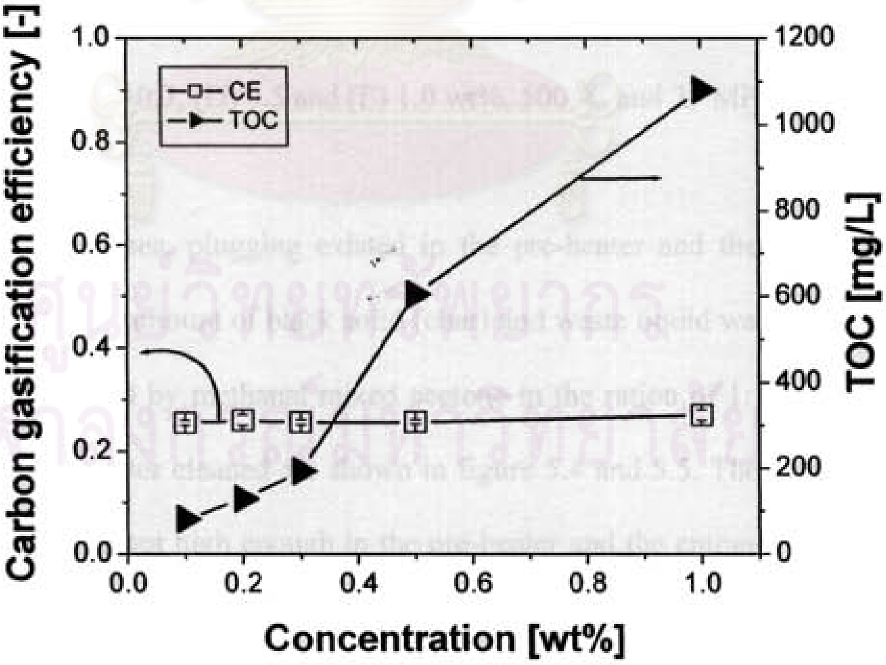

Figure 5.2 Carbon gasification efficiency of each concentration of cotton.

For liquid product, the color of liquid product became to dark yellow when concentration of feedstock was increased. That mean, an increasing in concentration of feedstock leads to amount of carbon in liquid product as shown in figure 5.3.

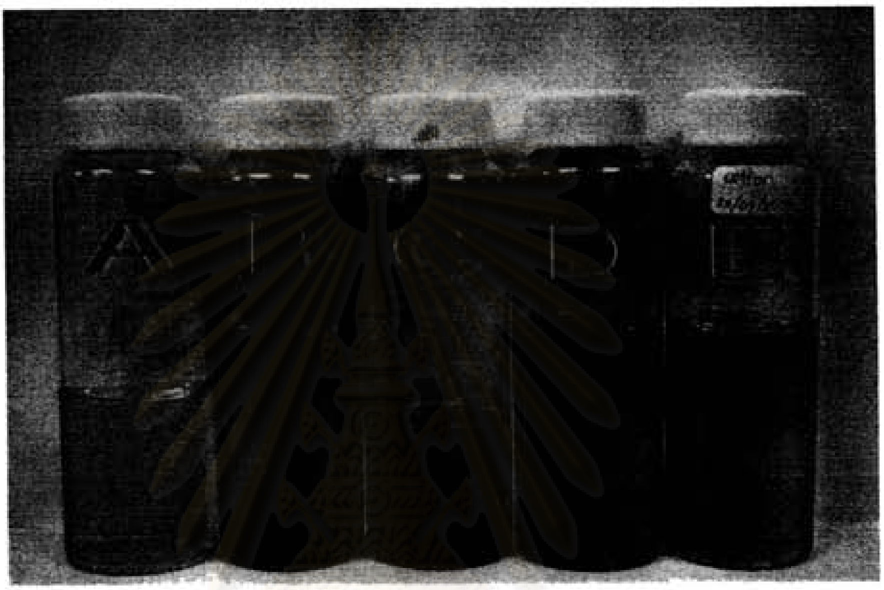

Figure 5.3 Liquid products of cotton gasification at concentration of (A) 0.1, (B) 0.2, (C) 0.3, (D) 0.5 and (E) 1.0 wt%, 500 °C and 25 MPa.

In some cases, plugging existed in the pre-heater and the entrance area of reactor. There was amount of black solid (char) and waste liquid was yellow when the reactor was cleaned by methanal mixed acetone in the ration of 1:1. The black solid and waste liquid after cleaned are shown in figure 5.4 and 5.5. The reasons might be the temperature is not high enough in the pre-heater and the entrance area of reactor. The temperature in that region might be not a range of temperature of supercritical water. At low temperature, biomass is gasified with the formation of char and tar which are difficult to decompose. These tar and char deposited on the wall of the line in pre-heater and the entrance area of reactor. Then, there was the plugging occurs.

Anyway, the ash from biomass gasification can also lead to reactor plugging. It can believe that high temperature, high heating rate (for batch reactor) and catalyst are required for gasification of high concentration feedstock.

Figure 5.4 Black solid (char)

Figure 5.5 Waste liquid after cleaned the reactor

In the case of non-catalyst gasification condition, cellulose was slightly decomposed over 200 °C to produce water-soluble products, which are almost sugars; no gas, no oil and no char or tar were produced. Over 300 °C, char and tar production was obtained (Minowa T., 1998). From observation, the reaction scheme of this biomass gasification might be as follows:

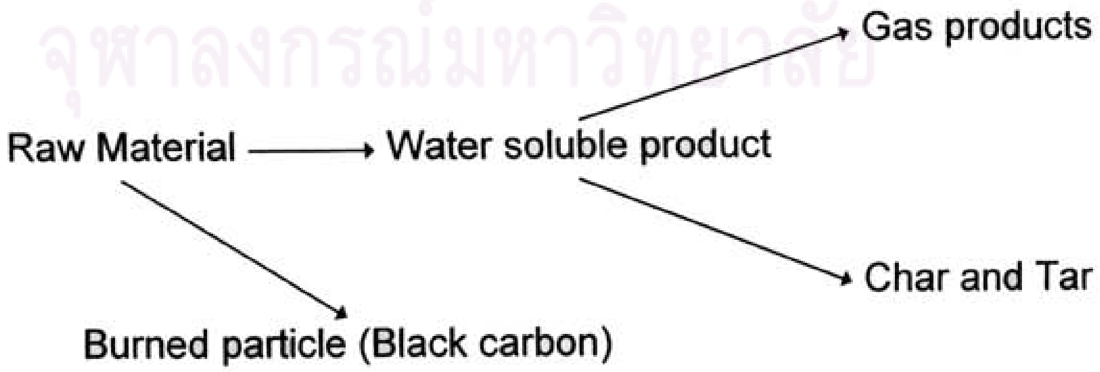

Figure 5.6 Model schematic

5.1.2 The effect of temperature

From the previous study, we know that only increasing concentration cannot improve the fraction of hydrogen. Guo et al., (2005) et al. studied the effect of temperature on biomass gasification. It found that temperature has significant effect on gasification. Feedstock of 1.0 wt% of cotton was gasified at 25 MPa. The feedstock were varies temperature in a range of 400 – 700 °C. The conditions in this studied are shown in table 4.7. The result is shown in figure 5.7. Temperature has a significant effect on biomass gasification in supercritical water. The fraction of hydrogen and methane were improved when increasing temperature while carbon dioxide and carbon monoxide were reduced. This would be attributed to that the selective formation of hydrogen and methane would be more enhanced under higher temperature conditions. Carbon gasification efficiency was improved when temperature was increased from 400 – 700 °C. The result is shown in figure 5.8. At lower temperature, the color of the liquid product became yellow and darker than the color of liquid at higher temperature. The reasons might be high temperature promotes the free-radical reactions (Buhler et al., 2002) which are needful for gas formations. Hence, the contents of the gases which are hydrogen and methane increase sharply. Xu et al. (1997) studied the glucose gasification in supercritical water with coconut shell activated carbon catalyst. They found that when temperature is raised from 500 °C to 600 °C, the carbon gasification efficiency increases from 51% to 98%, and hydrogen increases from 0.46mol to 1.7 mol. In our case, Hydrogen fraction increase sharply from 500 to 600 °C same as them, the carbon gasification efficiency improve with increasing temperature.

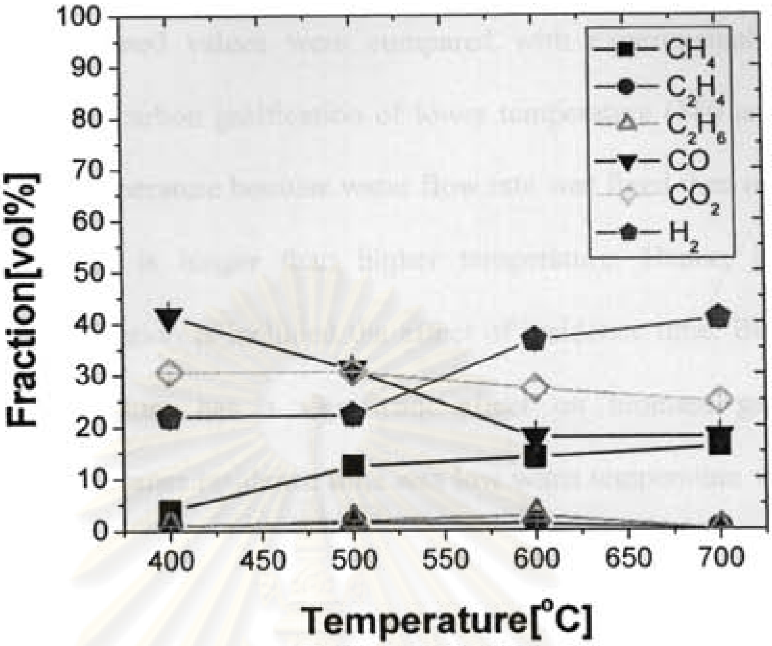

Figure 5.7 Gas products of each temperature of cotton.

