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นายชาตรี อัศยะธรรมานนท์

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คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
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FUEL GAS PRODUCTION FROM STEAMED RICE BY HYDROTHERMAL TREATMENT IN SUBCRITICAL WATER

Mr. Chatree Asayatamanon

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Thesis Title	FUEL GAS PRODUCTION FROM STEAMED RICE BY HYDROTHERMAL TREATMENT IN SUBCRITICAL WATER
By	Mr. Chatree Asayatamanon
Field of Study	Chemical Engineering
Thesis Advisor	Associate Professor Tawatchai Charinpanitkul, D.Eng.
Thesis Co-advisor	Achariya Suriyawong, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master’s Degree

…………………………………. Dean of the Faculty of Engineering
(Associate Professor Boonsom Lerdhirunwong, Dr.Ing.)

THESIS COMMITTEE

…………………………..…… Chairman
(Assistant Professor Varong Pavarajarn, Ph.D.)

……………………………..… Thesis Advisor

(Associate Professor Tawatchai Charinpanitkul, D.Eng.)

………………………………….. Thesis Co-advisor
(Achariya Suriyawong, Ph.D.)

………………………………….. Examiner

(Assistant Professor Apinan Soottitantawat, D.Eng.)

……………………………..… Examiner
(Supawat Vivanpatarakij, D.Eng.)

………………………………….. External Examiner
(Jintawat Chaichanawong, D.Eng)

ชาตรี อัศยะธรรมานนท์ : การผลิตแก๊สเชื้อเพลิงจากข้าวสวยด้วยกระบวนการไฮโดรเทอร์มอลในน้ำสภาวะกึ่งวิกฤติ. (FUEL GAS PRODUCTION FROM STEAMED RICE BY HYDROTHERMAL TREATMENT IN SUBCRITICAL WATER) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร. ธวัชชัย ชรินพาณิชกุล, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: อ.ดร. อัจฉริยา สุริยะวงค์, 101 หน้า.

คาร์โบไฮเดรตเป็นสารอินทรีย์ที่สามารถนำมาประยุกต์ใช้เป็นแหล่งพลังงานเชื้อเพลิงได้ ซึ่งทางงานวิจัยนี้ได้เสนอแนวทางการเปลี่ยนคาร์โบไฮเดรตเป็นเชื้อเพลิงด้วยกระบวนไฮโดรเทอร์มอล โดยการเพิ่มอุณหภูมิ และความดันให้แก่สารอินทรีย์ เพื่อให้เกิดการสลายตัวเป็นสารประกอบอินทรีย์ที่มีขนาดโมเลกุลเล็กลง ในงานวิจัยนี้ได้ใช้ข้าวสวยที่ผ่านการหุงสุกเป็นวัตถุดิบ ซึ่งใช้เป็นตัวแทนของเศษขยะอาหาร โดยที่มีองค์ประกอบหลักเป็นคาร์โบไฮเดรต โดยวัตถุประสงค์ของการวิจัยนี้คือ ศึกษาการแปรสภาพของคาร์โบไฮเดรตผ่านกระบวนการไฮโดรเทอร์มอล ในการทดลองโดยใช้ระบบแบบกะจะศึกษาอิทธิพลของอุณหภูมิที่ใช้ในการทำปฏิกิริยาอยู่ในช่วง 200 ถึง 300 องศาเซลเซียส และอัตราการให้ความร้อนตั้งแต่ 8 ถึง 13 องศาเซลเซียสต่อนาที พบว่าการเกิดขึ้นของแก๊ซเชื้อเพลิงจะเกิดได้ดีที่สุด ที่อุณหภูมิสูง และอัตราการให้ความร้อนสูง และเมื่อพิจารณาผลิตภัณฑ์ที่เป็นของแข็งจะพบว่า เกิดการรวมตัวของคาร์บอนในลักษณะที่เป็นอนุภาคคาร์บอนทรงกลมระดับไมโครเมตร ซึ่งทั้งนี้เราสามารถนำผลผลิตดังกล่าวมาประยุกต์ใช้เป็นตัวรองรับตัวเร่งปฏิกิริยา

ในส่วนของการทดลองโดยใช้ระบบแบบต่อเนื่องนั้นจะทดลองโดยใช้อุณหภูมิในช่วง 400 ถึง 600 องศาเซลเซียส และมีขนาดของอนุภาคตั้งแต่ 60 ถึง 250 ไมโครเมตร พบว่าที่อุณหภูมิสูงจะส่งผลให้เกิดการกลายเป็นแก๊สได้ดีกว่าที่อุณหภูมิต่ำ และเมื่อยิ่งใช้สารตั้งต้นที่มีขนาดอนุภาคขนาดเล็กจะส่งผลให้เกิดปริมาณของแก๊สได้มากกว่าการทดลองที่ใช้สารตั้งต้นที่มีอนุภาคใหญ่ เมื่อทดลองโดยใช้ร่วมกับไฮโดรเจนเปอร์ออกไซด์เป็นตัวปรับแต่ง จะพบว่าประสิทธิภาพของการกลายเป็นแก๊สนั้นดียิ่งขึ้นในทุกการทดลอง เพราะว่าไฮโดรเจนเปอร์ออกไซด์ช่วยเพิ่มปฏิกิริยาออกซิเดชั่นกับคาร์บอนได้ดีขึ้น

ภาควิชา.........วิศวกรรมเคมี......... ลายมือชื่อนิสิต..
สาขาวิชา.........วิศวกรรมเคมี......... ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก..................................
ปีการศึกษา.........2554......... ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม ....

5370595221 : MAJOR CHEMICAL ENGINEERING
KEYWORDS : HYDROTHERMAL/ HYDROGEN/ CARBOHYDRATE

CHATREE ASAYATAMANON : FUEL GAS PRODUCTION FROM STEAMED RICE BY HYDROTHERMAL TREATMENT IN SUBCRITICAL WATER. ADVISOR : ASSOC. PROF. TAWATCHAI CHARINPANITKUL, D.Eng., CO-ADVISOR : ACHARIYA SURIYAWONG, Ph.D., 101 pp.

Carbohydrate is an organic compound that could be an alternative source of fuel gas. Hydrothermal treatment makes use of high temperature and pressure to decompose organic compounds. In this research, steamed rice which is considered as simulated waste carbohydrate is subject to the hydrothermal treatment process for producing fuel gas with a tubular reactor in the batch system with a reaction temperature range of 300 to 400°C and heating rate ranging from 8 to 13°C/min. The result shows high temperature and high heating rate would promote the hydrogen production rate. In addition, solid residue, which is agglomerates of carbonaceous microsphere, was examined for its potential utilization.

In part of continuous process, steamed rice was used as a feed stock which used the continuous system. There investigate on the effect of temperature in range of 400, 500 and 600^{o}C and particle size in range of 60, 140 and 250 µm. The result is shown that the small particle size and high temperature could be produced the highest gas product. When using the H_2O_2 as an additive, it could be promoted carbon gasification efficiency in all experiment because of H_2O_2 was promoted oxidation process.

Department : Chemical Engineering Student's Signature ....
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NOMENCLATURES

^oC	Degree celsius
$^oC/min$	Degree celsius per minute
MJ	Megajoule
MPa	Megapascal
µm	Micrometer
m	Meter
mm	Millimeter
mm^3	Cubic millimeter
cm^3	Cubic centimeter
g	gram
kg	kilogram
H_2	Hydrogen
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
N_2	Nytrogen
H_2O_2	Hydrogenperoxide
5-HMF	5-Hydromethylfurfural
KOH	Potassium hydroxide
K_2CO_3	Potassium carbonate
H_2O	Water
NaOH	Sodium hydroxide
CH3COONa	Sodium acetate
$NaHCO_3$	Sodium bicarbonate
Na_2CO_3	Sodium carbonate
Ni	Nickel
SiO_2	Silicon dioxide
HCO3-	Hydrogen carbonate ion
HCOOK	Potassium formate

Pt	Platinum
AlO_3	Aluminium oxide
ZrO_2	Zirconium oxide
Ru	Ruthenium
TiO_2	Titanium oxide
CaO	Calcium oxide
$Ca(OH)_2$	Calcium hydroxide
VS	Volatile solid
GC	Gas chromatography
TOC	Total organic carbon
FTIR	Fourier transform infrared spectroscopy
SEM	Scanning electron microscope
TGA	Thermogravimetric analysis
IC	Inorganic carbon
NPOC	Non-purgeable organic carbon
NGV	Natural gas vehicles
RE	Renewable energy
SCW	Supercritical water
HTL	Hydrothermal liquefaction

CHAPTER I

INTRODUCTION

1.1 Background and motivation

Currently, natural sources of energy, such as oil, natural gas and coal, decrease rapidly. The nonrenewable sources in the natural could be combusted that produce the amount energy, but common byproducts of this process also produce carbon dioxide, carbon monoxide and nitrogen. There are the major effects of greenhouse effect what is a process by which thermal radiation from a planetary surface is absorbed by atmospheric greenhouse gases. From this reason, many researchers would investigate on the substituting energy sources to decrease demand from petroleum energy and enhance to use a clean energy such as geothermal, solar cell, biogas and biomass. Nowadays, petroleum products would be used for supplying demand as shown in Figure 1.1. Then, electricity is the 2nd energy that be used. For the renewable energy products including commercial renewable energy and tradition renewable energy, there would be the alternative resources. Energy from these resources may significantly contribute to the glowing future demand of energy [1]. Renewable energy is an alternative energy that refers to any source of usable energy intended to replace fuel sources. In a general sense in contemporary society, alternative energy is that which is produced without the undesirable consequences of the burning of fossil fuels, such as high carbon dioxide emissions, which is considered to be the major contributing factor of global warming. It is a renewable and clean energy source. It could also avoid the net increase of carbon dioxide in the atmosphere.

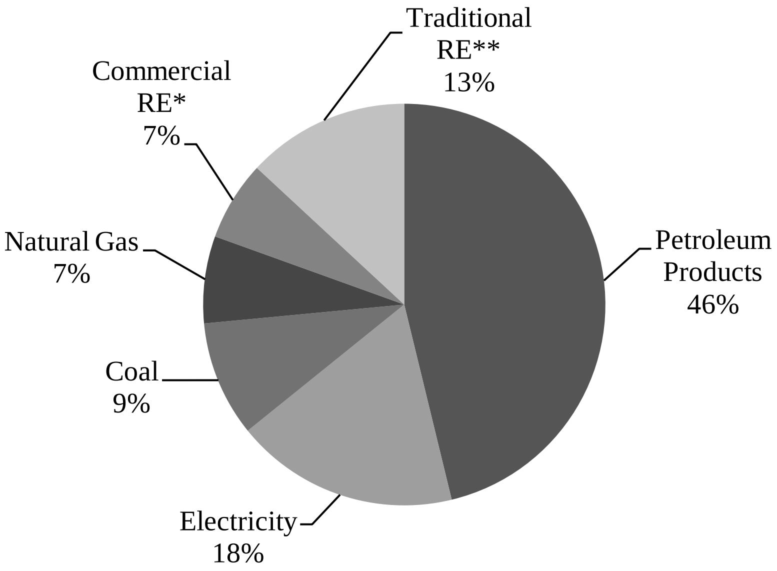

Figure 1.1 Energy consumption of Thailand in 2011

** Including solar, fuel wood, paddy husk, bagasse, agricultural waste, garbage and biogas*

*** Including fuel wood paddy husk and agricultural*

Figure 1.2 shows the alternative consumption of Thailand in 2011. The alternative energy was used as heat energy more over 50 percentage which is including solar, biomass, garbage and biogas. Then natural gas vehicles (NGV) were used as a second product of alternative energy. The electricity was the 3^{rd} energy consumption [1]. From this report, Thailand used the energy for heat in daily life while the energy sources decreased in day by day. So, many researchers enhance the renewable energy to be supplied for demand energy consumption in the future.

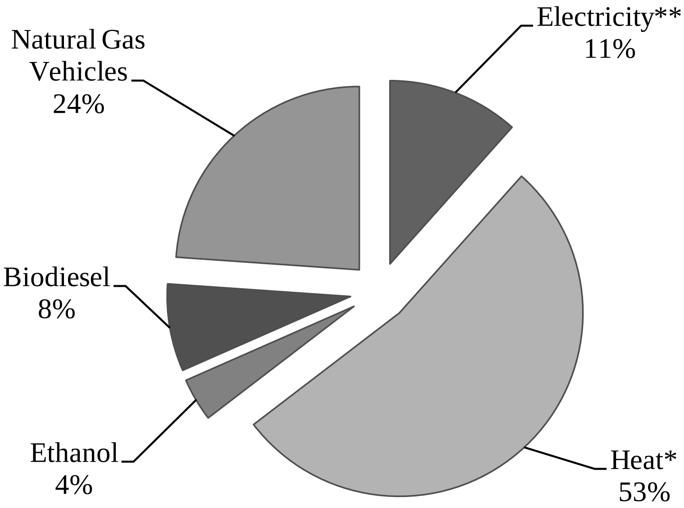

Figure 1.2 Alternative energy consumption of Thailand in 2011

**Including solar, biomass, garbage and biogas*

***Including solar, wind, hydro, biomass, garbage and biogas*

Among various biomass, it is a biological material that could be degradable by itself and can be used as fuel or industrial production. In generally, biomass consists of carbon, hydrogen and oxygen as a based element. Biomass is including the biodegradable wastes that could be burnt for energy source. Especially, biodegradable wastes such as food wastes which contain organic components that represent in carbohydrate, protein and lipids or fats. Nowadays, food wastes are the big problem for Thailand which is the pollution in community. Food wastes from food industries or human daily life activities could be converted to various forms of energy by using appropriate technologies and would be sustainable energy source. Food wastes would also lead to revenue gains by recovering waste energy and reducing waste disposal costs including reduce the impact on the environment [2]. Table 1.1 shows the amount of wastes in Thailand during 2005 to 2010. Wastes would be increased as increased population. In the other hand, the peoples would be growing up with technology by using energy for supplying the convenience. If these wastes could be generated into sustainable energy source, it will be helpful for pollution problems and wastes management in the future [3].

Table 1.1 The amount of wastes in Thailand during 2005 to 2010

Area	Wastes (Ton for a day)					
	2005	2006	2007	2008	2009	2010
Bangkok	8291	8403	8532	8780	8834	8766
Municipal area	12635	12912	13600	14915	16368	16620
External municipal area	18295	18697	18200	17369	16208	16146
Total	**39221**	**40012**	**40332**	**41064**	**41410**	**41532**

In this research, we assumed the food waste from the typical daily foods for example, Stirred fried pork with chili and mint, Wide noodles in a creamy sauce and Rice noodles in red soup. The typical foods were homogenized in each food for using as a material for characterizing the components. The sample 1 (s1) was the homogenized Stirred fried pork with chili and mint. The sample 2 (s2) was the homogenized Wide noodles in a creamy sauce. The sample 3 (s3) was the homogenized Rice noodles in red soup. Then, sample 4 (s4) was the mixed sample of s1, s2 and s3 in the same ratio as shown in Figure 1.3.

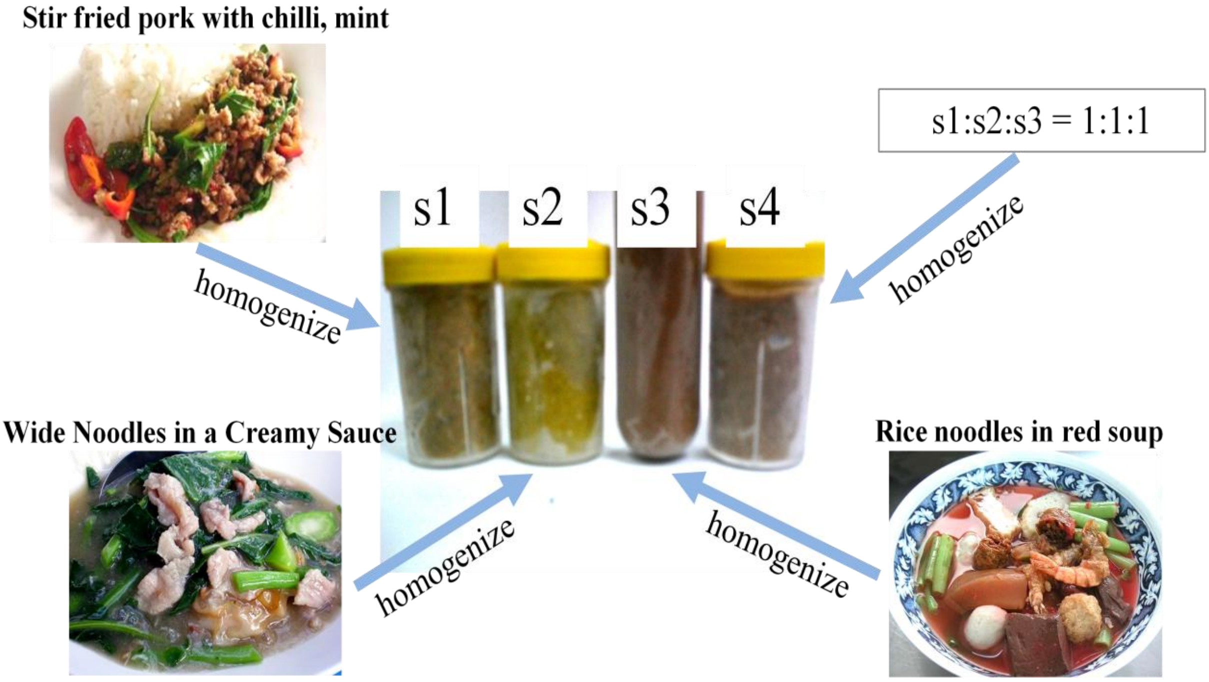

Figure 1.3 the typical foods after homogenization

When the samples were prepared, the samples would be analyzed for characterization the nutrient component including carbohydrate (Compendium of methods for food analysis 2003: 2-9), fat (Acid hydrolysis Method), Protein (ISO 2005: 5983-2), fiber (AOAC 2000: 978.10) and ash (AOAC 2005: 942.05). The result was shown that the major component of all samples was moisture. Also carbohydrate was the secondary component, protein was the third and fat was the fourth component. From these result, almost component in food waste was carbohydrate. So, the steamed rice was chosen for comparing the component with the typical food waste as shown in Figure 1.4. The steamed rice was the carbohydrate as a major component. In this research, all of experiments were used steamed rice as a raw material.