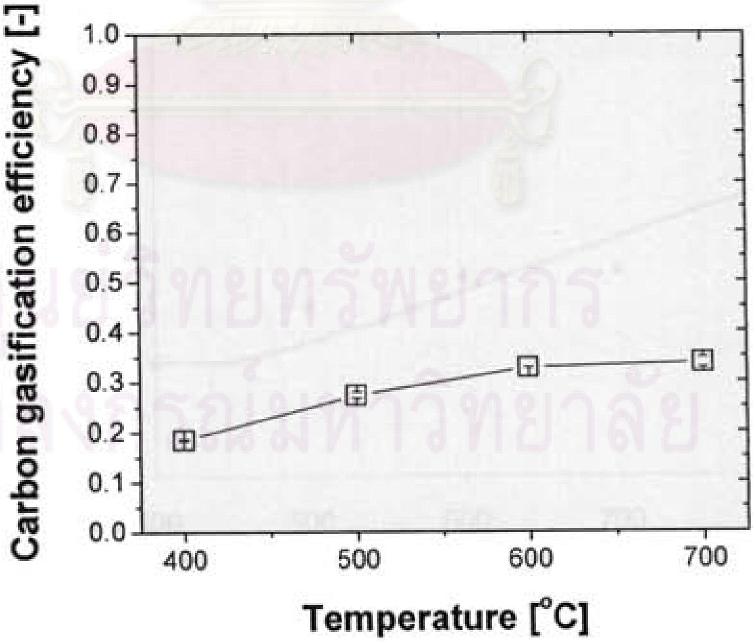

Figure 5.8 Carbon gasification efficiency of each temperature of cotton.

The calculated values of carbon gasification efficiency are shown in figure 5.9 and 5.10. The calculated values were compared with experimental values. For calculated values, the carbon gasification of lower temperature (380 and 390 °C) is higher than higher temperature because water flow rate was fixed then residence time of lower temperature is longer than higher temperature. Hence, the effect of temperature on gasification is included the effect of residence time. But it could be confirm that temperature has a significant effect on biomass gasification in supercritical water. Because residence time was low when temperature was high with fixed water flow rate but carbon gasification efficiency was improved when increasing temperature.

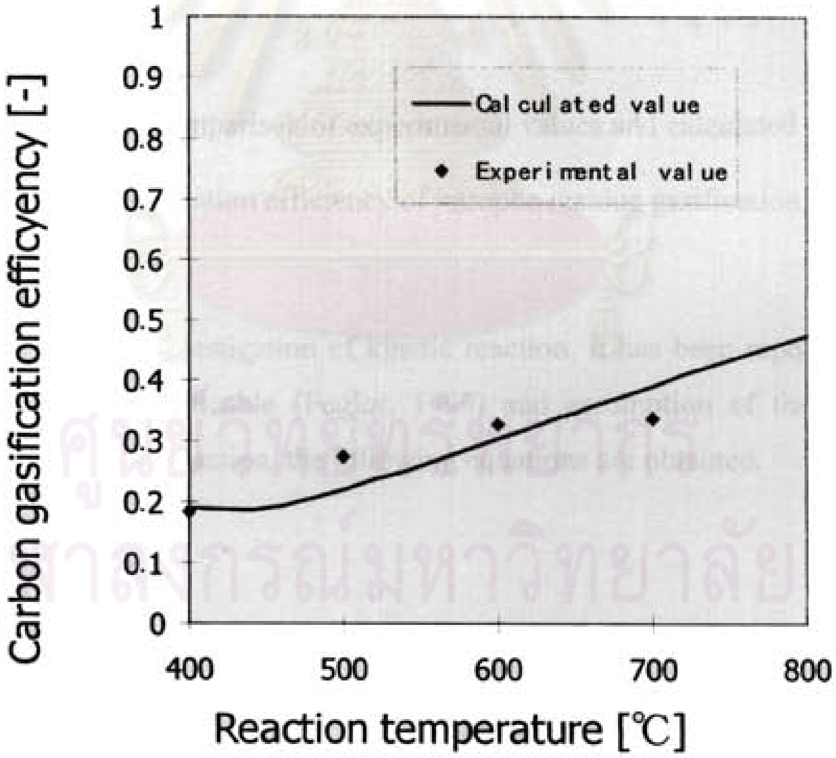

Figure 5.9 Comparison of experimental values and calculated values on Carbon gasification efficiency of cotton gasification.

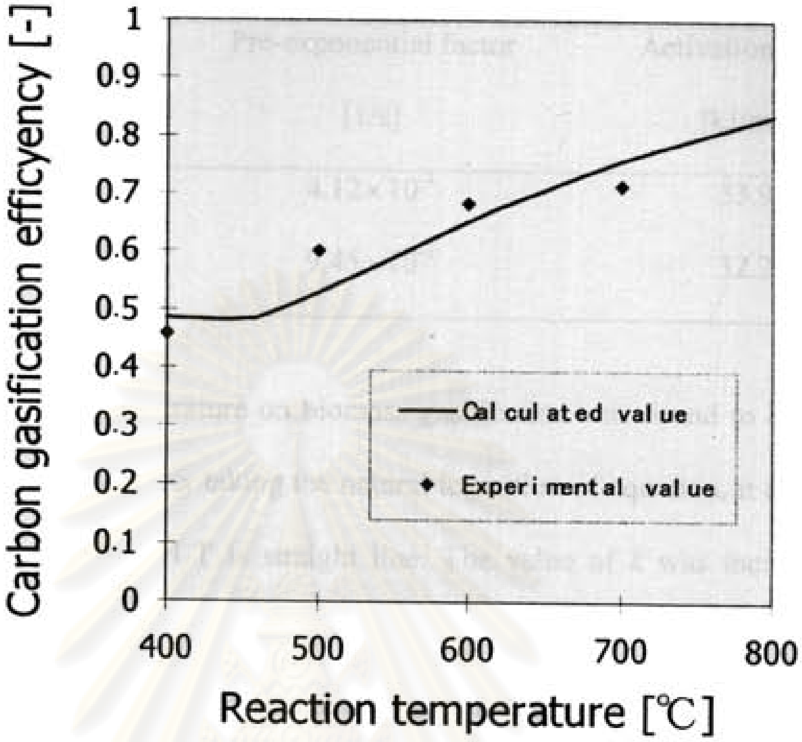

Figure 5.10 Comparison of experimental values and calculated values on Carbon gasification efficiency of jatropha residue gasification.

For the investigation of kinetic reaction, it has been reported that the Arrenius rate law is applicable (Foglor, 1999) and assumption of the first order reaction for gasification reaction, the following equations are obtained.

$$-r = kC^n \tag{1}$$

$$\frac{dC}{dt} = -k_0 \exp\left(\frac{-E_a}{RT}\right)C \tag{2}$$

$$x = 1 - \exp\left[-k_0 \exp\left(\frac{-E_0}{RT}\right)t\right] \tag{3}$$

The values are shown in table 5.1

Table 5.1 Parameters of reaction rate

	Pre-exponential factor [1/s]	Activation energy [kJ/mol]
Cotton	4.12×10^{-1}	33.97
Jatropha residue	9.45×10^{-1}	32.21

The effect of temperature on biomass gasification was found to be complied with the Arrhenius law. After taking the natural logarithm of equation, it can bee seen that a plot of ln *k* versus 1/T is straight line. The value of *k* was increased when increasing temperature. The graphs are shown in figure 5.11 and 5.12. From this result, it can believe that the temperature has essential effect on biomass gasification.