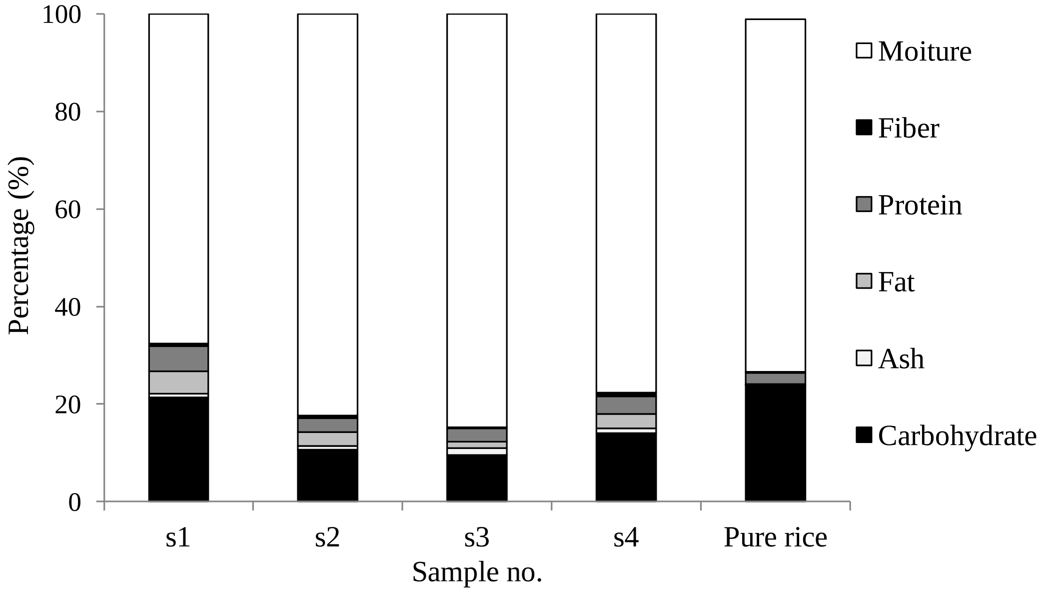

Figure 1.4 The component of typical food and steamed rice

Among various conversion methods, hydrothermal gasification, using super- or sub-critical water as a reacting medium, has been recognized as a promising technique to produce hydrogen from biomass with high efficiency. This process can be applied to the conversion of biomass with high moisture content without drying them. Furthermore, hydrogen can be obtained in a form of compressed gas with much higher reaction rate than those in the conventional fermentation processes. Wastes from the agricultural and food industries, which are mainly composed of carbohydrates, can be converted to gaseous or liquid fuels via hydrothermal processing. Also, hydrothermal reaction involves applying heat under pressure to achieve reaction in an aqueous medium. It has been attracting worldwide attention because of the fascinating characteristics of water as reaction medium at elevated temperatures and pressures, such as the organic compounds could not be dissolved in water at ambient temperature and ambient pressure. In addition, sub- or supercritical water behaves like an organic solvent that could be dissolved on it. For example, enhanced solubility of oxygen in aqueous solutions at high temperature and pressures provides a strong driving force for oxidation. When exceeding its critical point (374^{o}C and 22.1 MPa) the values of density, dielectric constant and ionic product of water drop down drastically. Under this condition, supercritical water (SCW) acts as a non-polar solvent of high diffusivity and excellent transport properties [4]. Because of the distinctive characteristics of water described above, hydrothermal reaction can be performed under performed under sub- or supercritical condition. Thus, the reaction environment can be manipulated by varying the operating conditions.

The available energy production processes from biomass can be divided into two general categories: gas fuels such as hydrogen and methane production. For liquid fuels, there are produced biodiesel, ethanol and 5-Hydroxymethylfurfural (HMF) as shown in Figure 1.5. In this research sets its aim to investigate the gas generation from carbohydrate by using hydrothermal treatment and study the effect of reacting temperature, treating time and concentration of steamed rice as well as catalyst on the yield of fuel gas generated.

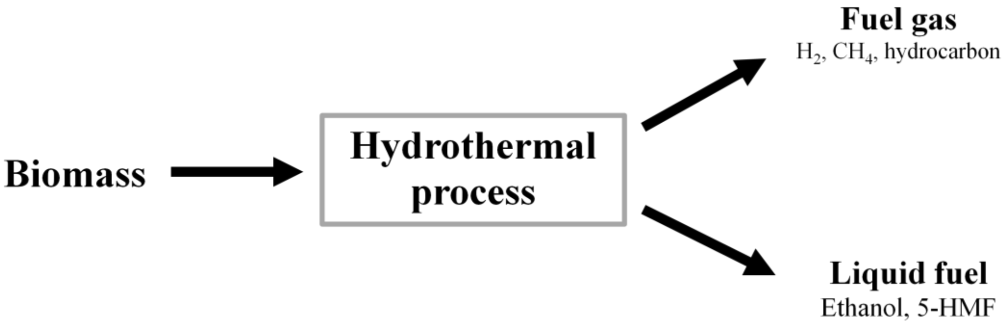

Figure 1.5 Path ways for converting biomass into fuel

1.2 Objectives

The object of this research is investigated the generation of fuel gas, especially hydrogen from steamed rice via its hydrothermal treatment in subcritical water and supercritical water.

1.3 Scope of the research

1.3.1 Steamed rice will be dried in the conventional oven at 100°C for 24 hours for removing volatile matter.

1.3.2 Dried steamed rice will be used as a raw material for hydrothermal treatment.

1.3.3 Investigate the influence of parameters on the hydrothermal treatment:

- Effect of reacting temperature in a range of 300 to 400°C.
- Effect of heating rate in a range of 8 to 13°C/min.
- Effect of particle size for continuous process in range of 60 to 250 micrometers.
- Effect of additive for continuous process (hydrogen peroxide (H_2O_2).

1.3.4 Investigate the optimum temperature of hydrothermal treatment which could provide the highest fuel gas yield.

1.4 Expected benefits

1.4.1 To obtain the guideline for preparing fuel gas from steamed rice under subcritical water and to find out the optimal condition for generating high yield of hydrogen products.

1.4.2 To gain additional experimental data to support biomass technology in Thailand as the renewable energy sources.

CHAPTER II

LITERATURE REVIEW

Before conducting experiments, literature survey has been conducted. It has been found that previous research works have been focused on various forms of biomass. Some conventional methods have been examined and reported. Some typical references are reviewed and summarized as shown below.

2.1 Anaerobic digestion process for produce biogas

Zong *et al*. investigated a two-step process of sequential anaerobic and photo-heterotrophic fermentation which was employed to produce hydrogen from cassava and food wastes. The result showed that the average yield of hydrogen in dark fermentation was approximately 199 cm^3 H_2/g of cassava and 220 cm^3 H_2/g of food wastes. In subsequent photo-fermentation, the average yield of hydrogen from the effluent of dark fermentation was approximately 611 cm^3 H_2/g of cassava and 451 cm^3 H_2/g of food wastes. These results demonstrate that cassava and food wastes could be ideal substrates for bio-hydrogen production and a two-step process combining dark and photo-fermentation was highly improving both bio-hydrogen production and removal of substrates and fatty acids [5].

EI-Mashad *et al*. investigated the effect of manure-screening on the biogas yield of dairy manure under 35^{o}C and determined the biogas production potential of different mixtures of unscreened manure and food wastes and compared them with the yield from manure or food wastes alone. The results showed the biogas yields of fine and coarse fractions of screened manure and unscreened manure after 30 days were 420, 380, and 340 mm^3/kg VS, respectively. The methane yield of the food wastes was 353 mm^3/kg VS after 30 days of digestion. Two mixtures of unscreened manure and food wastes, 68/32% and 52/48%, produced methane yields of 282 and 311 mm^3/kg VS, respectively after 30 days of digestion [6].

2.2 Hydrothermal gasification of biomass

Schmieder *et al*. reported on the wet biomass and organic wastes and effect of alkali metals that can be efficiently gasified under hydrothermal conditions to produce a hydrogen rich fuel gas. They demonstrated in two tubular flow reactors and in two batch autoclaves with glucose, aromatic, glycine and with real biomass (wood as saw dust, straw), wastes (sewage sludge and lignin). The results are showed at different residence times, temperatures and pressures. It was found that at 600^{o}C and 250 bar all compounds are completely gasified by addition of KOH or K_2CO_3. The main 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. The results of temperature influence in gasification shown that total organic carbon destruction efficiency was increased when increased temperature. The experiment with addition of KOH the carbon monoxide concentration in the product gas was decreased. 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 [7] according to the following equation:

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad \text{.....(1)}$$

Muangrat *et al*. investigated the gasification of some selected components (such as corn, mayonnaise, carrot, bean, cooked beef, mixed food wastes) by using H_2O_2 as the oxidant. In the presence of NaOH, there are investigated under subcritical water conditions. The reactor was heated to temperature of 330^{o}C at a heating rate of 20^{o}C/min, pressure in the reactor is 13.5MPa and held for 120 min. Hydrogen production was enhanced when both of NaOH and H_2O_2 were used compared to either NaOH or H_2O_2 was used alone or in their absence. Results indicated that the H_2O_2 acted to partially oxidize the samples while NaOH significantly increased hydrogen yields by promoting the water-gas shift reaction with subsequent CO_2 capture. In the presence of NaOH, the main components were $NaCO_3$, CH_3COONa and $CH_3COONa.3H_2O$. Char and tar production were suppressed in the presence of NaOH [8].

Ishida *et al*. examined the effect of alkali metal and a nickel catalyst, on the hydrothermal process to generate hydrogen from biomass with high selectivity at relatively low temperatures around 400^{o}C. A cellulose sample as model biomass was subjected to the hydrothermal process at 400^{o}C under 25 MPa in the presence of an alkali (Na_2CO_3) and a nickel catalyst (Ni/SiO_2). They concluded that the combination of these two additives led not only to highly efficient generation of hydrogen but also to effective dissolution of CO_2 into an alkaline liquid layer to form HCO_3^-. The hydrothermal process of real biomass, such as wood chips, organic fertilizer and food waste, in the presence of both the two additives resulted in highly selective production of hydrogen even at 400^{o}C [9].

Watanabe *et al.* investigated on glucose reactions in hot compressed water (200 to 500^{o}C, 4 to 40 MPa) by means of a batch-type reactor. The reactions in the heating period (about for 60 s) were observed. More than 80% of the glucose was consumed in the heating period above 300^{o}C. Gasification of glucose was promoted with increasing temperature. The effect of heating rate (from 4.2 to 15.8^{o}C/s) on glucose conversion was also examined, and gasification of glucose was enhanced with increasing the heating rate [10].

D'Jesus *et al*. investigated on the gasification of corn and cover glass in supercritical water in range of 500 to 700^{o}C, space time 3 to 15 minutes and alkaline addition by using tubular flow reactor. The result was shown that KOH concentration increased, the gasified product raised up because of KOH enhanced the formation of formate salt (HCOOK). CO reacted with KOH, which reacted further with water to produce H_2 production. In each temperature, the gasification yield increased with residence time that mean a function of time at high temperature which was the reaction rate constant increase with temperature as was expected from the Arrhenius equation. Increasing temperature promoted CO conversion by the water gas shift reaction. While high temperature, CH_4 production increased by formation of H_2 [11].

Jude A. *et al*. investigated on the hydrogen production from hydrothermal gasification by using glucose and other biomass samples. Experiments were carried out in range of 200 to 450^{o}C and were adding NaOH as an alkali catalyst. In experiment without NaOH, glucose decomposed to CO_2, char and tar as main products. In a presence of NaOH, H_2 increased with increased NaOH and less amount of char because the ability of alkali promoted the consumption of CO and captured CO_2 for produce H_2. The rate of generated hydrogen production was following order; glucose > cellulose, starch, rice straw > potato > rice husk [12].

Dolan *et al.* studied the hydrothermal gasification of cellulose at 315^{o}C in a presence of Pt/AlO_3 as catalyst. It was found that H_2 and CO_2 were increased with residence time while the experiment in a presence of $NaCO_3^-$ had a large impact on gasification yield that $NaCO_3^-$ would be promoted the water gas shift reaction. They implied that the intermediates from decomposed cellulose would be generated into acid. Then, the acid was decomposed into H_2 including a presence of the water gas shift reaction would be promoted to generate H_2 [13].

Byrd *et al.* studied on the catalysts for hydrogen production by gasification. Switchgrass was used as a material at 600^{o}C and 250 bar. Nickel, cobalt and ruthenium were used as catalyst and titania, zirconia and magnesium aluminium spinel were used as supports. The result was shown that the experiment in a presence of Ni/ZrO_2 as a catalyst was the highest gasification efficiency and Ru/TiO_2 was the second highest gas yield. After all experiments, the surface of catalyst was covered char particles. It was the coke formation more quickly that steam reforming reaction for generating gas production [14].

Youssef *et al.* studied the catalytic co-gasification of starch and catechol in range of 400 to 500^{o}C, 10 to 30 minutes with CaO and TiO_2 as catalysts. Result was shown that the highest H_2 yield and a complete elimination of CO and CO_2 when TiO_2 and CaO were used. TiO_2 enhanced to gasify the intermediate compounds. Meanwhile, CaO trapped the amount of CO_2 released from the reaction and then the water gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) contributed H_2 and CO_2 in the forward direction [15].

Kuramoto *et al*. investigated on the coal gasification in range of 600 to 700^{o}C and 0 to 30 minutes in a presence of a CO_2 sorbent. The result was shown that the residual solid at high temperature was less than low temperature. When the coal was heated, gas and tar formation took place with thermal decomposition. High soaking time increased H_2 and CO_2 yield which promoted water gas shift reaction. in a presence of $Ca(OH)_2$, no CO_2 was detected at any soaking time that CO_2 sorption by $Ca(OH)_2$ and the yield of H_2 and CH_4 clearly increased [16].

Muangrat *et al*. investigated on the effect of alkali-promoted hydrogen production from glucose, molasses and rice bran. The experiments were studied in range of 0 to 120 min and 330 to 390^{o}C. The result was shown that NaOH reduced CO_2 and enhanced H_2 as a main product via the water gas shift reaction. In a presence of alkali, products would not observe the tar and char. H_2 and CH_4 increased with high reaction time and would be steady state when it was over 30 minutes. High temperature would enhance biomass decomposition for producing H_2 and CH_4. While increasing feed concentration, CO, CO_2, CH_4 were increased but H_2 was decreased [17].

Garcia Jarana *et al*. studied the supercritical water gasification of industrial wastes. There had been tested on continuous-flow reactor which used Vinasses and Cutting oil wastes as raw materials. Experiments were studied in range of 450 to 550^{o}C, the amount of oxidant in the absence of oxygen and a presence of the KOH as a catalyst. Experimental result was shown that a presence of alkali decreased coke formation and decreased CO while KOH promoted the rate of the water gas shift reaction for increasing hydrogen yield. The major reaction pathways from the glucose gasification were converted glucose to water soluble intermediates and then contributed to produce CO. Meanwhile some of intermediates converted to CO_2 and H_2 by steam reforming reaction. CO was finally converted to CO_2 and H_2 through water gas shift reaction. The oxidant enhanced the steam reforming reaction for produce H_2 [18].

2.3 Liquefaction of biomass in sub- and supercritical water

Yin *et al*. investigated the cattle manure was converted to bio-oil by subcritical hydrothermal liquefaction (HTL) in the presence of NaOH. The bio-oil yield were studied in the effects of conversion temperature 270 to 350^{o}C, initial conversion pressure 0 to 100 psi, residence time ranged from 0 to 40 min and mass ratio of cattle manure to water were 0.25, 0.5, 1, 1.5 and 2. Results showed that the bio-oil yield depended on the conversion temperature and the process gas. In higher temperature (>315^{o}C), there are reduced bio-oil yields and the best conversion temperature for bio-oil production was in range of 295 to 305^{o}C. In HTL process, biomass (cellulose, hemicelluloses and lignin) in first hydrolyzed to unit structures like glucose and fructose with the minimum required temperature of 250^{o}C. Then, the bio-oil yield begins to decrease at higher temperature, due to the production of char/tar by self-condensation of bio-oil and the steam reforming of bio-oil. The higher initial conversion pressure would be dropped the bio-oil production because of self-condensation of bio-oil to solid. The effect of residence time, longer residence time also decreased the bio-oil yields while at high bio-oil yields are slightly 15 min. The higher heating value of bio-oil was 35.53 MJ/kg on average. The major non-polar components of bio-oil were toluene, ethyl benzene and xylene, which are components of crude oil, gasoline and diesel [19].

Kingler and Vogel studied the decomposition of glucose by using hydrothermal treatment in sub- and supercritical water in range of 250 to 420^{o}C with the reaction time 0 to 40 s and the effect of oxidation on glucose by adding H_2O_2. They found that glucose was decomposed to small molecules with increasing reaction time and temperature. A conversion of carbon would be held on 90% at 350^{o}C and 6s reaction time. At 250^{o}C, glucose isomerizes to fructose and mannose then would be converted to 1,6-anhydroglucose, 5-HMF and glyceraldehydes as major products. The derivative glucose decomposed to smaller molecules when temperature over 350^{o}C. In experiment with adding oxidant, the oxygen had no affect on decomposition rate of glucose in range of 250 to 350^{o}C. The first step of decomposed glucose in a presence of oxygen was not glucose but the intermediate hydrothermal product reacted with oxygen to form CO_2, CO, H_2 and organic acid [20].

Pourali *et al.* investigated the products from rice bran by using sub-critical water in range of 100 to 350^{o}C with the reaction time 5 minutes. The result was shown that the TOC rose up maximum yield at 232^{o}C then it was decreased with high temperature. Amino acids were found maximum yield at 127^{o}C but there were not observed when over 200^{o}C. In range of 150 to 250^{o}C, several soluble sugars were found (sucrose, fructose, glucose and glyceraldehyde). Organic acids were produced by decomposition from rice bran. Acetic acid, citric acid, formic acid, glycolic acid and levulinic acid were observed when temperature above 190^{o}C. Over 300^{o}C, the organic acids decreased with high temperature except acetic acid seems to be constant. Solid residue was observed for composition in each temperature. They found that the H/C in solid residue was decreased by increasing temperature because the pyrolysis reactions would enhance [21].

Pourali *et al.* studied the production of phenolic compounds from rice bran under subcritical water in range of 100 to 360^{o}C at the reaction time 10 minutes. Some phenolic compounds would be obtained from decomposition of rice bran under subcritical water: protocatechuic acid, p-hydrobenzoic acid, p-coumaric acid, syringic acid, vanillic acid, caffeic acid, gallic acid, ferullic acid and vanillin. The maximum product yields of the phenolic compounds were 230 to 295^{o}C then increasing temperature would enhance the decomposition reaction. The hydrolysis of rice bran in subcritical water was not only phenolic compounds but also carbohydrate was observed. Carbohydrate could be depolymerized into small sugar. It shows the soluble sugar yield increase with increasing temperature to reach at 190^{o}C, and then decreased to zero at 300^{o}C. The carbohydrate was hydrolyzed into water soluble oligomers and monomers, and then convert to other constituents, mainly to 5-HMF and soluble polymers [22].

CHAPTER III

FUNDAMENTAL KNOWLEDGE

Before exploring the experimental works, some fundamental information related to biomass and its utilization techniques have been reviewed to grasp the basic understanding which will be incorporated into the experimental analysis and discussion.

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 consists of carbon, hydrogen and oxygen based. This renewable energy source may also include biodegradable wastes that can be used as an energy source. There excludes organic material which has been transformed by geological processes into substances such as coal or petroleum. Environmentally, biomass is used as a replacement of fossil fuel, even though when they are burnt, the same amount of carbon dioxide (CO_2) is released into the atmosphere but when they are used for the energy production, it could be noted that a net amount of greenhouse gases are decreased because of the offset of methane (CH_4 is a much stronger greenhouse gas than CO_2) that would have otherwise entered the atmosphere.

3.2 Starch

Starch is the major form of stored carbohydrate in plants. Starch is composed of a mixture of two substances: amylose, an essentially linear polysaccharide, and amylopectin, a highly branched polysaccharide. Both forms of starch are polymers of α-D-Glucose. Natural starches contain 10-20% amylose and 80-90% amylopectin. Amylose forms a colloidal dispersion in hot water (which helps to thicken gravies) whereas amylopectin is completely insoluble.

3.2.1 Amylose molecules consist typically of 200 to 20,000 glucose units which form a helix as a result of the bond angles between the glucose units as shown in Figure 3.1.

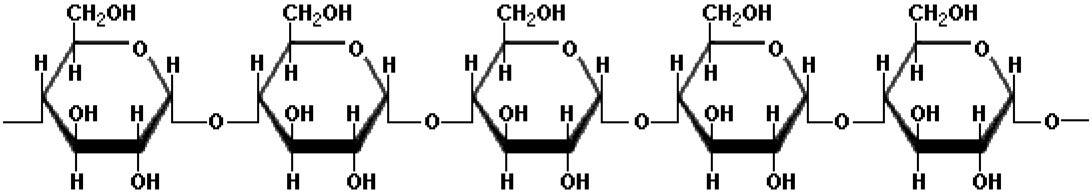

Figure 3.1 Amylase structure

3.2.2 Amylopectin differs from amylose in being highly branched. Short side chains of about 30 glucose units are attached with 1α→6 linkages approximately every twenty to thirty glucose units along the chain. Amylopectin molecules may contain up to two million glucose units as shown in Figure 3.2.

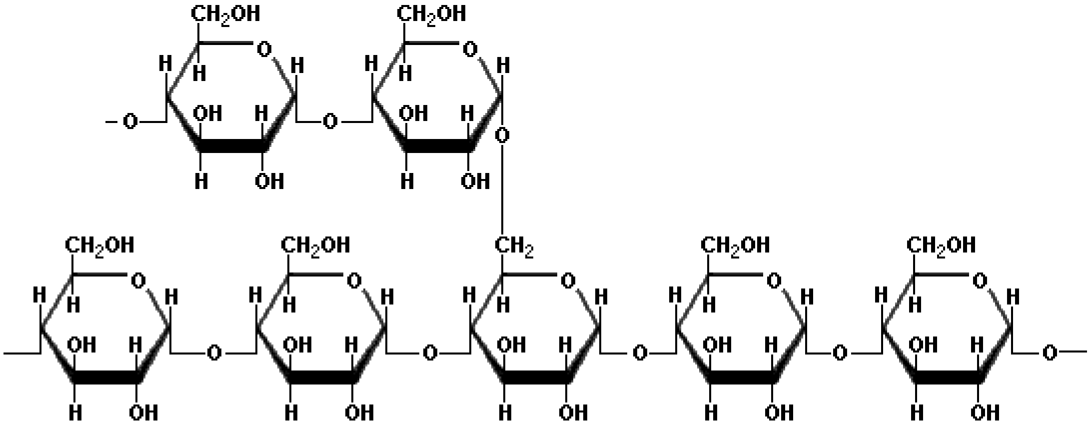

Figure 3.2 Amylopectin structure

3.2.3 Comparing starch and cellulose

Cellulose: Beta glucose is the monomer unit in cellulose. As a result of the bond angles in the beta acetal linkage, cellulose is mostly a linear chain shown in Figure 3.3: a) cellulose structure.

Starch: Alpha glucose is the monomer unit in starch. As a result of the bond angles in the alpha acetal linkage, starch-amylose actually forms a spiral much like a coiled spring shown in Figure 3.3: b).

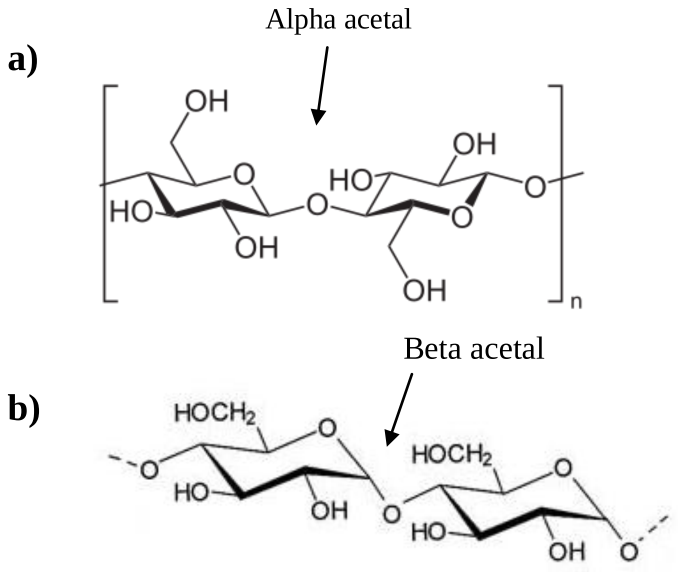

Figure 3.3 Unit structures; a) Cellulose structure, b) Starch structure

3.3 Hydrothermal treatment

Hydrothermal processing can be defined as any heterogeneous reaction in the presence of aqueous solvents or mineralizers under high pressure and temperature conditions to dissolve and recrystallize (recover) materials that are relatively insoluble under ordinary conditions. Definition for the word hydrothermal has undergone several changes from the original Greek, which contains ‘hydros’ for water and ‘thermos’ for heat. Hydrothermal reaction involves applying heat under pressure to achieve reaction in an aqueous medium. It has been attracting worldwide attention because of the fascinating characteristics of water as reaction medium at elevated temperatures and pressures as shown in Figure 3.4. The hydrothermal process will be enhanced solubility of oxygen in aqueous solutions at high temperatures and pressures provide a strong driving force for oxidation. The term subcritical water refers to liquid water at temperatures between the atmospheric boiling point and the critical temperature (374°C) of water. Very often interest is on temperatures above 200°C. Pressure is applied to keep water in liquid state. The pressure may be equal to the vapour pressure of water at a given temperature or higher. The necessary pressure range therefore is at least 16 bars at 200°C and up to 226 bars at 374°C. When exceeding its critical point at 374°C and 22.1MPa the values of density, dielectric constant and ionic product of water drop down drastically that supercritical water (SCW) acts as a non-polar solvent of high diffusivity and excellent transport properties as shown in Figure 3.4 and Figure 3.5. Even non-polar organic compounds and gases like oxygen become completely miscible with the SCW [4].

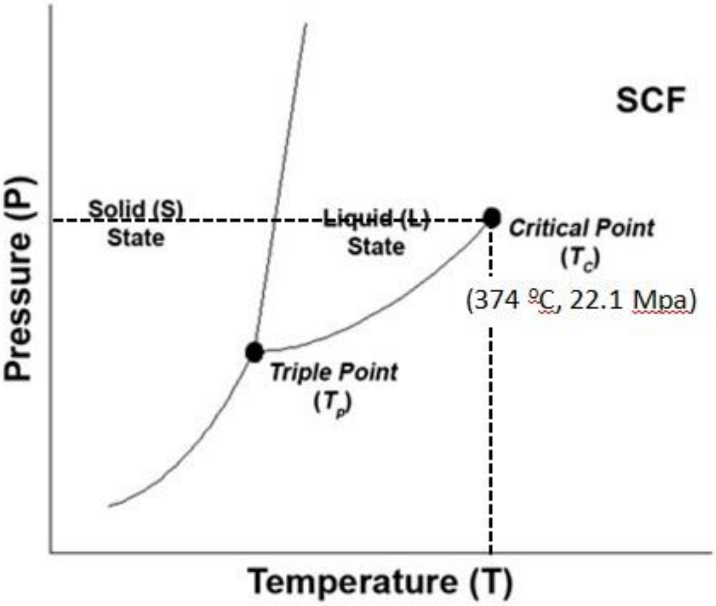

Figure 3.4 Phase diagram of water between temperature and pressure [4]

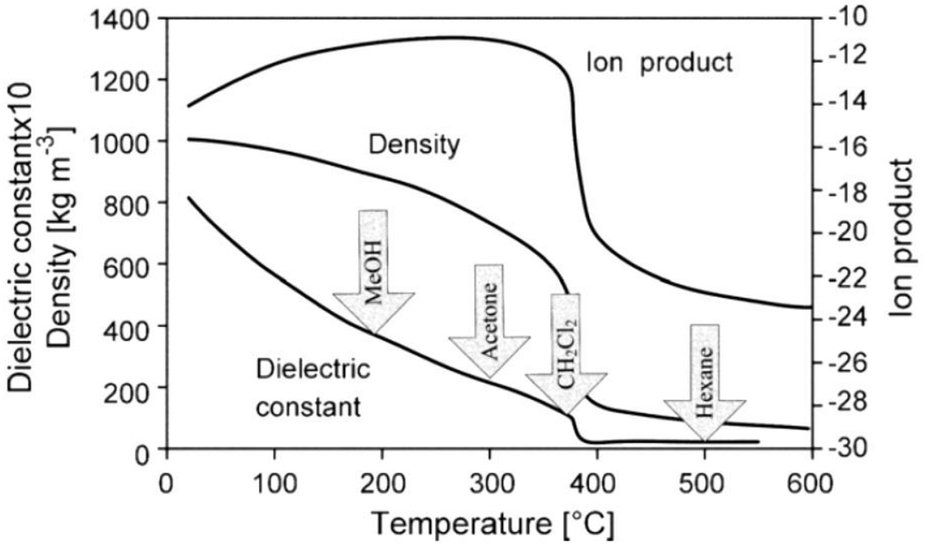

Figure 3.5 Physical properties of water at a pressure of 24 MPa vs. temperature [4] (dielectric constants of typical organic solvents at room temperature are indicated)

3.4 Biomass gasification principles

Gasification is partial thermal oxidation, which results in a high proportion of gaseous products, small quantities of char (solid product), ash, and condensable compounds (tars and oils). Steam, air or oxygen is supplied to the reaction as an oxidizing agent. The gas produced can be standardized in its quality and is easier and more versatile to use than the original biomass. Gasification adds value to low- or negative-value feedstock by converting it into marketable fuels and products. The gasification process consists of the following stages

- Drying. In this stage, the moisture content of the biomass is reduced. Typically, the moisture content of biomass ranges from 5% to 35%. Drying occurs at about 100 to 200°C with a reduction in the moisture content of the biomass of < 5%.
- Devolatilisation (pyrolysis). This is essentially the thermal decomposition of the biomass in the absence of oxygen or air. In this process, the volatile matter in the biomass is reduced. This results in the release of hydrocarbon gases from the biomass, due to which the biomass is reduced to solid charcoal. The hydrocarbon gases can condense at a sufficiently low temperature to generate liquid tars.

- Oxidation. This is a reaction between solid carbonized biomass and oxygen in the air, resulting in formation of CO_2. Hydrogen present in the biomass is also oxidized to generate water. A large amount of heat is released with the oxidation of carbon and hydrogen. If oxygen is present in substoichiometric quantities, partial oxidation of carbon may occur, resulting in the generation of carbon monoxide.
- Reduction. In the absence (or substoichiometric presence) of oxygen, several reduction reactions occur in the 800 to 1000°C temperature range. These reactions are mostly endothermic. The main reactions in this category are as follows equation:

  - Water carbon reaction:

    $$C + H_2O \longleftrightarrow CO + H_2 \qquad .....2)$$

  - Bounded reaction:

    $$C + CO_2 \longleftrightarrow 2CO \qquad .....3)$$

  - Water gas shift reaction:

    $$CO_2 + H_2 \longleftrightarrow CO + H_2O \qquad .....4)$$

  - Methane reaction:

    $$C + 2H_2 \longleftrightarrow CH_4 \qquad .....5)$$

3.5 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 reactions 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 the following equation:

$$-r_A = [k_A(T)]\,[\text{ fn } C_A, C_B, \ldots\,] \qquad .....6)$$

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.

$$k_A\,(T) = Ae^{-(E/RT)} \qquad \text{…..7)}$$

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

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 in the equation, 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 METHODOLOGY

4.1 Raw material

Thai jasmine rice was used as raw material in all experiment. Steamed rice will be dried in an oven at 100^{o}C for 24 hours to remove volatile matters. After drying, the dried sample will be sieved for controlling the particle sizes which are 250, 140 and 60 µm. Figure 4.1 shows steamed rice before drying process in a) and the powder of steamed rice after controlling the particle size in b).

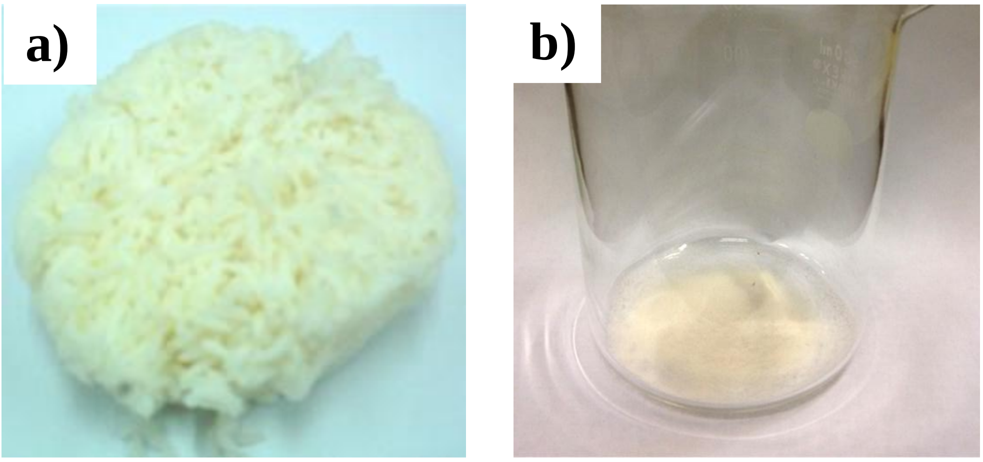

Figure 4.1 Image of carbohydrate material:
a) Steamed rice and b) Powder of steamed rice

4.2 Raw material characterization

4.2.1 Elemental composition

The elemental composition of sample powder are analyzed by Element Analyzer (Perkin Elmer, PE2400 Series II) and Thermalgravimetric analysis or TGA (TGA/DSC1 module, METTLER) to determine the chemical elements containing in sample powder.

Table 4.1 Chemical elements analysis of Steamed rice

Elemental composition	%wt
C	**43.6**
H	**5.9**
N	**1.89**
O(mass balance)	**64.19**

4.2.2 Particle size distribution

Sample powder are ground into smaller than 250, 140 and 60 μm by vibration ball mill and measured by using Particle size analyzer (Malvern, Master sizer 2000).

4.3 Biomass hydrothermal process

4.3.1 Batch reactor

Hydrothermal treatment of simulated food waste would be conducted in a tubular reactor which is schematically shown in Figure 4.2. Basically the reactor is made of a tubular stainless steel (SUS316) with an inner diameter of 21.18 mm and a length of 150 mm. At the top of the reactor, a pressure gauge (E Model, Swagelok) shows the internal pressure while a thermo couple is set at the bottom for monitoring the reacting temperature. Physical specification of the tubular reactor is summarized in Table 4.2.