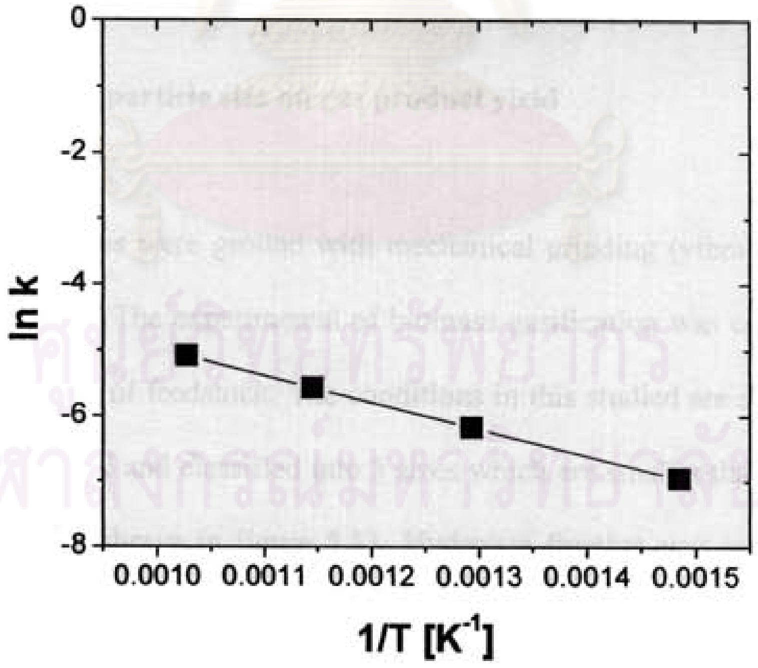

Figure 5.11 Arrhenius plot of reaction rate for cotton gasification

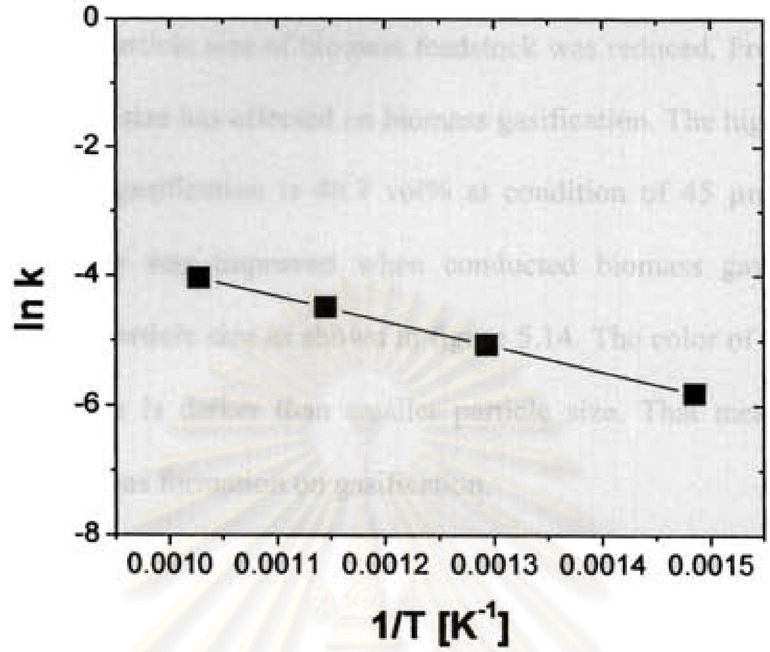

Figure 5.12 Arrhenius plot of reaction rate for jatropha gasification

5.1.3 Effect of particle size on gas product yield

Both of biomass were ground with mechanical grinding (vibration ball mill) before it was gasified. The experimental of biomass gasification was conducted with different particle sizes of feedstock. The conditions in this studied are shown in table 4.7. Cotton was ground and classified into 3 sizes which are smaller than 150, 90 and 45 μm. The result is shown in figure 5.13. Hydrogen fraction was improved when conducted the biomass gasification of smaller particle size of cotton feedstock. The trend of hydrogen fraction is same as previous condition that higher hydrogen fraction is obtained with gasification of high temperature. As expected the ground biomass feedstock with smaller particle size could provide the increased yield of hydrogen.

Base on the experimental results, carbon monoxide was decreased while hydrogen was increased when particle size of biomass feedstock was reduced. From this results found that the particle size has effected on biomass gasification. The highest hydrogen fraction from cotton gasification is 40.2 vol% at condition of 45 μm. The carbon gasification efficiency was improved when conducted biomass gasification at a condition of smaller particle size as shown in figure 5.14. The color of liquid product of bigger particle size is darker than smaller particle size. That mean the smaller particle size promote gas formation on gasification.

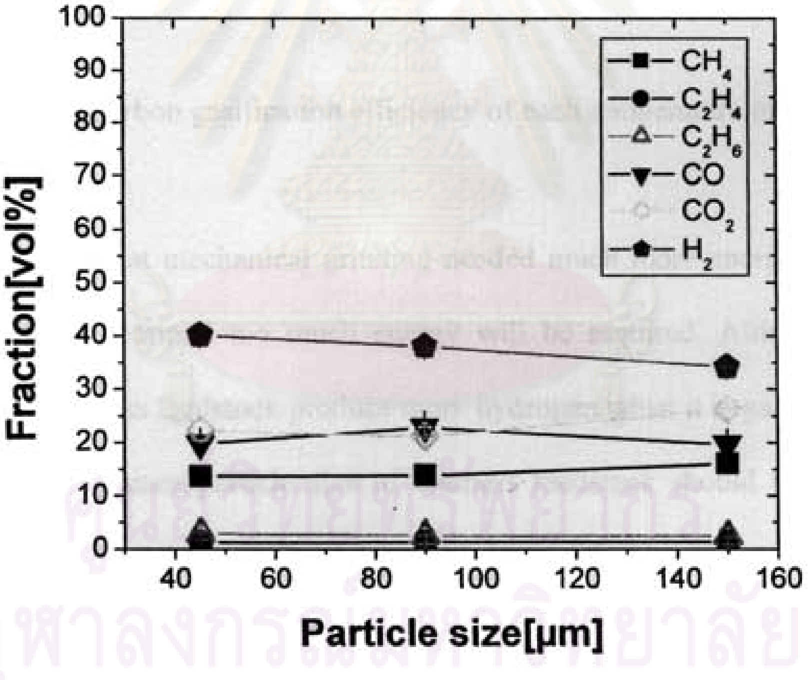

Figure 5.13 Gas products of each particle size of cotton.

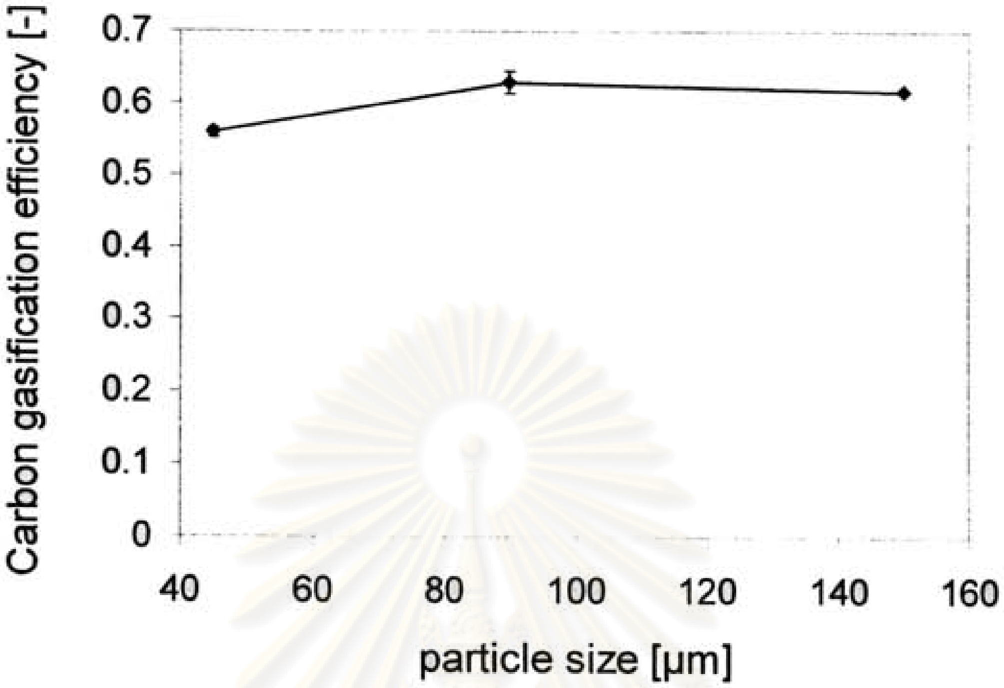

Figure 5.14 Carbon gasification efficiency of each temperature of cotton.

It is known that mechanical grinding needed much more energy. Hence, the smaller particle is obtained too much energy will be required. Although, smaller particle size of biomass feedstock produce more hydrogen when it is gasified. It is not economical. An optimum particle size of biomass feedstock should be found with considering economy and possibility.

5.1.4 Effect of residence time on gas product yield

Cotton powder was conducted under condition of 600 °C, 25 MPa and different water flow rate as shown in table 4.8. For water flow rate, it makes the residence time changes when the water flow rate is changed. The water flow rate was fixed into 3 values which are 1.5, 2.0 and 3.0 mL/min. Hence, the residence time was changed to 3 values which are 125, 93 and 63 second, respectively. From previous studied, it is known that higher temperature obtained the higher hydrogen fraction. Therefore in this studied, the temperature was fixed and varied in water flow rate for changed residence time. By varied the water flow rate is 1.5, 2.0 and 3.0 mL/min. The result is shown in figure 5.15. As shown in figure 5.15 for cotton gasification, it is shown that the hydrogen fraction increases sharply as the residence time increases from 63 to 93 s and methane fraction increases as the residence time increases from 63 to 125 s. At the same time, the carbon monoxide fraction has a sharp to decrease with increasing residence time from 63 to 125 s. The color of liquid products changed to light yellow with increasing residence time that mean organic carbon in raw material was gasified to gas product more than liquid product. It is shown in carbon gasification efficiency. Carbon gasification efficiency was improved when residence time was increased as shown in figure 5.16. Thus, Its can believe that residence time effect on biomass gasification. Longer residence time is need to biomass gasification. In this studied, the residence time of 125 s obtained the highest carbon gasification efficiency and high fraction of hydrogen and methane.