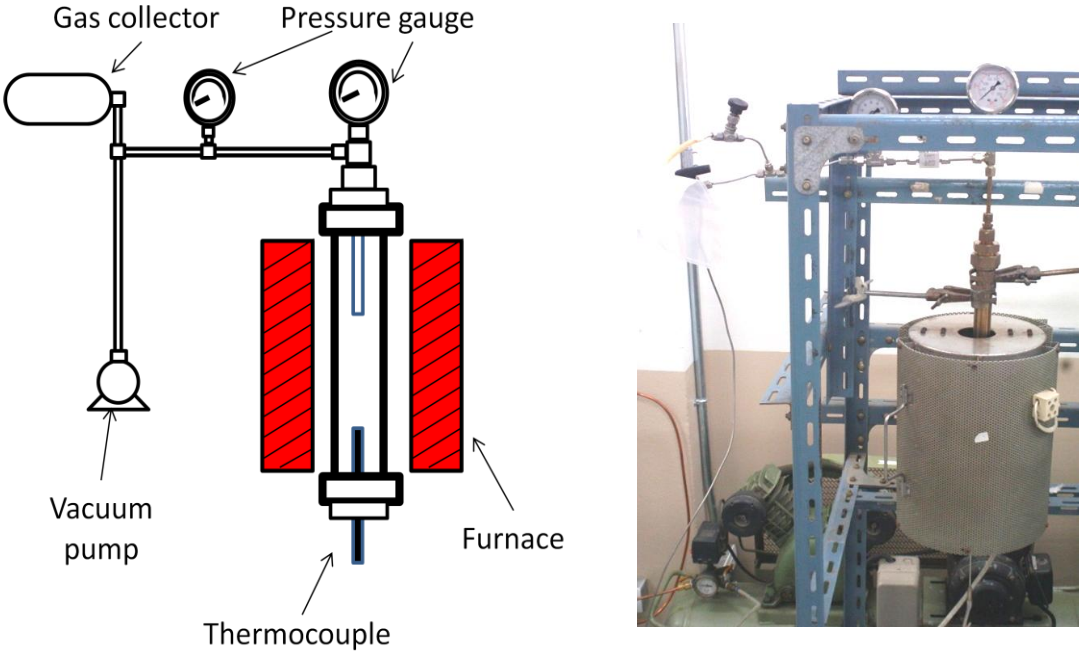

Figure 4.2 Tubular reactor in a batch system

Table 4.2 The physical properties of a tubular reactor used in this work

Material	SUS316
Volume (mm^3)	175
Inner diameter (mm)	21.18
Length (mm)	150
Wall thickness (mm)	2.11
Tolerant temperature (^oC)	649

All hydrothermal treatment would be performed in batch operation. Investigation of the influence of temperature and concentration on the gasification of simulated food wastes would be conducted with an aim to look into the generation gas yield. The reactor was heated using an electrical furnace to a designated temperature (300 to 400°C) with a heating rate (8 to 13°C/min) and kept at the set temperature for 10 min. Typical autogenously rising pressure with respect to temperature in each heating rate was shown in Figure 4.3. It was shown that the heating rate was not effect on the pressure inside reactor. Pressure increased with only increasing temperature. For sampling, the reactor was removed from the furnace and quickly quenched by soaking in a cold water bath to room temperature. Gas sample was collected using collecting gas bag while liquid and solid products were also taken for further analyses.

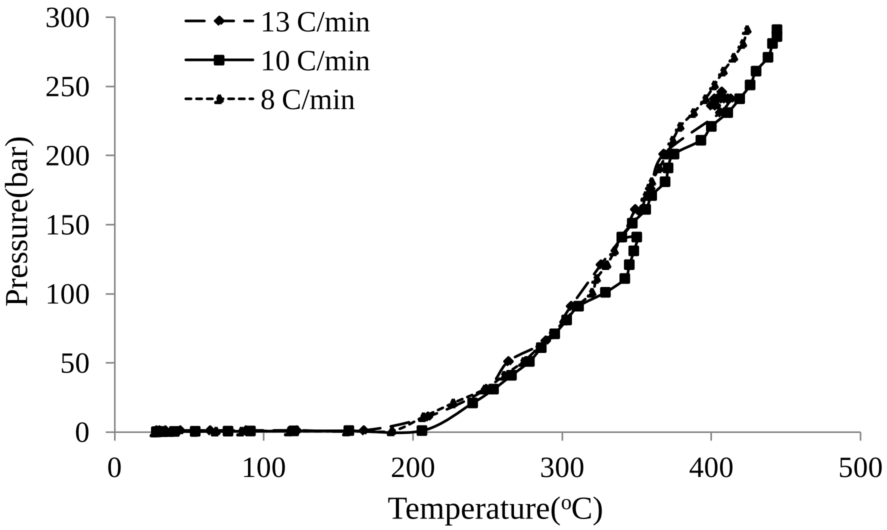

Figure 4.3 Autogenous pressure in the reactor with respect to rising temperature

4.3.2 Tubular flow reactor

In experimental continuous process, the carbohydrate feedstock was gasified by using the tubular flow reactor at Thermal Engineering Laboratory of Hiroshima University, Japan. The tubular flow reactor was used for gasification process as shown in Figure 4.4.

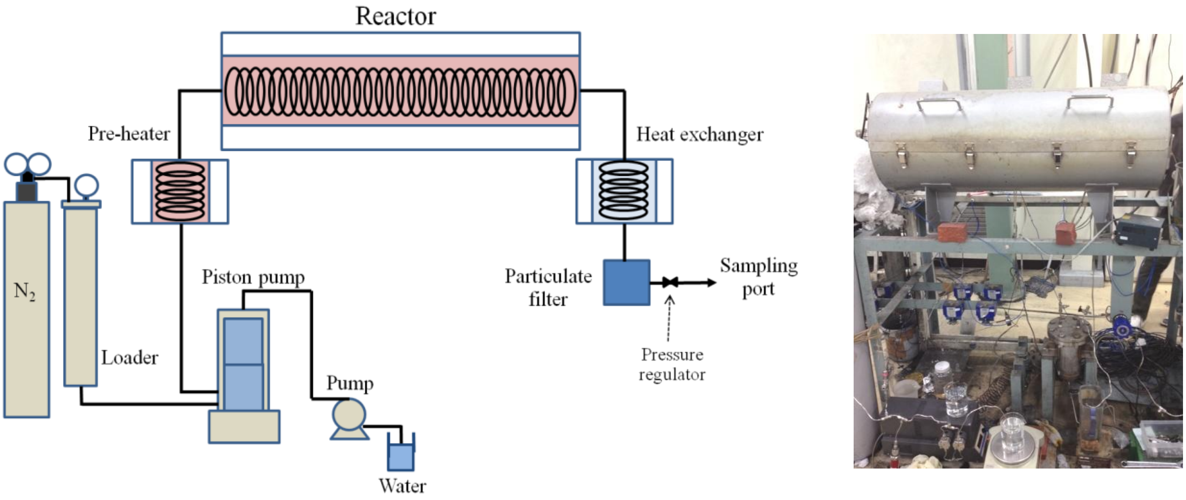

Figure 4.4 Tubular flow reactor in continuous system

All of experiments were investigated on the influence of temperature and particle size, the gasification of Steamed rice would be improved the yield of hydrogen in gas production. The tubular flow reactor was the inner diameter of 2.17 mm and the length of 12 m with Swagelok fitting. In a typical experiment, an accurately weighed amount of dried steamed rice on each condition and mixed with distilled water then were charged into loader as shown in Figure 4.5.

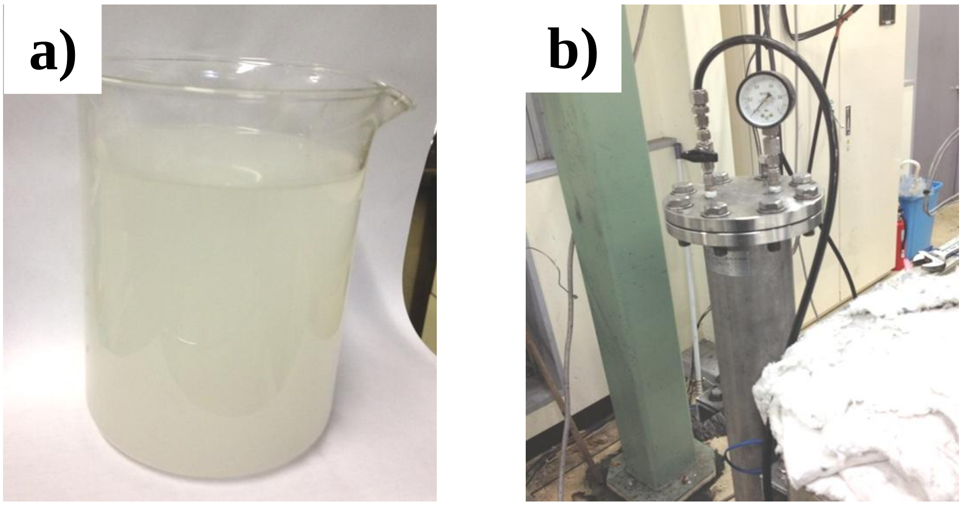

Figure 4.5 a) slurry feed stock (Steamed rice was mixed in distilled water) and b) loader

N_2 was fed into the loader. Then it forced the amount of feed stock inside the loader to go to Piston pump which was using 1400 rpm for stirring the slurry (Toyokoatu Co.) as shown in Figure 4.6.

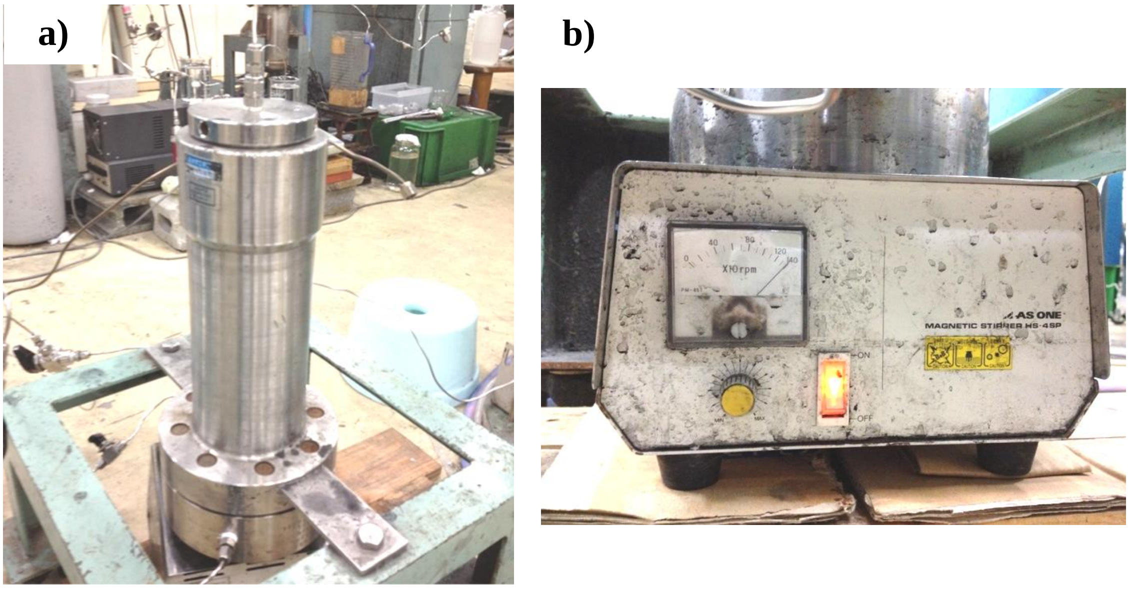

Figure 4.6 Piston pump details; a) Piston pump and b) Stirring speed

Then pump loaded the amount of water by the high pressure pump for forcing the feed stock into pre-heater and lead to reactor. After the feed stock passed the reactor, there would be cooled in the heat exchanger. Then the samples were separated by liquid-solid separator (ss-2TF-90, Swagelok) as shown in Figure 4.7. The gas samples were analyzed by using gas chromatography and the liquid samples were analyzed by using total organic carbon analyzer.

Figure 4.7 The picture of filter separator

All of experiments, the gas sample was collected by using the line of gas sampling port as U-shape under hydrochloric acid solution. The solution was prepared 0.1 mol/L of hydrochloric acid (purchased from Sigma Aldrich) and was diluted by deionized water (< 1 µs/cm; Organo water deionizer model BB-5A) as shown in Figure 4.8.

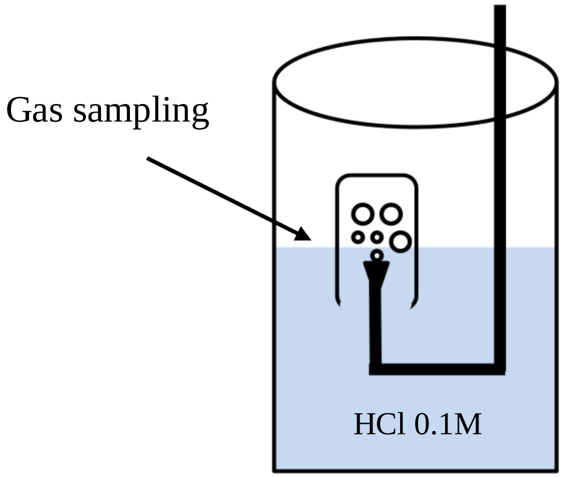

Figure 4.8 Schematic of gas sample collecting

4.4 Chemical analysis

Fuel products from carbohydrate hydrothermal treatment could be divided into gas, liquid and solid products. After treatment, product in each phase would be collected and subject to different analytical methods as shown in Figure 4.9.

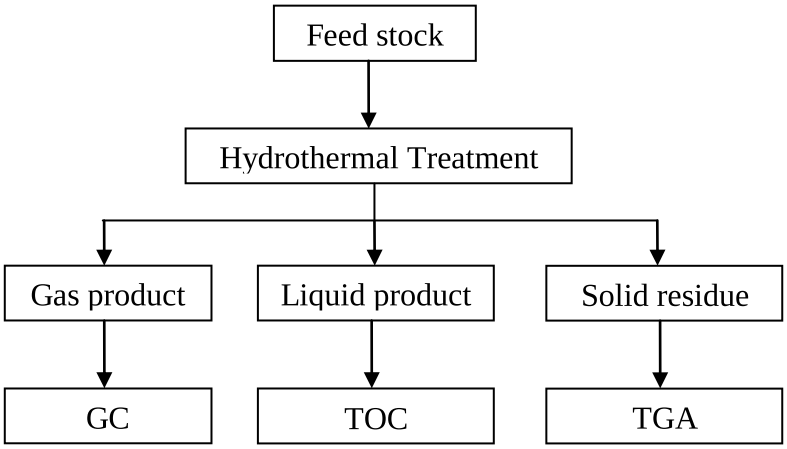

Figure 4.9 Scheme of the step product analysis

The gas product was analyzed with gas chromatography (GC-8A and GC-14B, Shimadzu) for hydrogen and carbon analysis in gas product as shown in Figure 4.10.

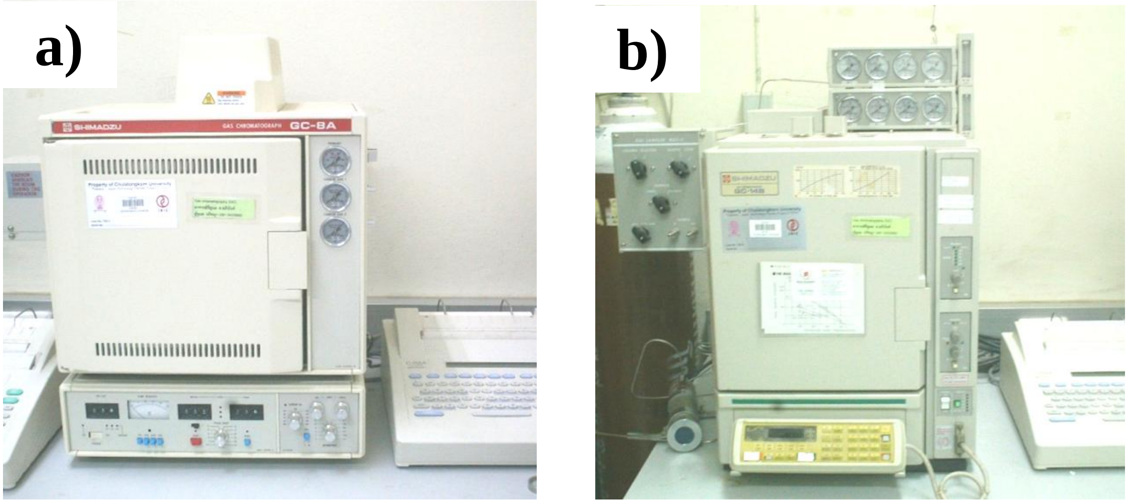

Figure 4.10 Gas chromatography; a) GC-8A model and b) GC-14B model

The liquid product was also analyzed by a Total Organic Carbon analyzer or TOC (TOC-V_{CPH}, Shimadzu) analyzer for measuring the amounts of carbon content in liquid product that was including non-purgeable organic carbon (NPOC) and the gas product was dissolved in liquid (inorganic carbon or IC) as shown in Figure 4.11.

Figure 4.11 Total Organic Carbon analyzer (TOC-V_{CPH}, Shimadzu)

Finally, solid residue would also be subject to Element Analyzer (Perkin Elmer, PE2400 Series II), was shown in Figure 4.12 and Thermalgravimetric analysis or TGA (TGA/DSC1 module, METTLER), was shown in Figure 4.13 for confirming the total hydrogen, carbon and oxygen balance.

Figure 4.12 Element Analyzer (Perkin Elmer, PE2400 Series II),

Figure 4.13 Thermalgravimetric analysis (TGA/DSC1 module, METTLER)

4.5 Experimental condition

4.5.1 The effect of temperature and heating rate on steamed rice (batch process)

Steamed rice powder was used as raw material in experiments that would be conducted in range of temperature 300 to 400^{o}C and heating rate 8 to 13^{o}C/min in batch hydrothermal process. To investigate the effect of both parameters, hydrothermal process would be generated the amount of gas. Steamed rice powder was classified into 250 µm. Table 4.3 shows the condition of hydrothermal process.

Table 4.3 the condition of experiments in batch process

Raw material	Steamed rice
Temperature (^{o}C)	300, 350, 400
Heating rate (^{o}C/min)	8, 10, 13
Concentration (%wt)	10
Pressure (MPa)	Autogenously
Particle size (µm)	250
Additive	-

4.5.2 The effect of temperature, particle size and catalyst on steamed rice (continuous process)

Steamed rice powder was used as a feed stock in the tubular flow reactor in each condition. In experiment, there investigated on the effect of temperature in range of 400 to 600^{o}C, the effect of particle size in range of 60 to 250 µm and the effect of additive by using H_2O_2 (0.5%wt) that was shown in Table 4.4

Table 4.4 the condition of experiments in continuous process

Raw material	Steamed rice
Temperature (^oC)	400, 500, 600
Heating rate (^oC/min)	-
Concentration (%wt)	0.1-0.2
Pressure (MPa)	25
Particle size (µm)	60, 140, 250
Additive	none, H_2O_2

CHAPTER V

RESULTS AND DISCUSSIONS

Based on the objective of the research, experimental works were operated into two parts. The first part was conducted using a batch tubular reactor. The other was conducted in Hiroshima University by using a continuous flow reactor. Experimental data obtained from the first part would be used as reference for low temperature condition. As an extension of investigation on temperature effect, the continuous flow reactor was examined using the same raw material.

5.1 Batch process

5.1.1 The effect of temperature on gaseous products

In order to examine effect of maximum temperature, an arbitrary heat rate of 13^{o}C/min was set to heat up each steamed rice sample filled into the batch tubular reactor until reaching the designated temperature. Temperature history with respect to each designated temperature (300, 350 and 400^{o}C) was shown in Figure 5.1. It would be noted that the total time which the reactor was heated from the room temperature to the designated temperature and cooled down to the room temperature again was almost the same. The reaction time was 70 minutes in each experiment. This information would suggest that reaching time period would be almost identical in each experiment. Therefore, it would reasonably be assumed that reaction time would exert insignificant effect on the reaction product.

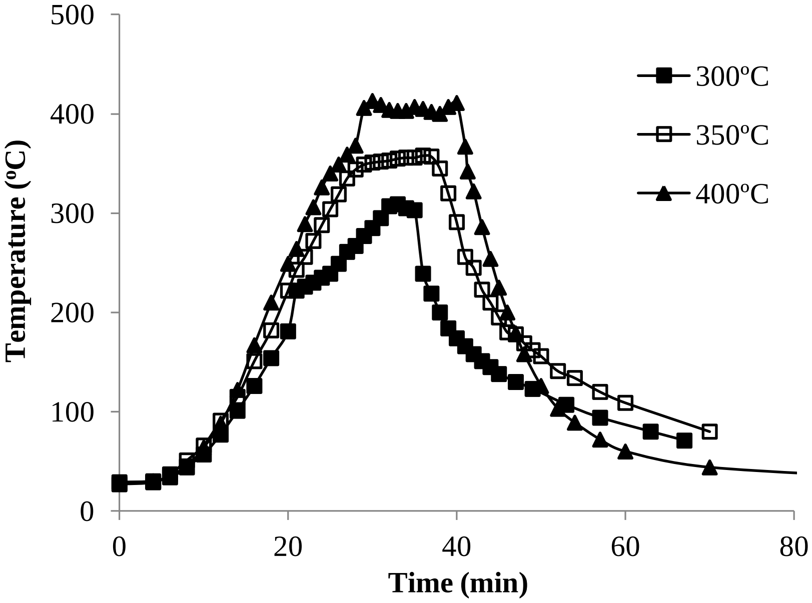

Figure 5.1 The history of temperature in hydrothermal process in temperature 300 to 400°C at heating rate 13°C/min

Effect of reaction temperature on the decomposition of steamed rice would be discussed by analyzing the fraction of carbon in gas, liquid and solid forms which is shown in Figure 5.2. It was found that the amount of carbon in gas was drastically increased with increasing temperature while the amount of carbon in liquid and solid was oppositely decreased. High temperature could enhance the carbon gasification for converting carbohydrate in steamed rice into gaseous product.

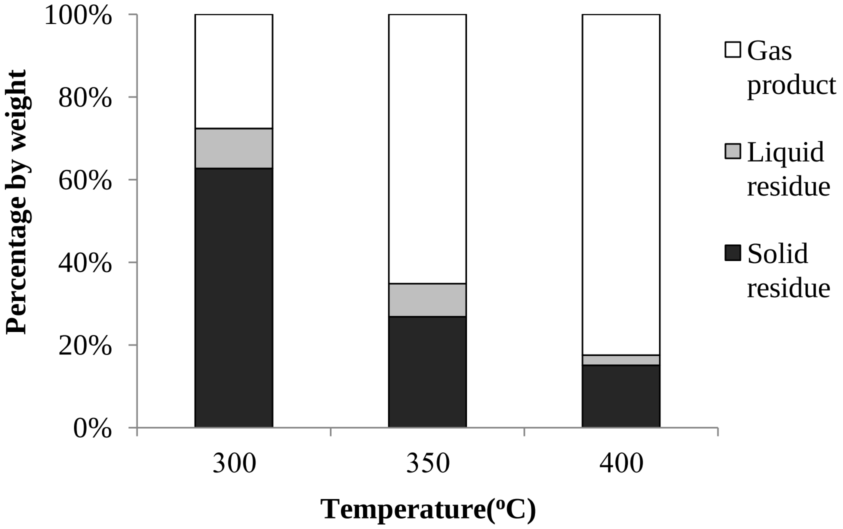

Figure 5.2 The carbon balance in each phase at difference temperature at heating rate 13°C/min

After hydrothermal treatment, gas samples were collected and then analyzed with gas chromatography. Yield of gaseous product with respect to the designated temperature is shown in Figure 5.3. H_2 yield is separately shown in Figure 5.4. It was found that amount of gaseous products which were H_2, CH_4 and CO_2 became higher with the increased temperature. High temperature would promote the decomposition of steamed rice, resulting in liquid yield of gaseous product. The major products of biomass gasification in hydrothermal treatment were H_2 and CO_2. Meanwhile CO was formed as intermediate before converted to CO_2 and H_2 increased by steam reforming reaction. In batch process, the amount of H_2 yield was lower than the amount of CO_2 yield because the reaction time is not enough for complete the steam reforming reaction [7-17].

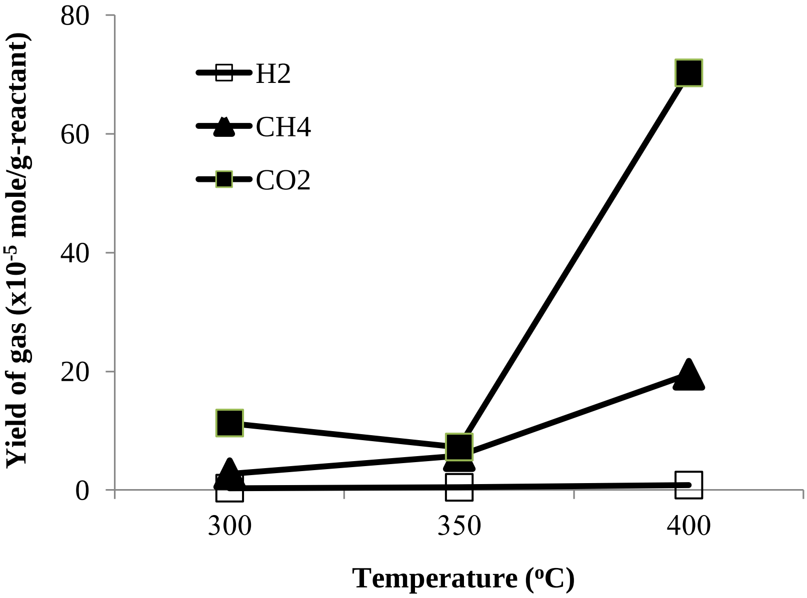

Figure 5.3 The yield of gas production at difference reaction temperatures at heating rate 13°C/min

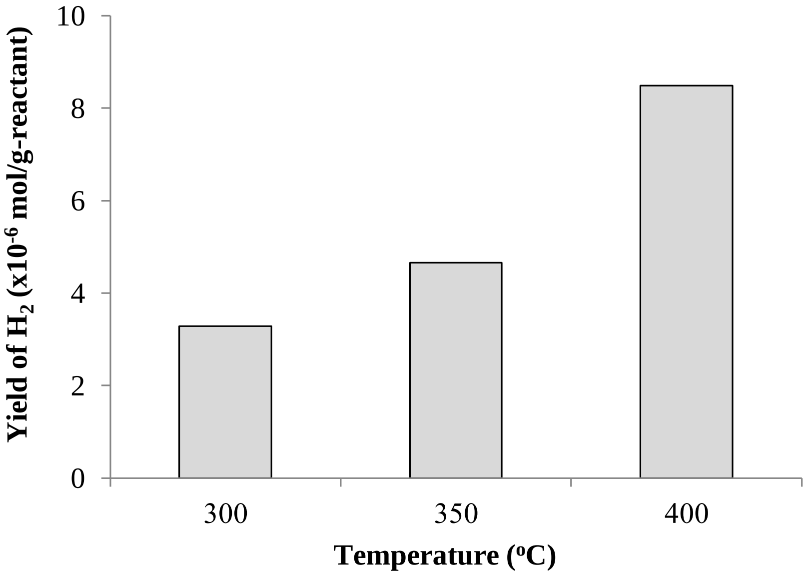

Figure 5.4 The yield of hydrogen production at difference reaction temperatures at heating rate 13°C/min

The liquid residues after hydrothermal treatment were observed by using TOC analyzer for detecting the amount of water soluble carbon. Figure 5.5 shows the amount of TOC in liquid residues after hydrothermal in difference temperature. TOC decreased with increasing temperature. The steam rice had carbohydrate as a major product. When temperature increased, carbohydrate could be depolymerized into small sugar. Many researchers studied the decomposition of glucose in hydrothermal treatment. They found that glucose decomposed to 1,6-anhydrousglucose and 5-HMF as major products. Then the derivatives were gasified into gas and decomposed into small molecules depending on selectivity of the reaction [19-22].

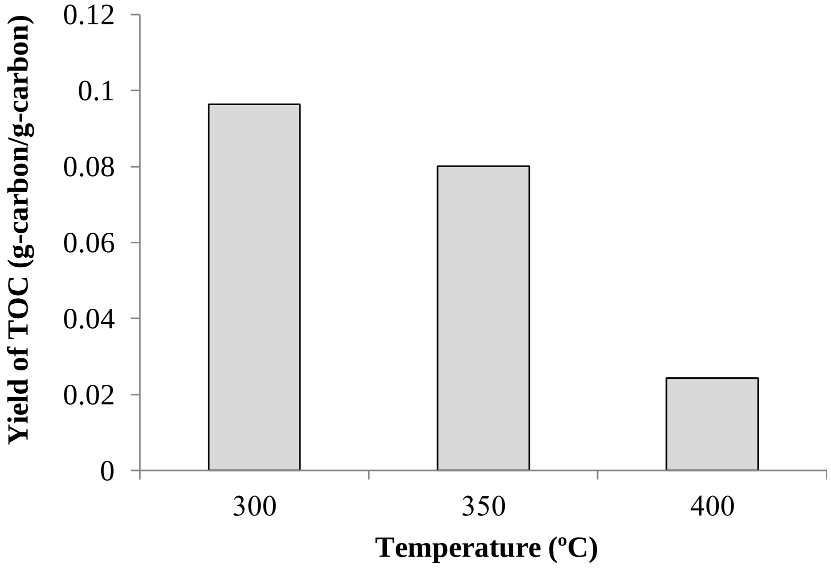

Figure 5.5 The yield of TOC in liquid residue at difference reaction temperatures at heating rate 13^{o}C/min

The solid residues were analyzed by using elemental analysis for comparing the amount of carbon, hydrogen and nitrogen between pristine steamed rice and the solid residues after hydrothermal treatment in each condition as shown in Figure 5.6. Every experiments, after hydrothermal treatment the amount of carbon was changed. It could suggest that the pristine steamed rice was the carbohydrate as a polymer of amylose and amylopectin. When the carbohydrate was hydrolyzed into monosacharides and some delivatives, there was reacted and become to carbonacious material such as carbon microsphere [23]. So, the solid residue contained the amount of carbon as a major product.

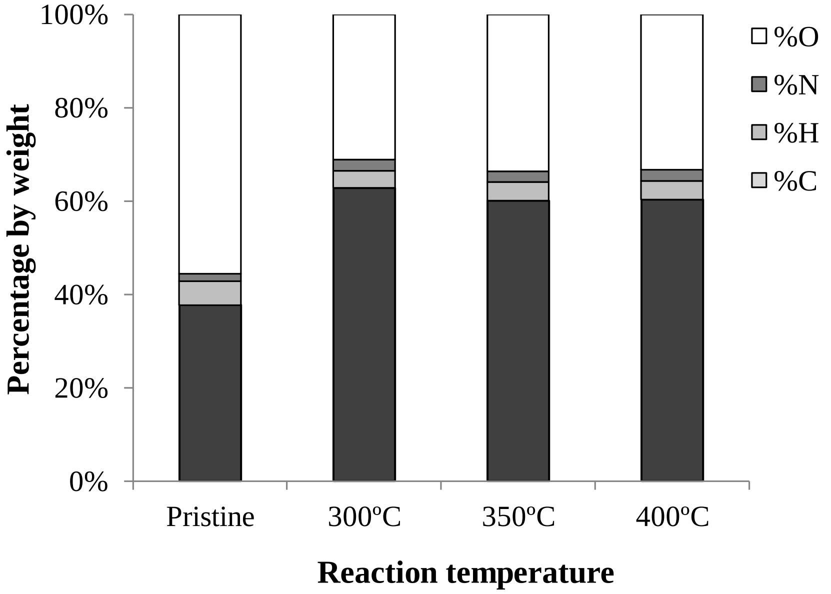

Figure 5.6 Elemental analysis of solid residue after hydrothermal treatment in each temperature at heating rate 13°C/min

Then, solid residues were analyzed by using TGA. Decomposition of pristine steamed rice was related with solid residue of each temperature as shown in Figure 5.7. the result of TGA, the pristine steamed rice was decomposed in range of 300^{o}C. After hydrothermal treatment, the solid residue was decomposed at different temperature. It could suggest that the morphology of steamed rice was changed into stable thermal decomposition during hydrothermal treatment, so it would change the temperature of decomposition in solid residue from pristine steamed rice as the same reason of generated carbonacious material [23].

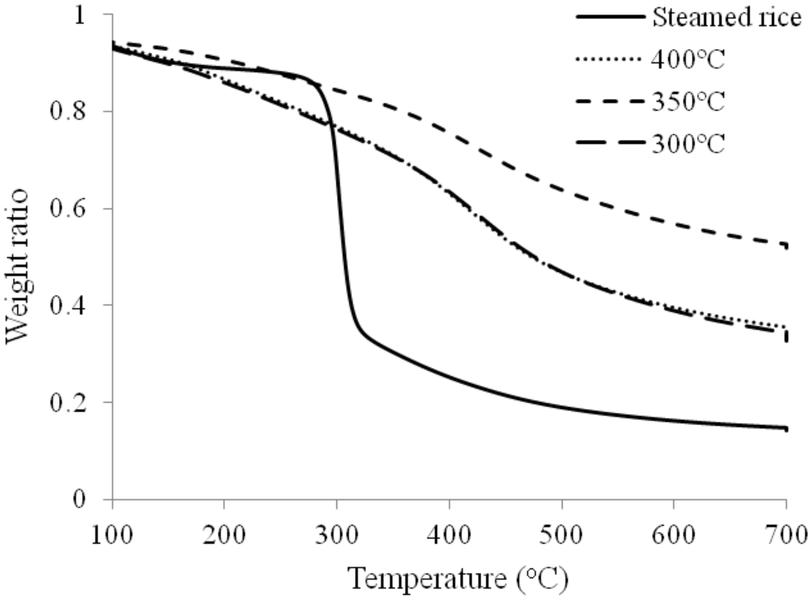

Figure 5.7 Effect of reaction temperature on solid residue after hydrothermal treatment at heating rate 13^{o}C/min

The chemical transformations that occur when the biomass was converted into cabonaceous products by means of hydrothermal treatment were examined by several spectroscopic techniques. FTIR spectra of the solid residues was shown in Figure 5.8. It could be seen that the FTIR spectra of the solid residue was difference from pristine steamed rice. There were contained a several bands which reveal that aromatization processes take place during hydrothermal process. The presence of aromatic rings was evidenced by the band at 1620 cm^{-1}, attributed to C=C vibrations, and the band at 875-750 cm^{-1}, assigned to aromatic C-H out-of-plane bending vibrations. The solid residues also contained aliphatic structures, could be observed from the band 3000-2815 cm^{-1}. Moreover the presence of oxygen groups was suggested by the band at 1710 cm^{-1} (C=O vibrations corresponding to carbonyl, quinone, ester or carboxyl) and 1000-1460 cm^{-1} (C-O streching vibrations in hydroxyl, ester or ether and O-H bending vibrations) [24].