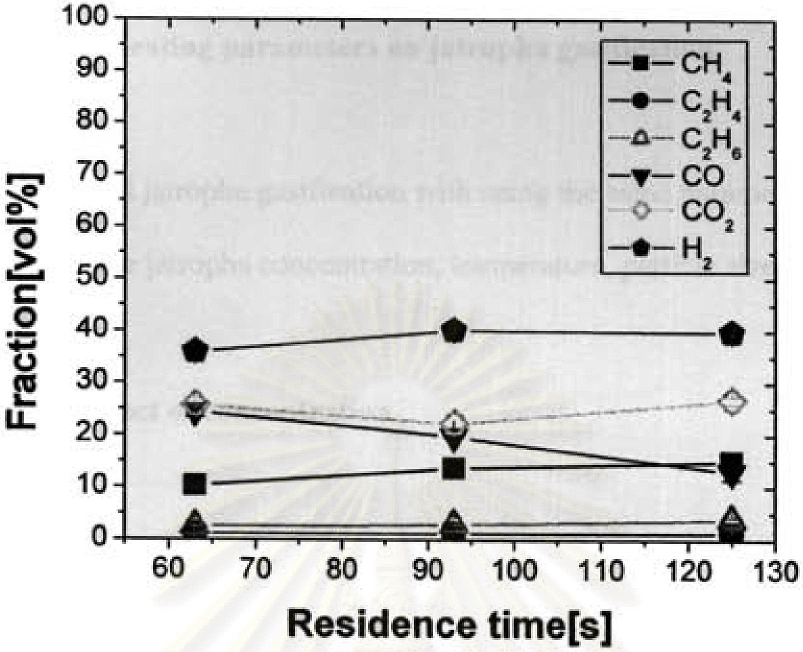

Figure 5.15 Gas product of cotton gasification with different residence time.

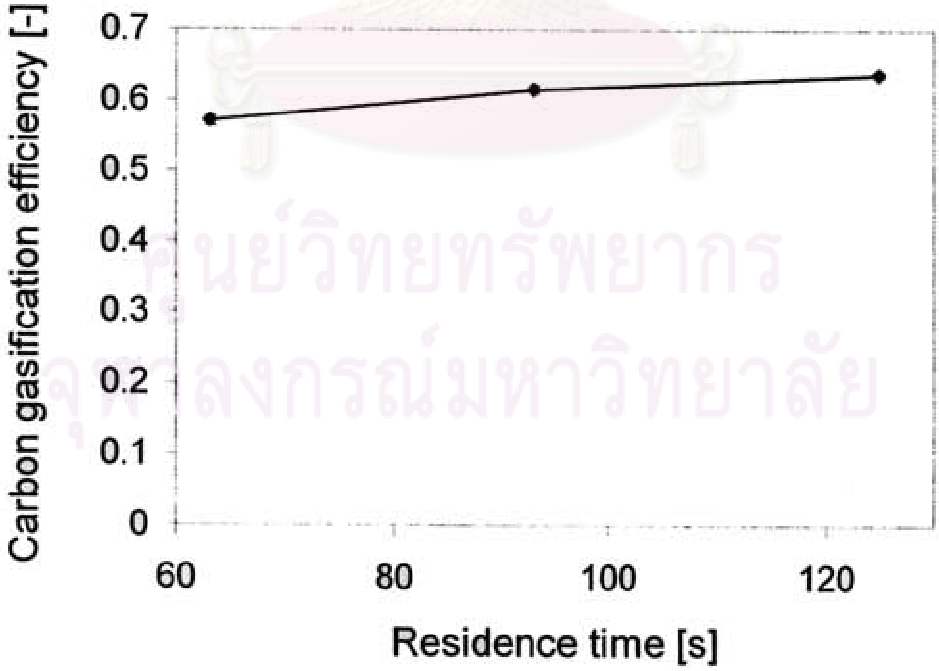

Figure 5.16 Carbon gasification efficiency of cotton with different residence time.

5.2 The study of operating parameters on jatropha gasification

We conducted jatropha gasification with using the same parameters as cotton gasification which are jatropha concentration, temperature, particle size and residence time.

5.2.1 The effect of concentration

The jatropha feedstock was varies concentrations in a range of 0.05 – 0.3 wt% and conducted with temperature of 500 °C and pressure of 25 MPa. The result is shown in figure 5.17. It is shown that the concentration of feedstock has essential effect on biomass gasification. For the gas product, the fraction of Hydrogen and carbon dioxide of low concentration feedstock gasification are higher than those of high concentration feedstock gasification. While the fraction of carbon monoxide was increased with increasing concentration of feedstock. But the carbon gasification efficiency does not improve with higher concentration feedstock. The effect of biomass concentration on carbon gasification efficiency is shown in figure 5.18. From graphs in figure 5.18, the carbon gasification efficiency of every concentration looks like a linear. The total organic carbon (TOC) was increased with increasing jatropha concentration. That mean, an increasing in concentration of feedstock leads to amount of carbon in liquid product.

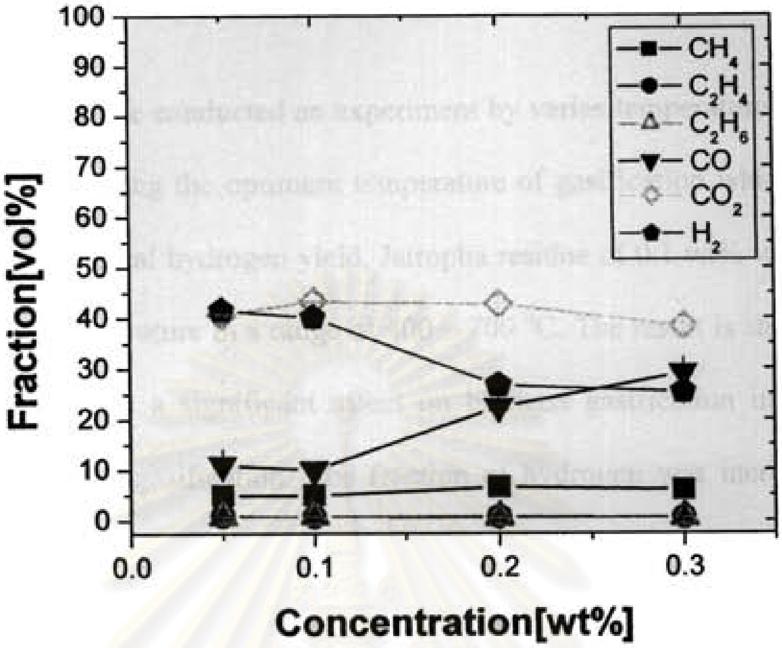

Figure 5.17 Gas products of each concentration of jatropha residue.

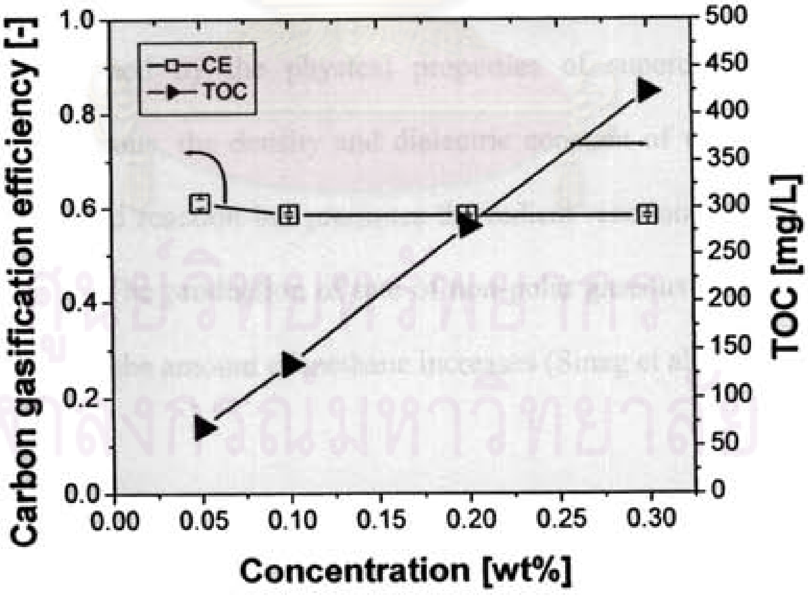

Figure 5.18 Carbon gasification efficiency of each concentration of jatropha residue

5.2.2 The effect of temperature

In this study, we conducted an experiment by varies temperature in a range of 400 – 700 °C for finding the optimum temperature of gasification which could give gas product with optimal hydrogen yield. Jatropha residue of 0.1 wt% was gasified at 25 MPa and the temperature in a range of 400 – 700 °C. The result is shown in figure 5.19. Temperature has a significant affect on biomass gasification in supercritical water same as cotton gasification. The fraction of hydrogen was increased sharply with increasing temperature from 500 – 700 °C. The fraction of methane was increased when temperature increased from 500 – 700 °C. But the fraction of carbon dioxide was decreased sharply with increasing temperature from 500 – 600 °C. The carbon gasification efficiency is increased when temperature increased. The carbon gasification efficiency is show in figure 5.20. The increase in the amount of product gas can be explained by the physical properties of supercritical water. Under supercritical conditions, the density and dielectric constant of water decrease which obstructs the ionized reaction but promotes the radical reaction (Buhler et al., 2002; Guan et al., 2008) The production of rate of non-polar gaseous such as methane can be improved. Thus, the amount of methane increases (Sinag et al., 2003).

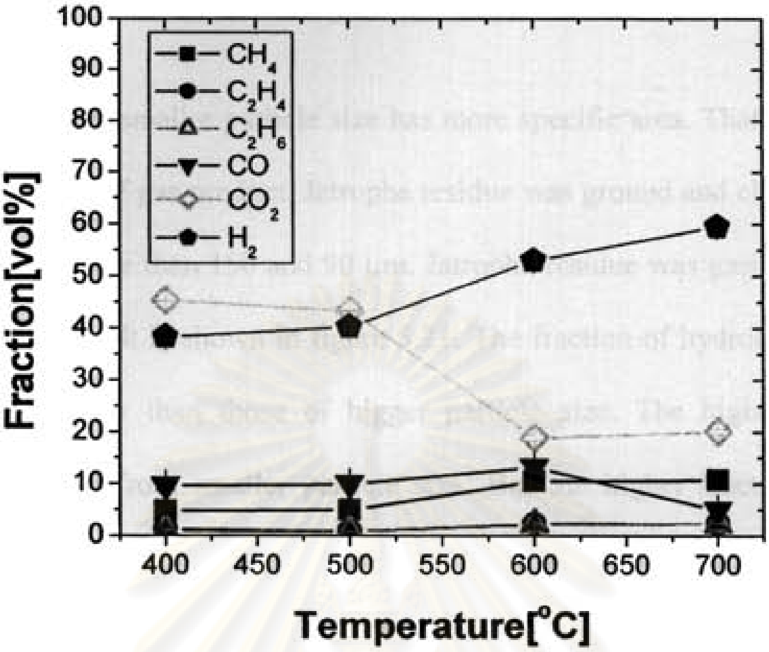

Figure 5.19 Gas products of each temperature of jatropha residue.

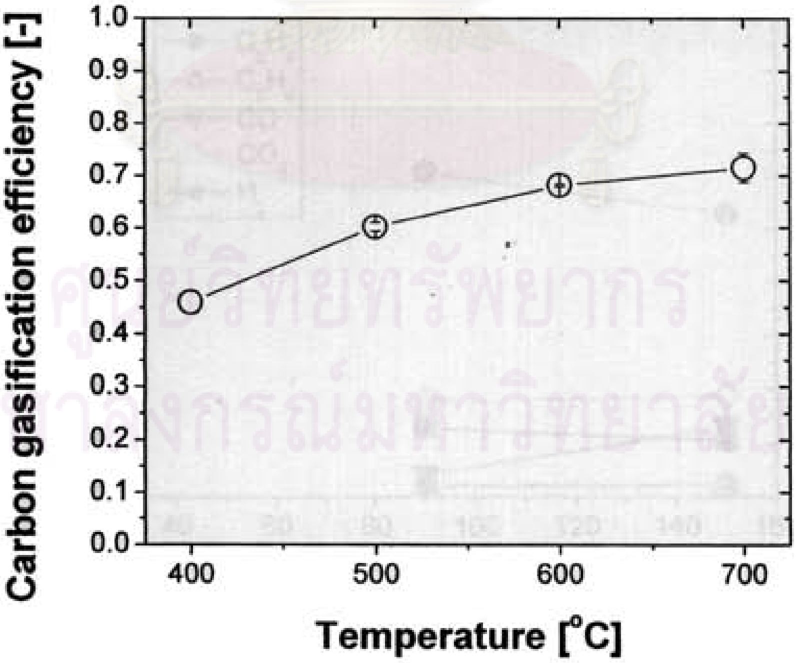

Figure 5.20 Carbon gasification efficiency of each temperature of cotton.

5.2.3 Effect of particle size on gas product yield

We know that smaller particle size has more specific area. That could help to improve the fraction of gas product. Jatropha residue was ground and classified into 2 sizes which are smaller than 150 and 90 μm. Jatropha residue was gasified at 600 °C and 25 MPa. The result is shown in figure 5.21. The fraction of hydrogen of smaller particle size is higher than those of bigger particle size. The higher fraction of methane is obtained from smaller particle size. But the higher fraction of carbon monoxide is obtained with bigger particle size. The carbon gasification efficiency is show in figure 5.22. The carbon gasification efficiency increase when conducting smaller particle size. That mean smaller particle size provide higher gas product.

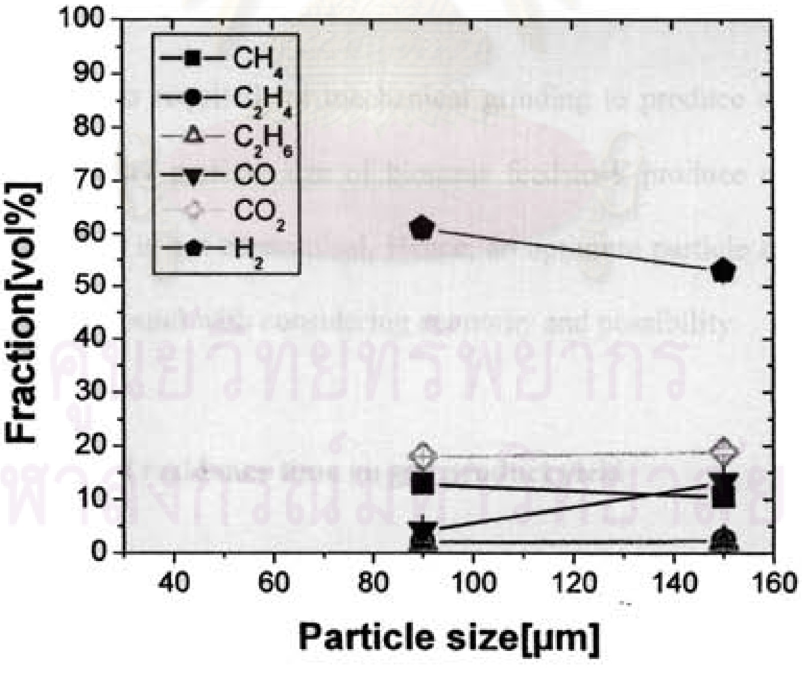

Figure 5.21 Gas products of each particle size of jatropha residue.

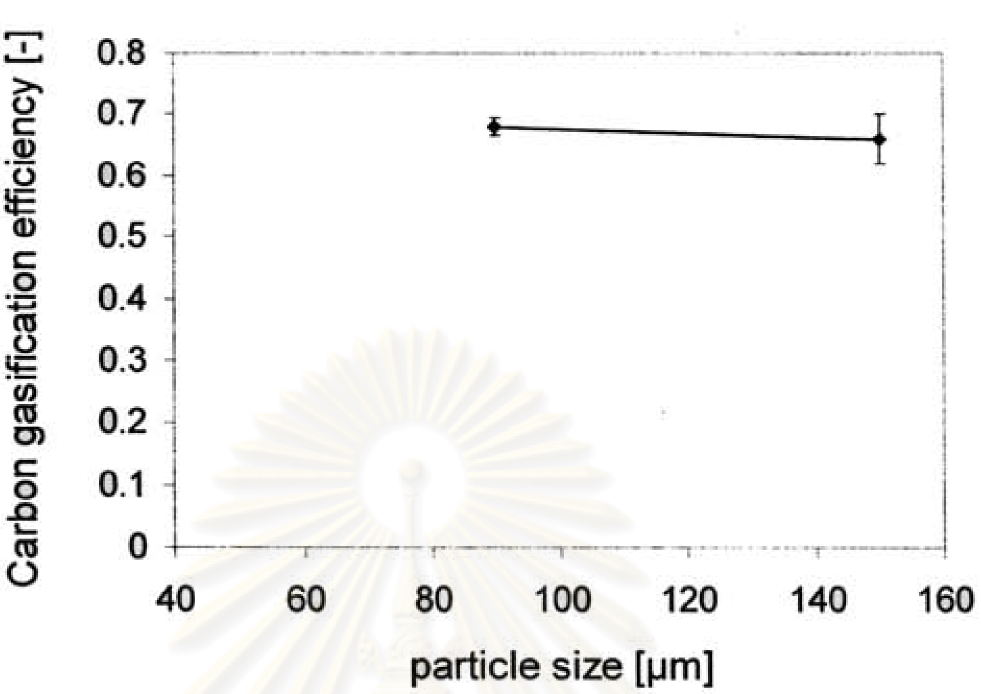

Figure 5.22 Carbon gasification efficiency of each temperature of jatropha.

High energy is required for mechanical grinding to produce smaller particle size. Although, smaller particle size of biomass feedstock produce more hydrogen when it is gasified. It is not economical. Hence, an optimum particle size of biomass feedstock should be found with considering economy and possibility.

5.2.4 Effect of residence time on gas product yield

From the literature review, we know that longer residence time is useful to produce higher fraction gas product. In this studied, we conducted an experiment under condition of difference residence time in a value of 63, 93 and 125 second. Jatropha residue was gasified at 600 oC and 25 MPa. We chose the particle size of jatropha residue which is smaller than 90 μm to use in this study. The result is shown in figure 5.23. The fraction of hydrogen was increased with increasing residence time. While the fraction of methane and carbon dioxide were decreased. The carbon gasification efficiency was increased with increasing residence time. The same result as cotton gasification, longer residence time provide higher fraction of hydrogen. That mean longer residence time is useful on gasification. The carbon gasification efficieny is show in figure 5.24.