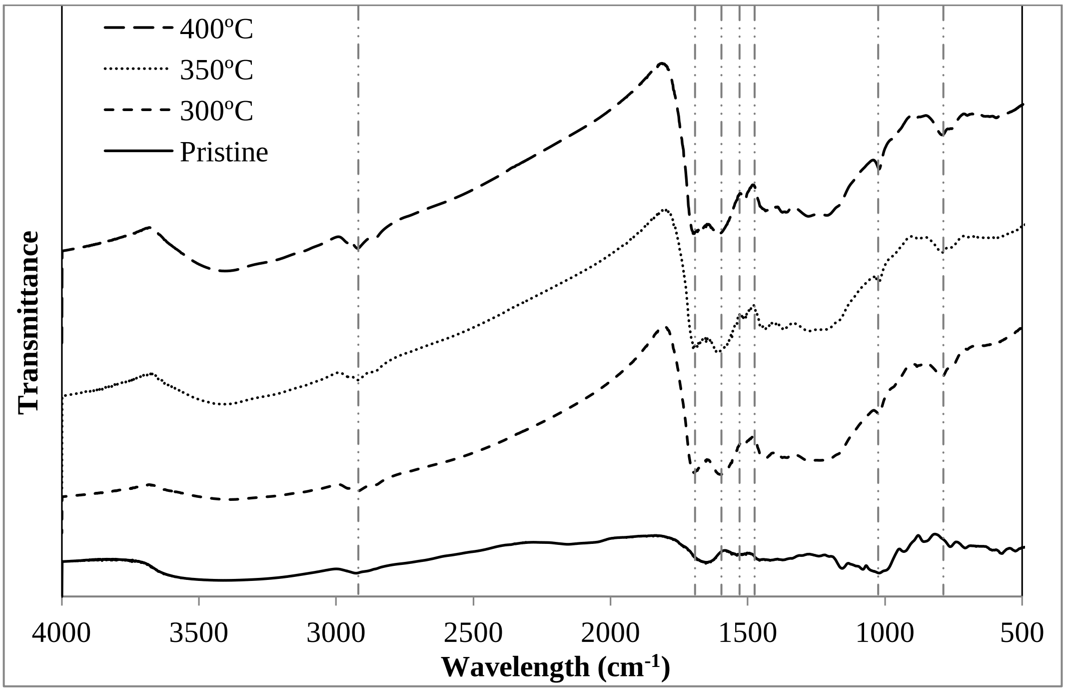

Figure 5.8 FTIR spectra for pristine steamed rice and solid residue after hydrothermal treatment in each temperature at heating rate 13°C/min

Also there were confirmed the changing morphology of solid residue after hydrothermal in each temperature as shown in Figure 5.9, it was shown SEM images of the pristine steamed rice (Figure 5.9 (a)) and solid residue obtained by hydrothermal treatment at each temperature. It could be noted that, whereas the products from hydrothermal treatment exhibit sphere morphology similar in each temperatures while pristine steamed rice similar as a large part. It shows that hydrothermal treatment would be changed characteristic of steamed rice. The particle in high temperature was smooth and large particle than particle at low temperature. The result of experiment could be suggest that hydrothermal treatment decomposed biomass and reformed into the carbonaceous material and then the properties in material were changed to more stability at high temperature as shown in Figure 5.6, Figure 5.7 and Figure 5.8.

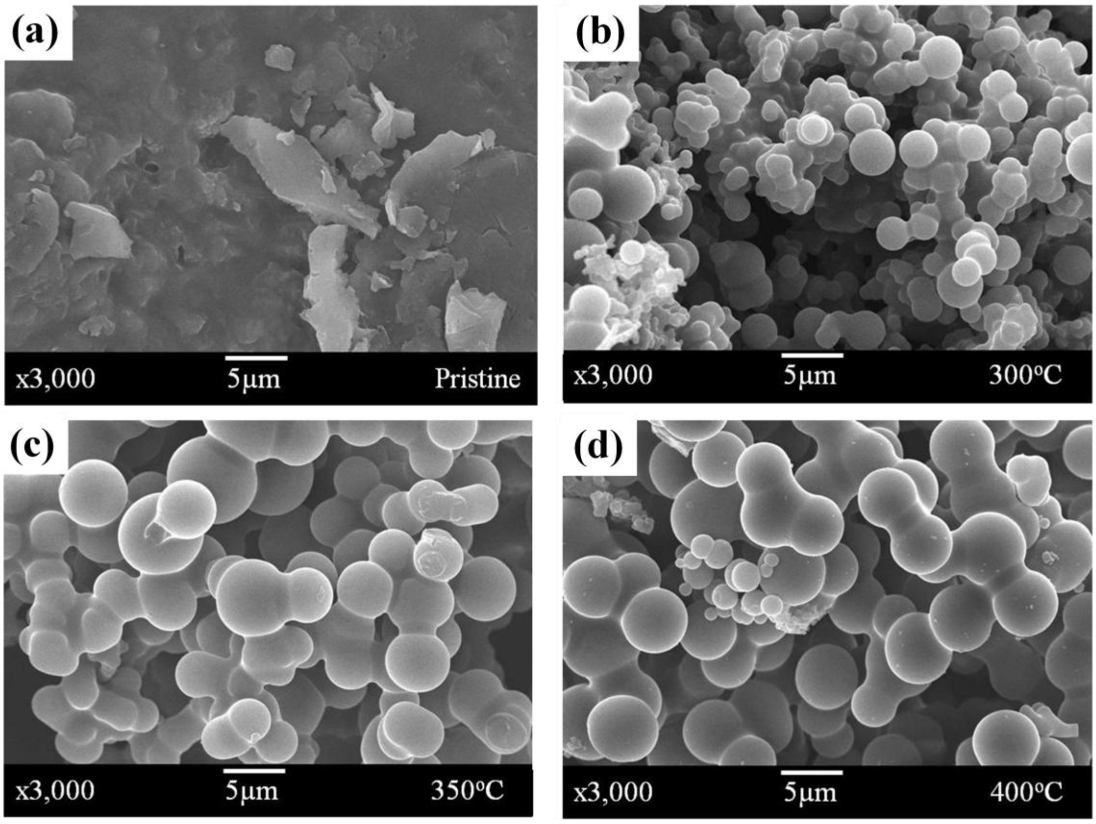

Figure 5.9 SEM images of a) Pristine steam rice, b) solid residue after hydrothermal treatment at 300°C, c) solid residue after hydrothermal treatment at 350°C and d) solid residue after hydrothermal treatment at 400°C with heating rate 13°C/min

5.1.2 The effect of heating rate on gas products

In this study, the effect of heating rate on gas production yield was investigated. Dried steamed rice was processed in hydrothermal treatment at reaction at temperature 400°C with heating rate 8, 10 and 13°C/min to observed hydrogen yield and methane yield. Figure 5.10 shows the temperature history inside the tubular reactor with reaction temperature and heating rate. In addition, heating rate is concerned that the contact times between feed stock and water vapor are reacted during the hydrothermal process.

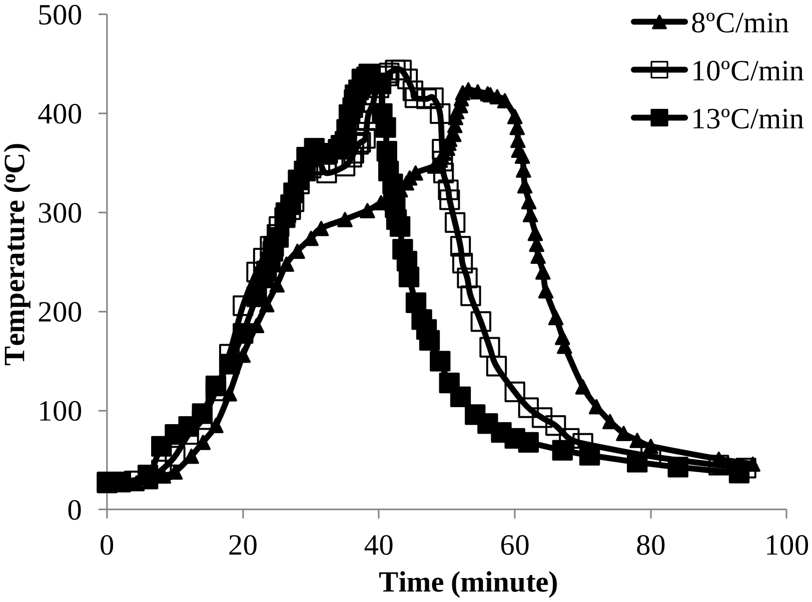

Figure 5.10 Temperature history of the hydrothermal process at 400°C in each heating rate

The carbon balance in each phase was shown in Figure 5.11. It shows that the amount of carbon in gas phase was highest at high heating rate while the amount of carbon in liquid phase was lowest at high heating rate. At the same temperature, high heating rate enhanced the amount of carbon in liquid and solid phase to gas formation. The small sugar was converted to derivatives of glucose and then gasified into CO and CO_2 [10].

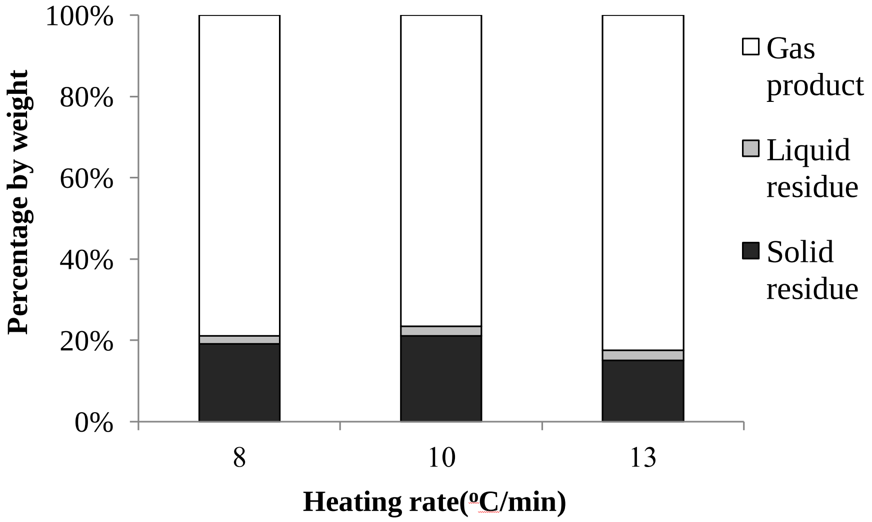

Figure 5.11 The carbon balance in each phase at difference heating rate at 400°C

The gas samples were collected after hydrothermal treatment and then analyzed with gas chromatography as shown in Figure 5.12. It shows that amount of gas products which were H_2 and CH_4 were increased with increasing heating rate. It could be suggest that the heating rate affected the gasification of biomass during hydrothermal process. The CO was increased with increasing heating rate and then H_2 was promoted in the water gas shift reaction pathway. The major products of the water gas shift reaction in hydrothermal treatment were H_2 and CO_2 [10].

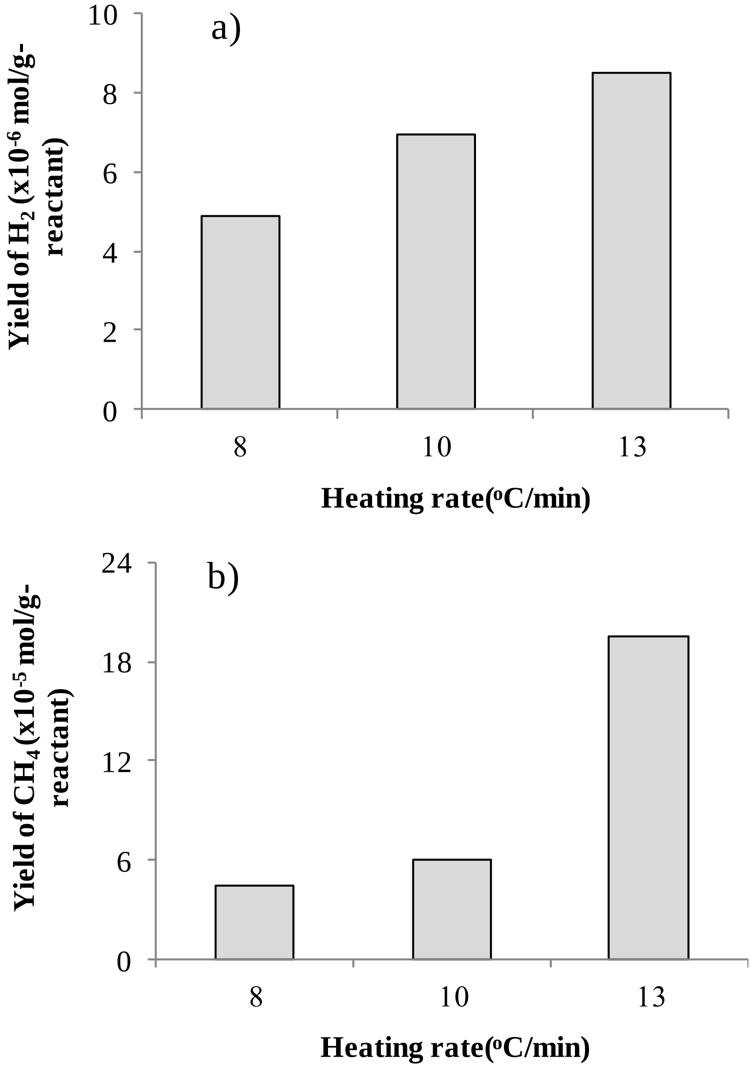

Figure 5.12 The yield of hydrogen production at 400°C in each heating rate; a) hydrogen yield and b) methane yield

Figure 5.13 shows the effect of heating rate on the liquid products of steamed rice at 400°C. The shortest reaction time (highest heating rate) showed the highest yield of TOC in liquid phase. Carbohydrate in steamed rice was depolymerized into small sugar and derivatives. At high heating rate, small sugar was converted to the derivatives of glucose that were 5-HMF and anhydroglucose. In addition, the longer time at lower temperature inhibited the formation of gas [10]. Thus, heating rate has a great influence for gasification of glucose at high temperature.

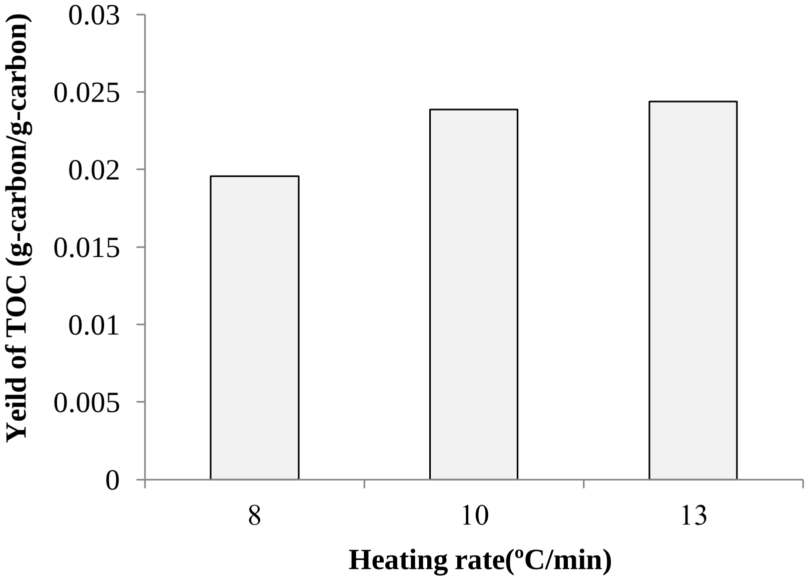

Figure 5.13 The yield of TOC in liquid residue at 400°C in each heating rate

The solid residues were analyzed by using elemental analysis for comparing the composition in pristine steamed rice and solid residues after hydrothermal treatment in each condition as shown in Figure 5.14. In all experiments, after hydrothermal treatment the amount of carbon in solid residues was changed from the pristine stemed rice. At high heating rate, the amount of carbon in solid residue was lower than the amount of carbon in solid residues at low heating rate. It could suggest that the pristine steamed rice was converted into small sugars with high tempeature and then high heating rate enhanced gasification of small sugar to gas. It confirmed that the effect of heating rate enhaced the gasification of carbon as shown in Figure 5.11, Figure 5.12 and Figure 5.13.

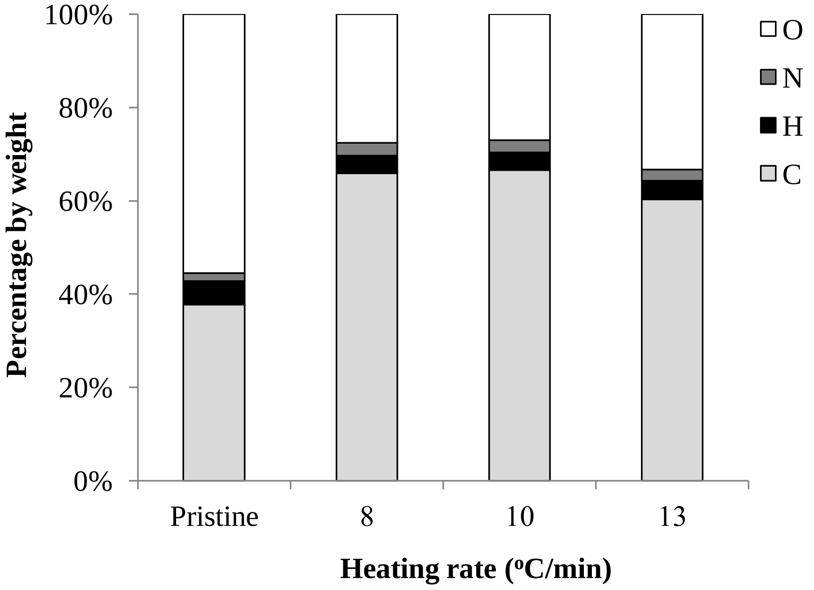

Figure 5.14 Elemental analysis of solid residue after hydrothermal treatment in each heating rate at 400^{o}C

Then, solid residues were analyzed by using TGA. Decomposition of pristine steamed rice was related with solid residue of each temperature as shown in Figure 5.15. the result shows that the pristine steamed rice was decomposed in range of 300°C while the solid residues after hydrothermal treatment were stable at high temperature. The effect of heating rate on solid residues (Figure 5.15) was the same results of the effect of temperature on solid residues as shown in Figure 5.7. It could suggest that the both effect of temperature and heating rate on the solid residues were changed into the same properties of solid residues.