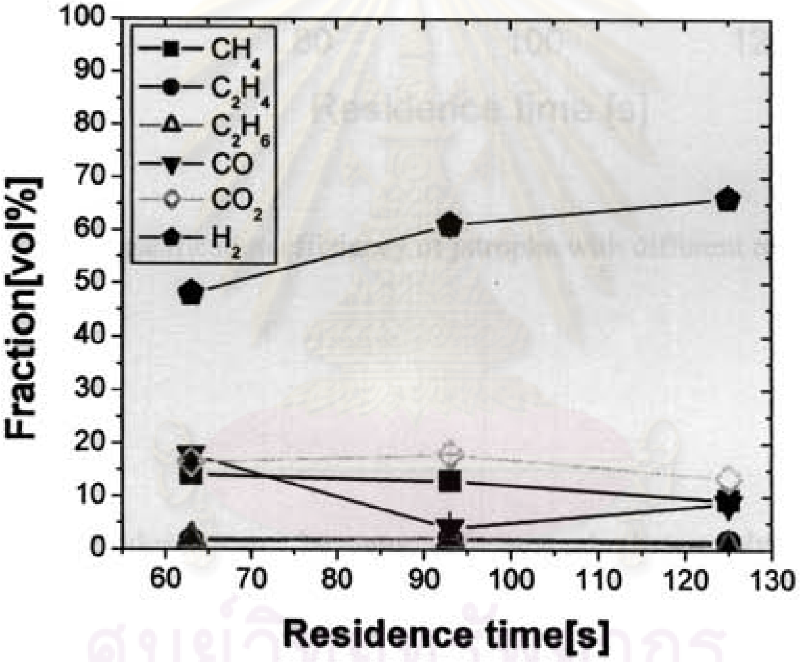

Figure 5.23 Gas product of jatropha gasification with different residence time.

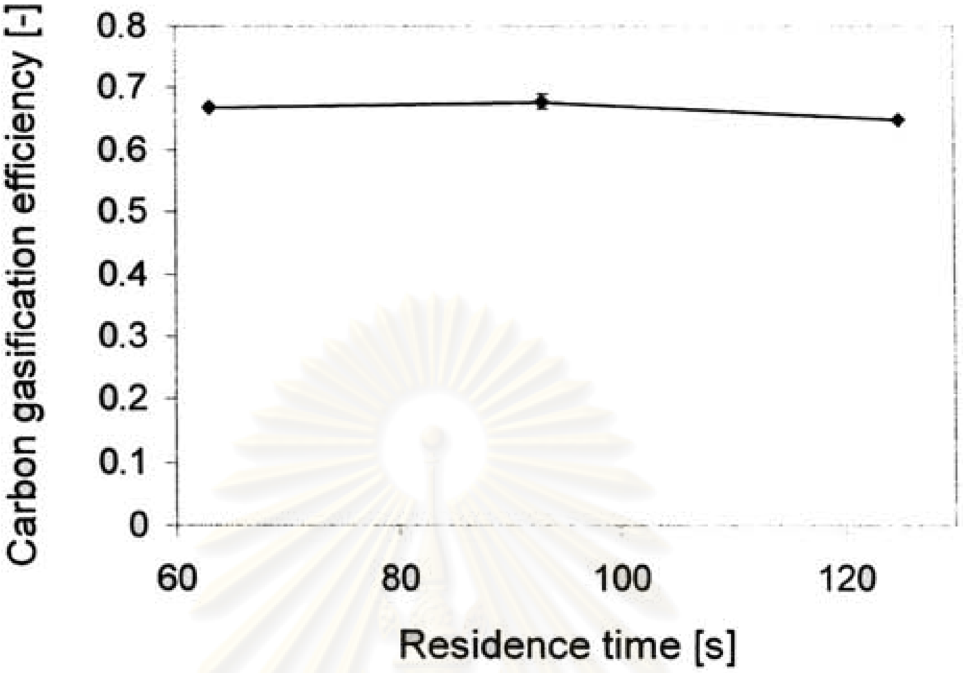

Figure 5.24 Carbon gasification efficiency of jatropha with different residence time.

5.3 Addition

A hemi-cellulose can be any of several heteropolymers (matrix polysaccharides) present in almost all plant cell walls along with cellulose. While cellulose is crystalline, strong, and resistant to hydrolysis, hemi-cellulose has a random, amorphous structure with little strength. It is easily hydrolyzed by dilute acid or base. Unlike cellulose, hemi-cellulose (also a polysaccharide) consists of shorter chains - 500-3000 sugar units as opposed to 7,000 - 15,000 glucose molecules per polymer seen in cellulose. In addition, hemi-cellulose is a branched polymer, while cellulose is unbranched. Then, it might be reason that jatropha residue, which is consist more hemi-cellulose (see table 4.4), give higher gas product than cotton.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Cotton and jatropha residue could be gasified in the tubular flow reactor without catalyst under supercritical water condition. The mechanical grinding of raw material was employed for preparation of biomass feedstock before its gasification. In this work, biomass feedstock was ground and classified into 3 sizes which were 45, 90 and 150 μm. The particle size of biomass feedstock could significantly affect the gaseous product yield. It was found that cotton with the optimum particle size of 45 μm could provide the hydrogen fraction of 40 vol% while jatropha residue with the particle size of 90 μm. could provide the hydrogen fraction of 61 vol%. Higher hydrogen fraction could be obtained with gasification of smaller particle sizes. It was well known that mechanical grinding required higher energy consumption. Though, smaller particle sizes produce more hydrogen when it was gasified, it would not be economical. The optimum particle size should be found with considering economy and possibility.

Carbon gasification efficiency was slightly be improved by increasing biomass concentration of feedstock. Then, the optimum concentration was 1.0 wt%. Because there was plugging occur when conducted with high concentration of biomass feedstock and using low temperature. At low temperature, biomass was gasified with the formation of char and tar which were difficult to decompose. It can believe that high temperature, high heating rate (for batch reactor) and catalyst are required for gasification of high concentration feedstock.

With the effect of temperature of biomass gasification, the temperature was varied in a range of 400 – 700 °C. From previous studied, It is known that low temperature provided char and tar. Carbon gasification efficiency is low when conducted at lower temperature. However, high temperature required more energy, it is not prudential. From this research, the highest hydrogen fraction is obtained from 700 °C. At 700 °C, the hydrogen fraction from cotton gasification was 41 vol% and the hydrogen fraction from jatropha residue gasification was 59 vol%. The effect of temperature on this gasification can explain by the Arrhenius law. With plot the relationship between 1/T and natural logarithm of k (ln k), it can be seen that a plot of ln k versus 1/T should be straight line. The value of k was increased when increasing temperature. From this result, it can believe that the temperature has essential effect on biomass gasification.

The effect of residence time on biomass gasification was studied with varied of water flow rate. The water flow rate was varied in a range of 1.5, 2 and 3 mL/min that are make the residence time changed into 3 values which are 125, 93 and 63 s, respectively. From this research, longer residence time provided high gas product. The highest hydrogen fraction is obtained from the residence time of 93 s for cotton gasification which was 40 vol%. The highest hydrogen fraction from jatropha gasification was 66 vol% regarding to the residence time of 125 s.

Recommendations

Systematic investigation on gasification of both biomass materials would be beneficial to Thailand and Southeastern Asian countries because of their abundance in this region. Due to the smaller particle size of biomass feedstock was obtained higher hydrogen fraction. Comparison with 45 and 90 μm, the hydrogen fraction does not different too much. It is only 2.5 vol% difference. For economical, particle size of 90 μm would be appropriate for gasification. The lowest temperature of gasification that could be provided high fraction of hydrogen should be considered in the future work. Additional of catalyst in gasification would be studied. What kind of catalyst is good for economical gasify.

REFFERENCES

Adhikari, D.K.; Seal, D.; Saxena R.C.; Goyal, H.B. Biomass based energyfuel through biochemical routes: A review. Renewable and Sustainable Energy Reviews 13 (2009): 156-167

Buhler, W.; Dinjus, E.; Ederer H.J.; Kruse, A.; Mas C. Ionic reactions and pyrolysis of glycerol as competing reaction pathways in near- and supercritical water. Journal of Supercritical Fluids 22 (2002): 37-53

D'Jesus, P.; Boukis, N.; Kraushaar-Czarnetzki, B.; Dinjus, E. Gasification of corn and clover grass in supercritical water. Fuel 85 (2006): 1032–1038

Fogler, H.S. Elements of Chemical Reaction Engineering: Third Edition; United States of America.