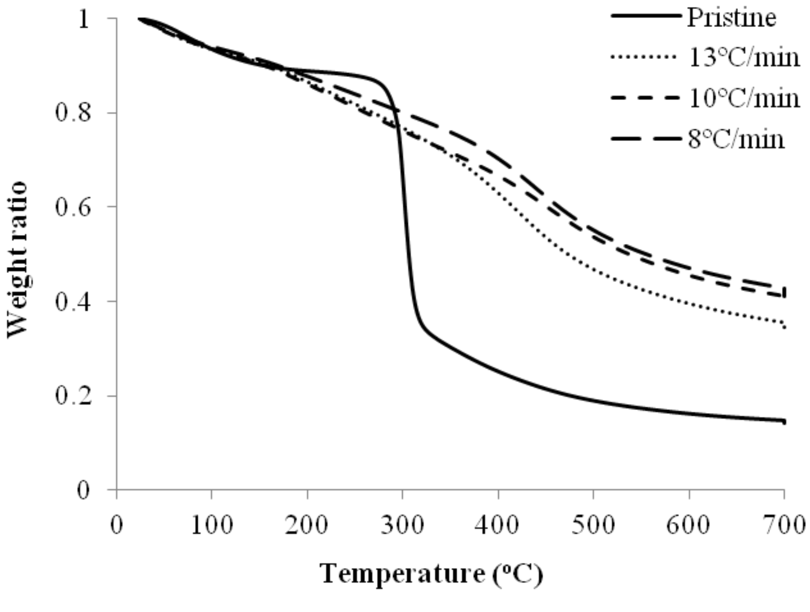

Figure 5.15 Effect of heating rate on solid residue after hydrothermal treatment at 400°C

The solid residues were observed for the chemical transformations that was converted into cabonaceous products by using FTIR spectra as shown in Figure 5.16. It could be seen that the FTIR spectra of the solid residues in difference heating rate were difference from pristine steamed rice. There were contained a several bands which reveal that aromatization processes take place during hydrothermal process. The aromatic rings was observed by the band at 1620 cm^{-1}, attributed to C=C vibrations at 875-750 cm^{-1}, assigned to aromatic C-H out-of-plane bending vibrations. The solid residues also contained aliphatic structures that was shown in the band 3000-2815 cm^{-1} and the oxygen groups was suggested by the band at 1710 cm^{-1} (C=O vibrations corresponding to carbonyl, quinone, ester or carboxyl) and 1000-1460 cm^{-1} (C-O streching vibrations in hydroxyl, ester or ether and O-H bending vibrations) [24]. The chemical transformations on the solid residues at difference heating rate was similar the solid residues at difference temperature as shown in Figure 5.8.

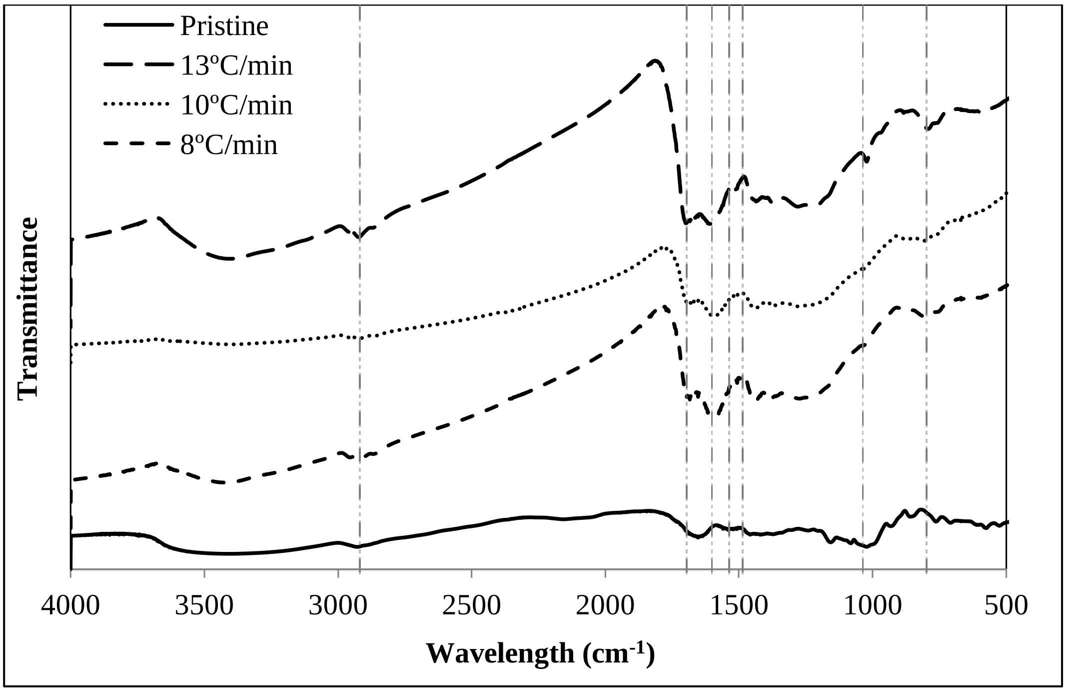

Figure 5.16 FTIR spectra for pristine steamed rice and solid residue after hydrothermal treatment in each heating rate at 400°C

There were confirmed the changing morphology of solid residue after hydrothermal in each temperature by using scanning electron microsphere as shown in Figure 5.17, it was shown SEM images of the pristine steamed rice (Figure 5.17, a) and solid residue obtained by hydrothermal treatment in each heating rate. It could be noted that the morphology of the solid at high heating rate exhibit sphere morphology and then sphere morphology agglomerated to tube morphology with long reaction time while pristine steamed rice similar as a large part. It shows that hydrothermal treatment would be changed characteristic of steamed rice even the difference reaction time could be changed the morphology in solid particle. The solid particle in low heating rate was sintered than particle at high heating rate.

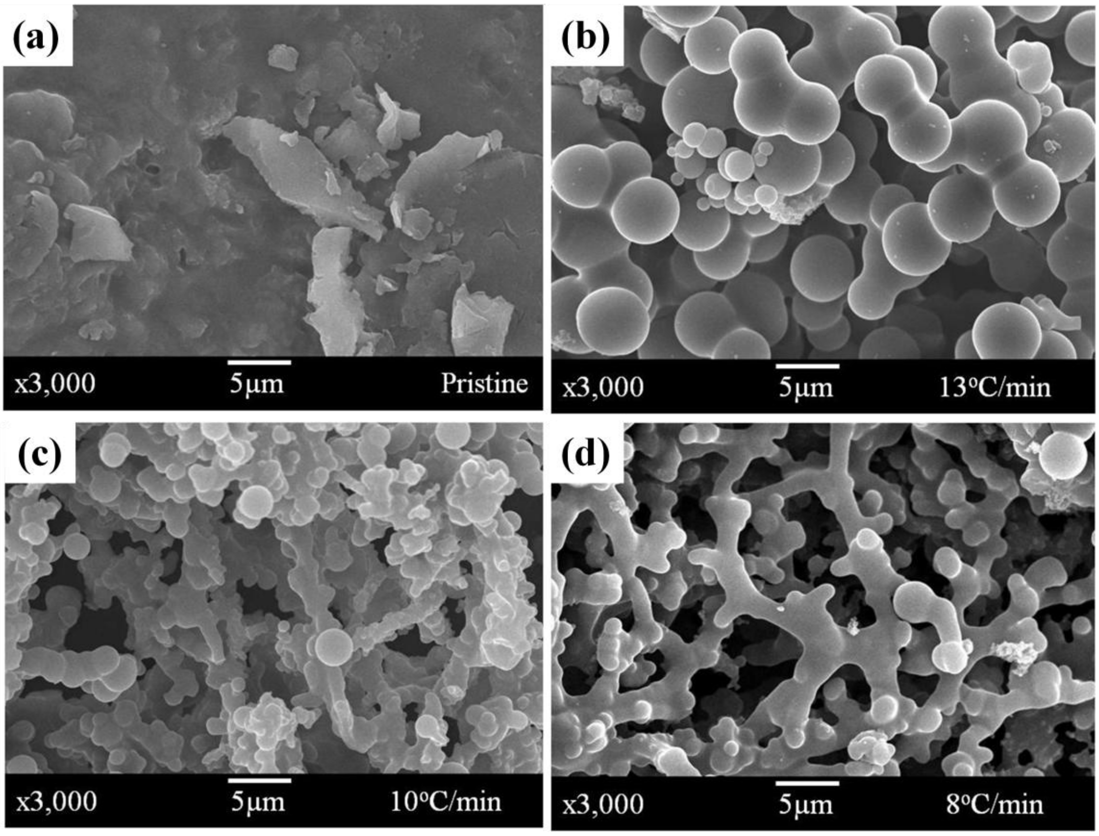

Figure 5.17 SEM images of a) Pristine steam rice, b) solid residue after hydrothermal treatment with 8°C/min, c) solid residue after hydrothermal treatment with 10°C/min and d) solid residue after hydrothermal treatment with 13°C/min at 400°C

From this experiment, hydrogen yield was increased when increased temperature and heating rate. The path way of carbohydrate conversion could suggest that the steamed rice was converted into monosaccharide and then gasified to gas but some derivatives of glucose still contained in liquid phase instead of gas production. The decomposed glucose was starting at temperature in range of 250 to 280^{o}C. In the other hand, high temperature and high heating rate could make better reaction than low temperature and low heating rate because of lower condition was just a partial reaction or not complete reaction with carbohydrate [9 - 12]. Then it confirmed that the amount of organic carbon in liquid phase could be generated to gas production that including hydrogen gas [24]. A presence of carbonaceous microsphere, some carbohydrate was hydrolyzed during hydrothermal treatment that became monosaccharide. Then, they were decomposed to organic acids. At the same time, the aromatization of polymers takes place. When the concentration of aromatic clusters that was converted from small sugars in the aqueous solution reaches the critical super saturation point, a burst nucleation takes place. From the results, the path ways of steamed rice conversion in hydrothermal process was proposed in Figure 5.18.

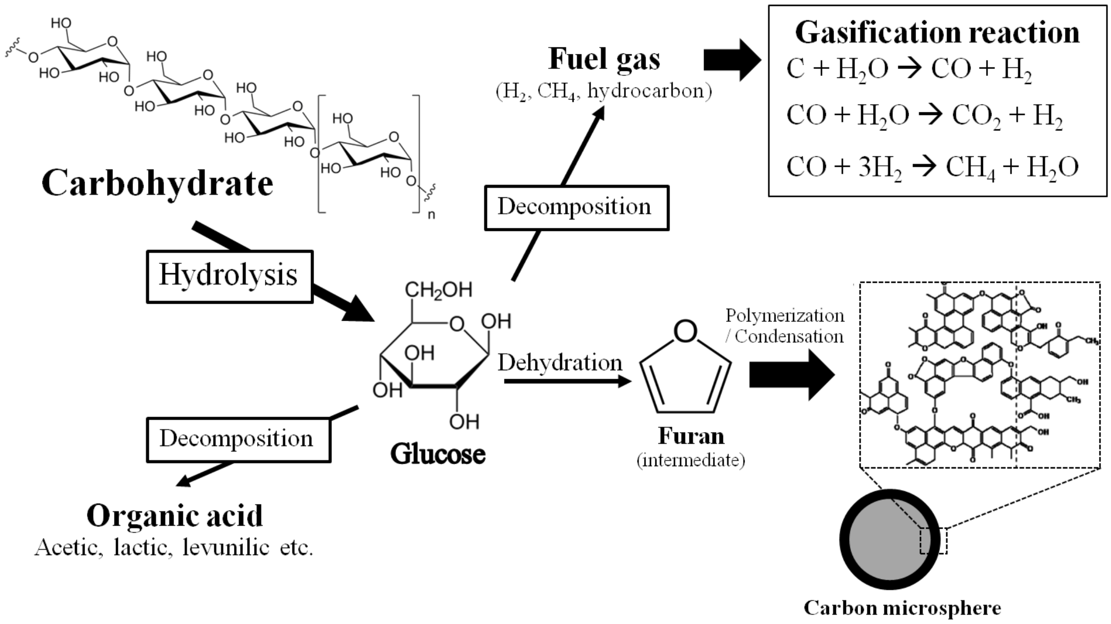

Figure 5.18 Path ways of the reaction in hydrothermal process

5.2 Continuous process

The result of the experiment in low temperature shows that temperature was increased, the amount of gaseous products were increased. It could be suggested that the gasification model was endothermic reaction. So, the experiments were conducted at high temperature at Hiroshima University by using tubular flow reactor.

5.2.1 The effect of temperature on gas products

The steamed rice was used as the feed stock in concentration 0.1-0.2 wt% and then it was heated the tubular flow reactor at designated temperature 400 to 600°C with pressure 25 MPa. The samples were collected in every hour for testing the amount of TOC in liquid phase and the gas generation rate of the system as shown in Figure 5.19 and Figure 5.20. The results show that concentration of TOC was increased with increasing time. Concentration of TOC reached to the maximum concentration at 3 hours and then the concentration was stable at 4 to 5 hours. The gas generation rate was stable at 4 to 5 hour. So, every experiments were collected the gas sample and liquid sample after 5 hours. The samples were analyzed the amount of gas product by using gas chromatography and the amount of carbon in liquid phase by using TOC.

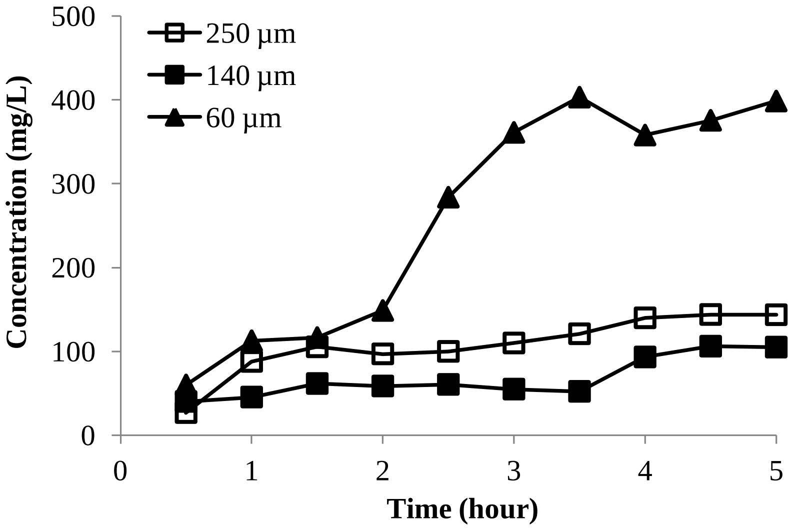

Figure 5.19 Concentration of TOC with time in each particle size at temperature 600°C

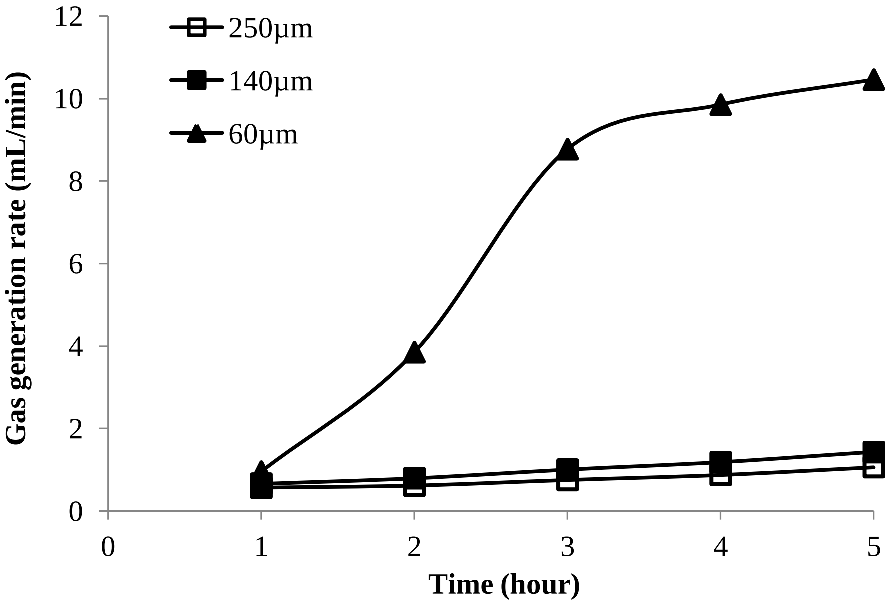

Figure 5.20 Gas generation rate of the gas product in each particle size at temperature 600°C

In this study, steamed rice which controlled particle size at 250 µm was used as a raw material for hydrothermal treatment in supercritical water. Many researches were reported that the reaction of biomass is similar 1st order reaction [18]. In this research, the gasification of steamed rice was assumed 1st order reaction for calculation the effect of temperature on carbon gasification as shown in Figure 5.21. It is the amount of carbon in gas phase divided by the amount of carbon in feed stock. The result shows that the 1st order reaction was not correctly the gasification of steamed rice. It shows when the temperature was increased, the efficiency of gasification would be increased. At high temperature, the amount of carbon in liquid phase was promoted the gasification. The gasification of steamed rice with particle size 250 µm was reached to 90% when reached temperature at 650°C. It could be noted that the steamed rice with particle size 250 µm would be completely gasified at above 650°C. So, the experiment in a part of subcritical water could not completely convert the steamed rice to gas product in range of 300 to 400°C. There were observed the solid residues after hydrothermal treatment at low temperature.