Gaun, Y.; Pei, A.; Guo, L. Hydrogen production by catalytic gasification of cellulose in supercritical water. Front. Chem. Eng. China 2 (2008): 176-180

Kersten, S.R.A.; Prins, W.; Drift, B.V.; Wam, P.M.; Swaaji, V. Principles of a novel multistage circulating fluidized bed reactor for a biomass gasification. Chem. Eng. Sci. 58 (2003): 725–731

Lu, Y.J.; Guo, L.J.; Ji, C.M.; Zhang, X.M.; Hao, X.H.; Yan, Q.H. Hydrogen production by biomass gasi.cation in supercriticalwater: Aparametric study. International Journal of Hydrogen Energy 31 (2006): 822 – 831

Matsumura, Y.; Minowa, T.; Potic, B.; Kersten, S.R.A.; Prins, W.; Van Swaaij, P.M.W.; Van de Beld, B.; Elliott, D.C.; Neuenschwander, G.G.; Kruse, A.; Antal Jr., M.J. Biomass gasification in near- and super-critical water: Status and prospects. Biomass and Bioenergy 29 (2005): 269-292

Meng, N.; Leung, D.Y.C.; Leng, M.K.H.; Sumathy, K. An overview of hydrogen production from biomass. Fuel Process Technology 87 (2006): 461–472

Minowa, T.; Fang, Z.; Ogi T.; Varhegyi, G. Decomposition of cellulose and glucose in hot-compressed water under catalyst-free conditions. Journal of Chemical Engineering of Japan 31 (1998): 131 – 134

Qian, Y.; Zuo, C.; Tan, J.; He, J. Structural analysis of bio-oils from sub-and supercritical water liquefaction of woody biomass. Energy 32 (2007): 196–202

Saxena, R.C.; Seal, D.; Kumar, S.; Goyal, H.B. Thermo-chemical routes for hydrogen rich gas from biomass: A review. Renewable and Sustainable Energy Reviews 12 (2008): 1909–1927

Schmieder, H.; Abeln, J.; Boukis, N.; Dinjus, E.; Kruse, A.; Kluth, M.; Petrich, G.; Sadri, E.; Schacht, M. Hydrothermal gasification of biomass and organic wastes. Journal of Supercritical Fluids 17 (2000): 145–153

Sinag, A.; Kruse, A.; Schwarzkopf, V. Key compounds of the hydropyrolysis of glucose in supercritical water in the presence of K_2CO_3. Ind. Eng. Chem. Res. 42 (2003): 3516-3521

Xu, X.; Matsumura, Y.; Stenberg, J.; Antal Jr., M.J. Carbon-Catalyzed Gasification of Organic Feedstocks in Supercritical Water. Ind. Eng. Chem. Res. 35 (1996): 2522-2530

Yanik, J.; Ebale, S.; Kruse, A.; Saglam, M.; Yuksel, M. Biomass gasi.cation in supercritical water: Part 1. Effect of the nature of biomass. Fuel 86 (2007): 2410–2415

Yoshida, T.; Oshima, Y.; Matsumura, Y. Gasification of biomass model compounds and real biomass in supercritical water. Biomass and Bioenergy 26 (2004): 71 – 78

APPENDICES

APPENDIX A

USDA method

Equipment:

1. crucible
2. Shallow enamel pan
3. Suck dry
4. Oven
5. Cooling bath
6. Reflux set

Reagents:

1. ***acid-detergent fiber** (1 L)*

Sulfuric acid	49.04	g
Cetyl trimethylammonium bromide (CTAB)	20	g

Weigh sulfuric acid and make up to volume with distilled water at 20°C. Check normality by titration before addition of detergent. Then add CTAB and stir.

2. Decahydronaphthalene
3. Acetone
4. Hexane
5. ***Saturated potassium permanganate*** (1 L)

- Distilled water	1	L
- Potassium permanganate	50	g
- Silver sulfate	0.05	g

Dissolve potassium permanganate and silver sulfate in distilled water. Keep out of direct sunlight.

6. ***Lignin buffer solution*** : (1 L)

-	Ferric nitrate nanohydrate	6	g
-	Silver nitrate	0.15	g
-	Acetic acid	500	ml
-	Potassium acetate	5	g
-	Tertiary butyl alcohol	400	ml
-	Distilled water	100	ml

Dissolve ferric nitrate nonahydrate and silvernitrate in distilled water. Combine with acetic acid and potassium acetate. Add tertiary butyl alcohol and mix.

7. ***Combined permanganate solution*** : (1 L)

Combine and mix *saturated potassium permanganate* and *lignin buffer* solution in the ratio of 2:1 by volume, before use. Unused mixed solution kept about a week in a refrigerator. (purple)

8. ***Demineralizing solution*** (1 L)

Oxalic acid dehydrate	50	g
Ethanol 95 %	700	ml
Hydrochloric acid	50	ml
Distilled water	250	ml

Dissolve oxalic acid dehydrate in ethanol .Add concentrated hydrochloric acid and distilled water and mix.

9. ***Ethanol 80 %***

95 ethanol	845 ml
Distilled water	155 ml

Step;

1. Dry sample at less than 65 °C. And grind through 20-30 mesh (1 mm). Add *acid-detergent fiber* to 1(g) samples in crucibles in a shallow enamel pan containing cold water 1 cm.

   Acid-detergent fiber:

   1) Weight 1 g air dry sample ground to pass 1 mm.
   2) Add 100 ml acid detergent solution and 2 ml decahydronaphthalene. Heat to boiling in 5 to 10 minutes. Reflux 60 min.
   3) Filter on a previously tared crucible and suck dry. Break up the filtered and wash twice with hot water (90-100 °C)
   4) Repeat wash with acetone until remove no more color : break up all lumps.
   5) Optional wash with hexane. Suck dry the acid detergent fiber free of hexane. Dry at 100 °C. overnight.

2. Add 25 ml of combined **saturated potassium permanganate** and **Lignin buffer solution** *(2:1 by volume)* to crucibles in the enamel pan containing cold water. Adjust level (2-3cm.) of water in pan. Stir contents to break lump and draw ***permanganate solution*** up on side of crucibles to wet all particles.

3. Allow crucible to stand at 20-25 °C. for 90-100 min. add more mixed ***permanganate solution*** if necessary. Purple color must be present at all time.
4. Remove crucibles to filtering apparatus. Suck dry. Do not wash. Place in a clean enamel pan, and fill crucibles no more than half full with ***Demineralizing solution*** , maybe added directly to crucible . Care must be taken foaming.

   After 5 min, suck dry on filter and refill haft full with ***Demineralizing solution.*** Repeat after second interval of solution is very brown. Rinse side crucible with solution from a wash bottle with a fine stream. Treat until fiber is white. (20-30 min)
5. Fill and thoroughly wash crucible and contents with ethanol. Suck dry and repeat two time. Wash twice in similar manner with acetone. Suck dry.
6. Dry at 100 °C overnight. And weigh. Calculate lignin content as loss weight from ADF
7. Ash at 500 °C. for 3 hr, cool , and weigh. Calculate residual ash as the difference between the weigh original tare of crucible. Calculate cellulose by weight loss upon ash.

APPENDIX B

Publications

International Proceedings

T. Samanmulya, Y. Matsumura and T. Charinpanitkul, "Gasification of cotton and jatropha residue using supercritical water" *Proceeding of Japan Institute of Energy*, January 13-14, 2009, Kitami, Hokkaido, Japan

T. Samanmulya, T. Charinpanitkul and Y. Matsumura "Gasification of cotton and jatropha residue using supercritical water" *Proceeding of Thailand-Japan International Academic Conference (TJIA2008)*, November 21-22, 2008, Tokyo, Japan

社団法人 日本エネルギー学会
JIE The Japan Institute of Energy

第4回　バイオマス科学会議
発表論文集

開催日：平成21年1月13日(火)～1月14日(水)
会　場：北　見　工　業　大　学

主催：社団法人　日本エネルギー学会　バイオマス部会

共賛：北見工業大学、北見市、「エネルギー学」部会、PEGASUS研究会

協賛：アルコール協会、エネルギー・資源学会、環境経済・政策学会、科学技術振興機構、化学工学会、紙・パルプ技術協会、訓子府・新エネルギー研究会、触媒学会、新エネルギー・産業技術総合開発機構、新エネルギー財団、森林バイオマス利用学会、森林利用学会、石油学会、日本ガス協会、日本機械学会、日本下水道協会、日本森林学会、日本太陽エネルギー学会、日本農学会、日本木材加工技術協会、日本木材学会、日本木材学会北海道支部、日本有機資源協会、農業土木学会、農林水産技術情報協会、バイオインダストリー協会、バイオマス利用研究会、廃棄物学会、木質バイオマス利用研究会

P225 GASIFICATION OF COTTON AND JATROPHA RESIDUE IN SUPERCRITICAL WATER

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ABSTRACT

Among various biomass materials available in Thailand, cotton and jatropha are abundant biomass which has potential as renewable energy resources. Powdery cotton and jatropha residue has been gasified by supercritical water in a tubular flow reactor to produce fuel gas. Effects of gasification temperature in a range of 400 – 700°C and biomass loading of 0.1-0.5 wt % have been experimentally examined. The gaseous product is composed of hydrogen, carbon dioxide, carbon monoxide, methane and a small amount of ethane and ethene. The hydrogen yield was dependent on the increasing biomass loading. Elevated temperature and catalyst addition would be required for the gasification of high concentration of feedstock.

1. Introduction

Biomass is one of the most abundant renewable energy resources. A variety of biomass resources can be used as energy resource. Biomass conversion to energy is undertaken with two main process technologies: thermochemical and biochemical processes. Thermochemical gasification of biomass is likely to be a cost-effective process to produce fuel gas [1].

One method for hydrogen production is the steam reforming of biomass. The major problem in gasification by steam reforming is the formation of tars and char as the biomass does not react directly with steam at atmosphere pressure [2].

Supercritical water has an excellent extracting capability which is superior to that of liquid water. Generally, the dielectric constant of supercritical water is much lower than that of water and other solvents. As a result, supercritical water behaves like an effective solvent for many biodegradable materials. It is well known that supercritical water has the ability to dissolve biomaterials which are not normally soluble in water or steam. These properties make supercritical water a very promising reaction medium for the conversion of biomass to value-added products. The objective of this research is to produce a fuel gas from biomass, which are cotton and jatropha seed residues, by gasification in supercritical water. Investigation on effects of temperature and biomass loading on gasification yield has been conducted experimentally. Analyses of gas compositions obtained from gasification have also been carried out.

2. Experimental

All gasification has been performed within a tubular flow reactor shown schematically in Fig. 1. The tubular flow reactor had the inside diameter of 2.17 mm and the length of 12 m. Cotton or jatropha residue powder suspension was fed into the reactor by a piston pump (Toyokoatu Co., designed for our use). Except otherwise stated, the reactor temperature and pressure were 500°C and 25 MPa, respectively. The reactor was cooled down by the cooler before solid remaining was separated from suspension by the solid-liquid separator. Meanwhile, the exit gas flow was separated by the liquid-gas separator. The gas generation rate was measured by the gas meter (W-NK0.5A, Shinagawa Co.). The gas and liquid samples were analyzed with gas chromatograph (GC-14B, Shimadzu) and TOC (TOC-V_{CPH}, Shimadzu), respectively. In this work, the reaction temperature was varied from 400 to 700 °C and residence time in the range of 80 – 222 s.

3. Results and Discussions

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Effect of biomass loading (0.1-0.3 wt %) in the reactor on gasification product by supercritical water was studied at 500°C, 25 MPa. Figure 2 shows that with an increase in the biomass loading from 0.1 to 0.2 %wt, relative yield of methane, ethene, ethane and carbon monoxide concentration was reduced while that of carbon dioxide and hydrogen was increased. As the biomass loading was further increased from 0.2 to 0.3 %wt, the hydrogen fraction was reduced while carbon monoxide was increased slightly. Based on these results, it would be implied that the gasification of low solid loading of biomass feedstock would be preferable to gaseous product with small molecular size.

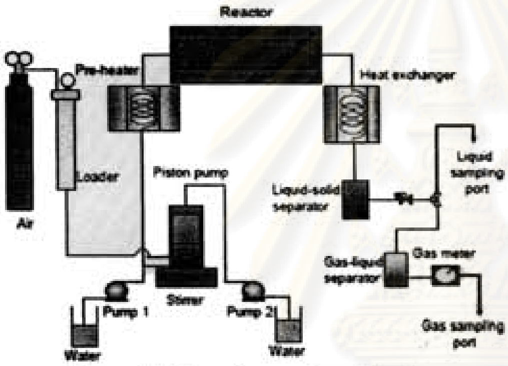

Figure 1 Schematic experimental set-up

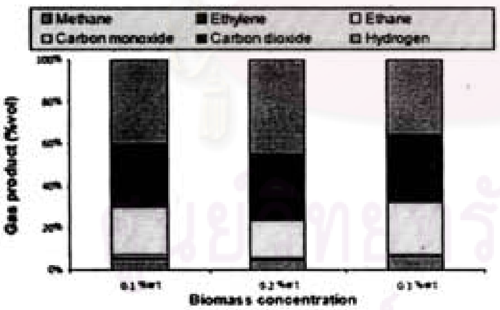

Figure 2 Effect of loading on gaseous product synthesized from cotton gasification in supercritical water (500°C and 25 MPa.)

Meanwhile, effect of temperature (500-600°C) on gasification of cotton and jatropha residue is shown in Figure 3. When temperature was increased from 500 to 600°C, the yield of hydrogen and methane were increased while the fraction of carbon monoxide and carbon dioxide were reduced. These would be attributable that the selective formation of hydrogen and methane would be more enhanced under higher supercritical conditions.

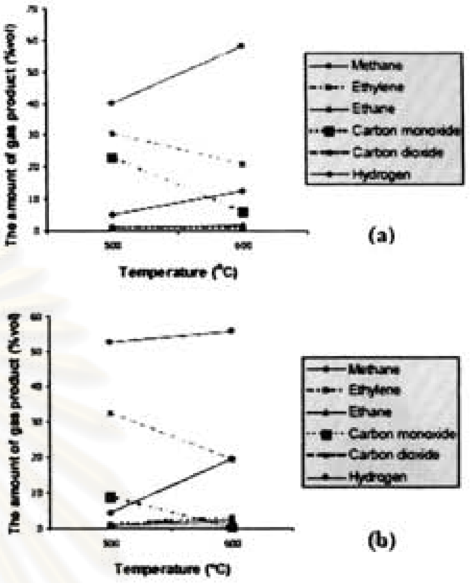

Figure 3 Gaseous products synthesized from gasification of biomass in supercritical water (25 MPa.); (a)Cotton powder (b)Jatropha

4. Conclusion

Cotton and jatropha residue could be gasified by supercritical water to produce fuel gas which contained hydrogen, methane, carbon monoxide, carbon dioxide and small amount of ethene and ethane. Hydrogen production was clearly influenced by operating parameters which were biomass loading, temperature and residence time. With a high solid loading, hydrogen fraction was decreased. Systematic investigation on gasification of both biomass materials would be useful for Thailand because of their abundance in many areas in Thailand.

5. Reference

[1]. Y.J. Lu et al. Hydrogen Energy 31 (2006) 822 – 831

[2]. M. J. Antal et al. Ind Eng Chem Res 39 (2000) 4044 - 4053

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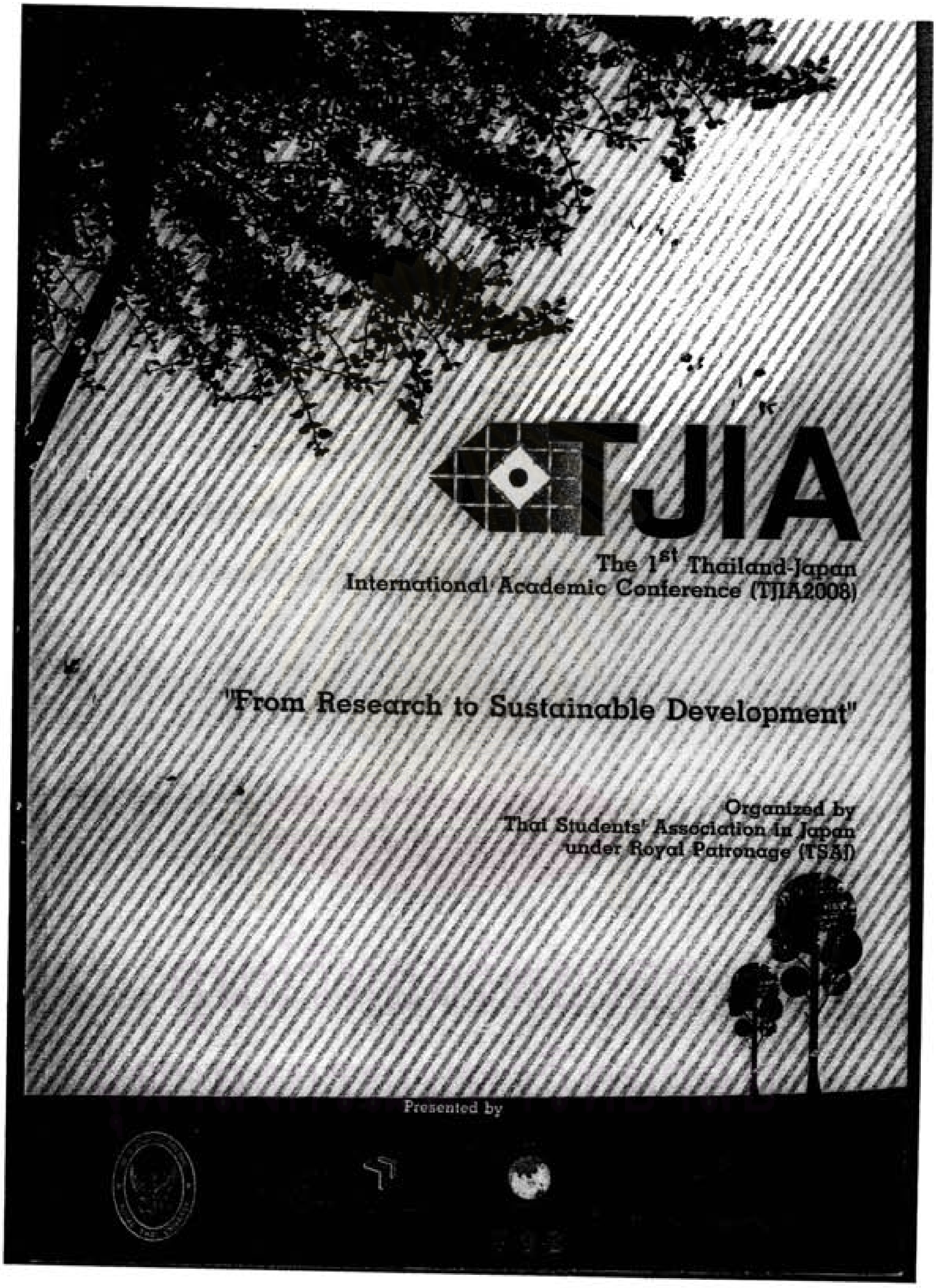

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VITA

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