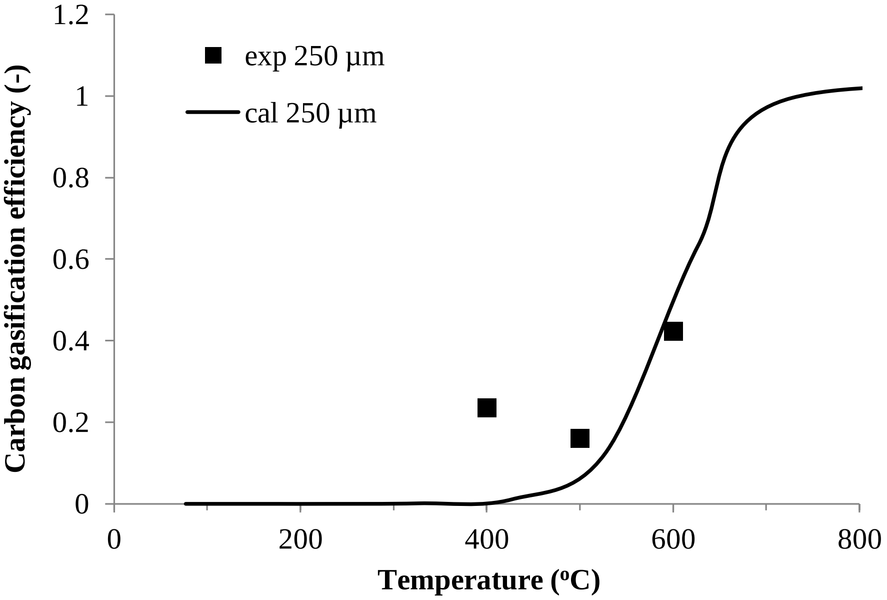

Figure 5.21 Carbon gasification efficiency of steamed rice in each temperature with particle size 250 µm

Figure 5.22 shows the yield of gas production at difference temperatures. It shows that at the high temperature, the amount of hydrogen would be increased while the amount of carbon monoxide was reduced. Carbon dioxide and methane would be increased at highest temperature but still less than the amount of hydrogen. This would be attributed to selective formation of hydrogen and methane that would be enhanced under higher temperature conditions. Carbon gasification efficiency was improved when temperature was increased from 400 to 600^{o}C. It might be high temperature to promote the free-radical reactions which enhance the gas formation in supercritical water process. Hence, the amount of hydrogen and methane increase sharply [9 - 18].

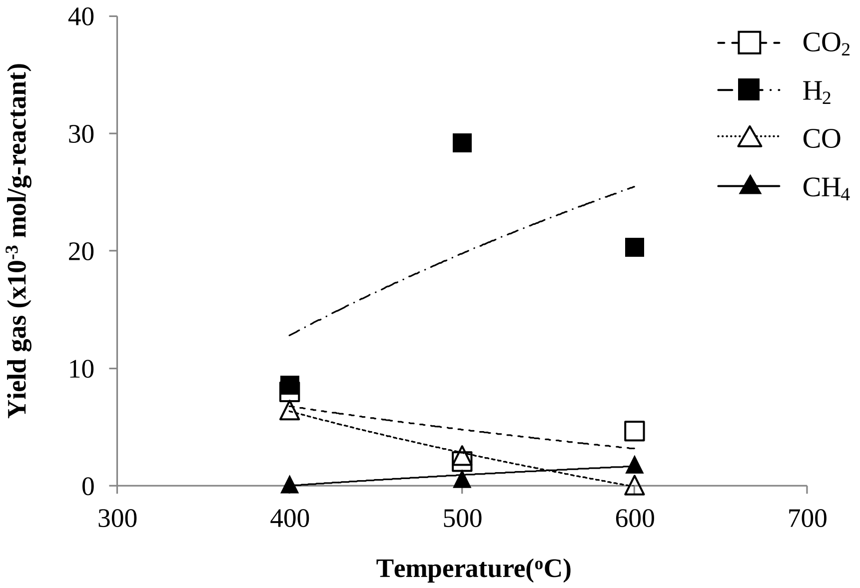

Figure 5.22 The yield of gas production at difference temperatures with particle size 250 µm

The gasification process was increased with increasing temperature that was gasified from water soluble sugars in liquid phase. So, the amount of carbon that dissolved in liquid product was analyzed by TOC analyzer. The result shows that the amount of carbon in liquid product was decreased while increasing temperature as shown in Figure 5.23. The carbohydrate in steamed rice was depolymerized into small sugar with increasing temperature and then the sugar was gasified to gas products and derivative sugar which dissolve in liquid phase. So, the gas product was enhanced with high temperature from decomposition of sugars in liquid phase.

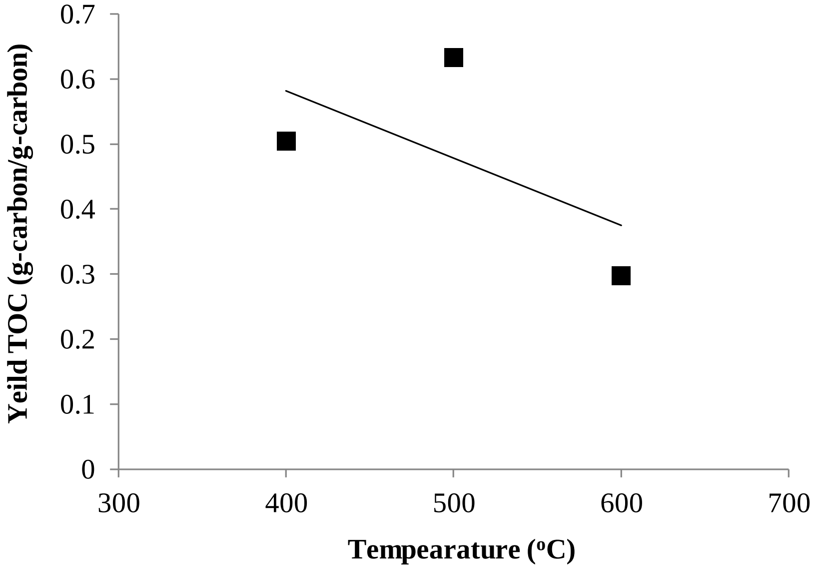

Figure 5.23 The yield of TOC in liquid product at difference temperatures with particle size 250 µm

The carbon balance in each phase was shown in Figure 5.24. It shows that the amount of carbon in gas would be increased with increasing temperature. The amount of carbon in liquid and solid phase was decreased with increasing temperature. There are confirmed that the effect of temperature enhanced the gasification of carbon that was gasified carbon in liquid phase and carbon in solid phase as shown in Figure 5.21, Figure 5.22 and Figure 5.23.

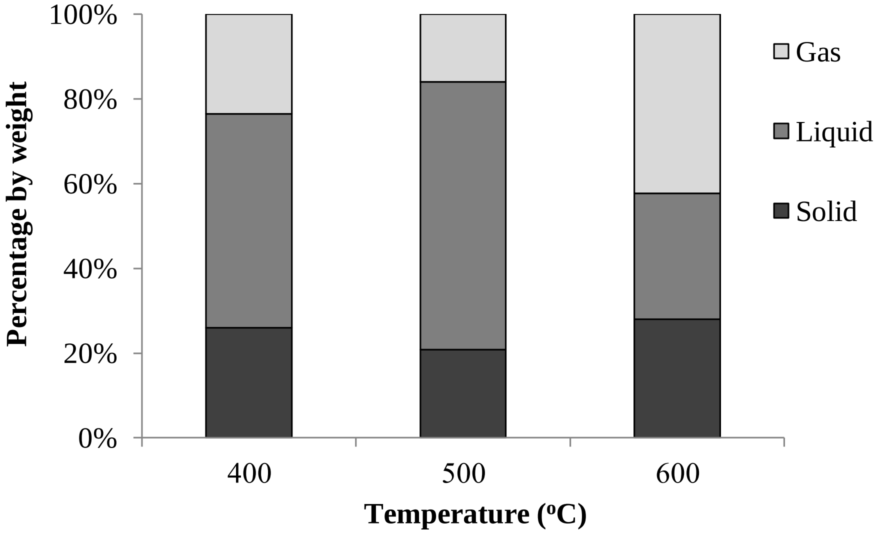

Figure 5.24 Carbon balance in each phase at difference temperatures with particle size 250 µm

5.2.2 The effect of particle size on gas products

Steamed rice with the controlled particle size in range of 60 to 250 µm was used as a feed stock for hydrothermal treatment in supercritical water. The effect of temperature and particle size on carbon gasification was shown in Figure 5.25. The result shows that the efficiency of gasification increased with increasing temperature. The gasification of steamed rice with a largest particle size was reached to 90% when reached temperature at 650°C while the gasification in the smallest particle size was reached to 90% at 550°C. It could be noted that the effect of temperature was the most influence for gasification of carbon and the effect of particle size was enhanced the gasification of carbon. The efficiency of gasification in lower particle size is better than higher particle size that caused the area of smaller particle has a larger area for reaction in hydrothermal treatment.

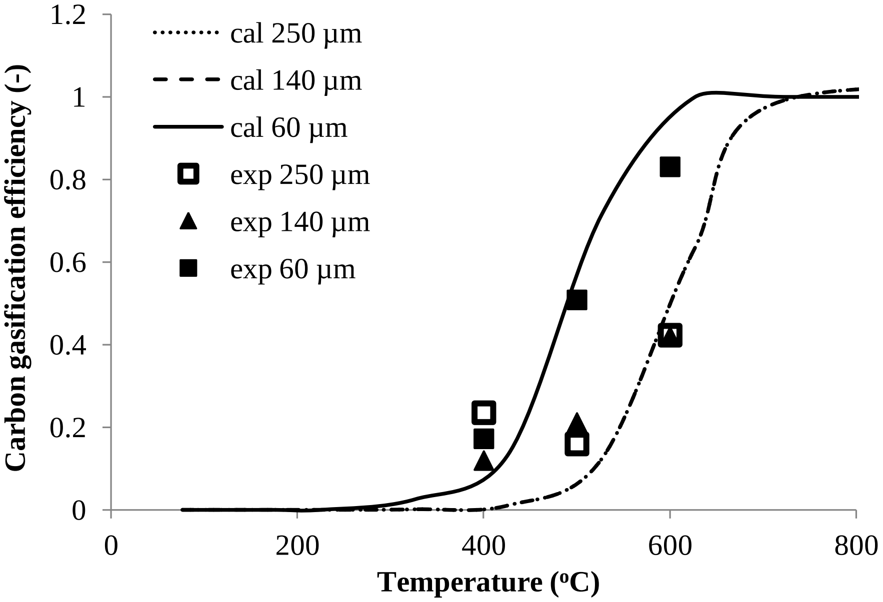

Figure 5.25 Carbon gasification efficiency of steamed rice at difference temperatures in each particle size

Figure 5.26 shows the yield of gas production in each particle size at temperature 600°C. It shows that the amount of H_2 would be decreased at the small particle size while the amount of CO_2 and CH_4 was increased. CO was low in each particle size. It could be noted that the carbon gasification efficiency was enhanced with decreasing particle size of material. It affected to carbon reaction for converting CO_2 and H_2 by the water gas shift reaction while the selectivity of gas formation at high temperature and small particle size would be enhanced the amount CH_4 instead of formation H_2. Hence, the amount of CO_2 and CH_4 increase sharply with increasing temperature where as used a small particle size by the methanation reaction [9 - 18].

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad \text{....8)}$$

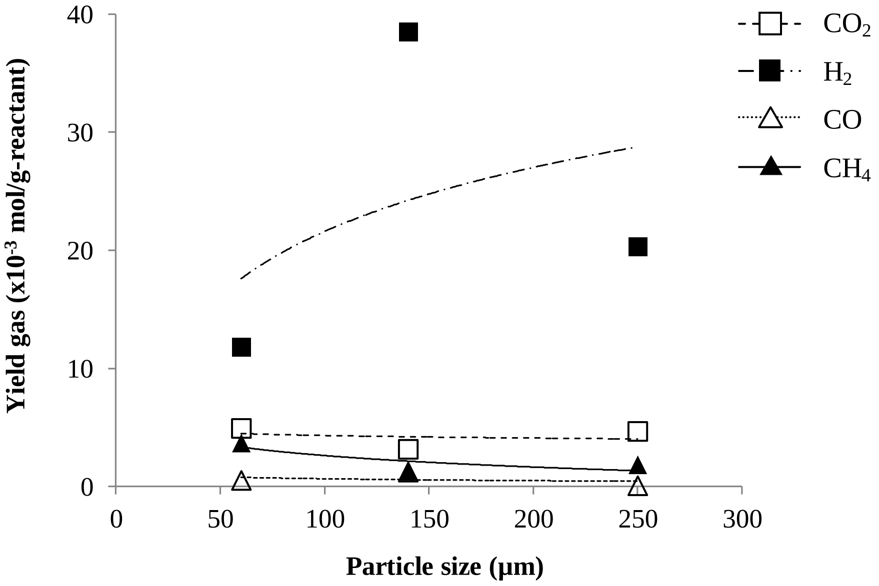

Figure 5.26 The yield of gas production in each particle size at temperature 600°C

The amount of carbon that dissolved in liquid product was analyzed by TOC analyzer. The result shows that the amount of carbon in liquid product was decreased with increasing temperature. When the particle size of steamed rice decreased, the amount of carbon in liquid phase was decrease sharply as shown in Figure 5.27. Figure 5.28 shows the amount of carbon in gas was dissolve in liquid phase that was analyzed by TOC. The small particle size was contained the carbon gas in liquid more than the carbon gas in a large particle size. The steamed rice has carbohydrate as a major component that was depolymerized into small sugar with increasing temperature and also the small particle size was enhanced the reaction. The small sugar was gasified to gas products and derivative sugar which dissolve in liquid phase.

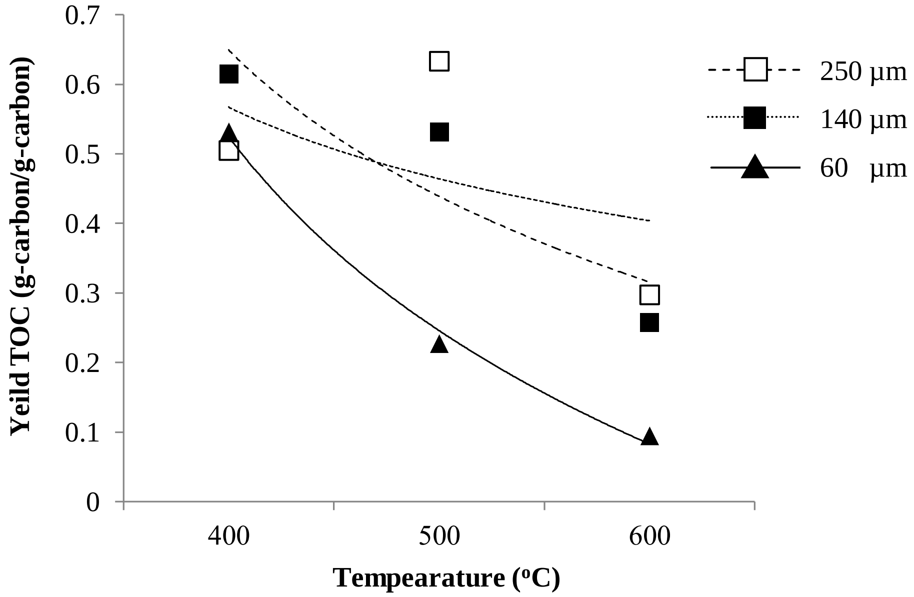

Figure 5.27 The yield of TOC in liquid product in each particle size at difference temperature

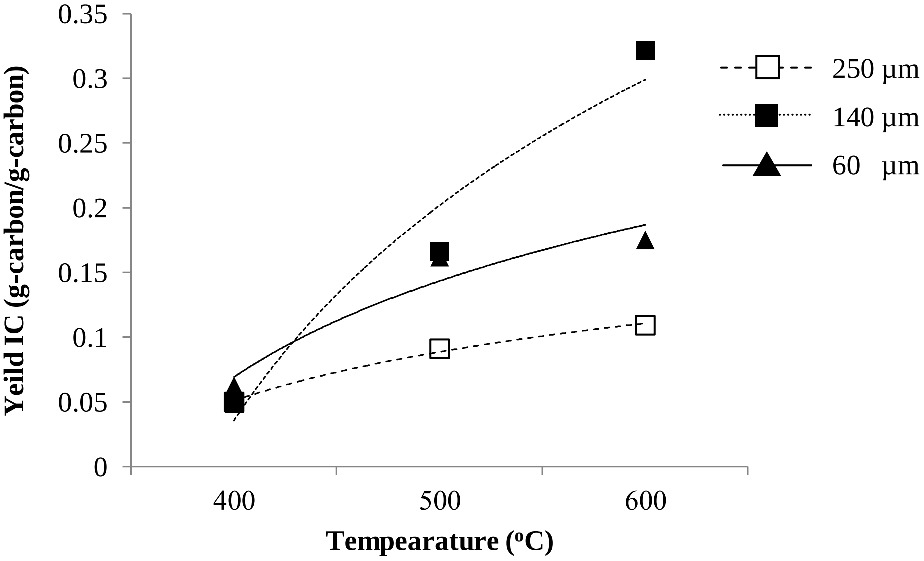

Figure 5.28 The yield of IC in liquid product in each particle size at difference temperature

The carbon balance in each phase was shown in Figure 5.29. It shows that the amount of carbon in gas would be increased with decreasing particle size of a raw material. The amount of carbon in liquid and solid phase was decreased with decreasing particle size. There are confirmed that the effect of particle size enhanced the gasification of carbon that was gasified carbon in liquid phase and carbon in solid phase as related in Figure 5.25, Figure 5.26 and Figure 5.27.

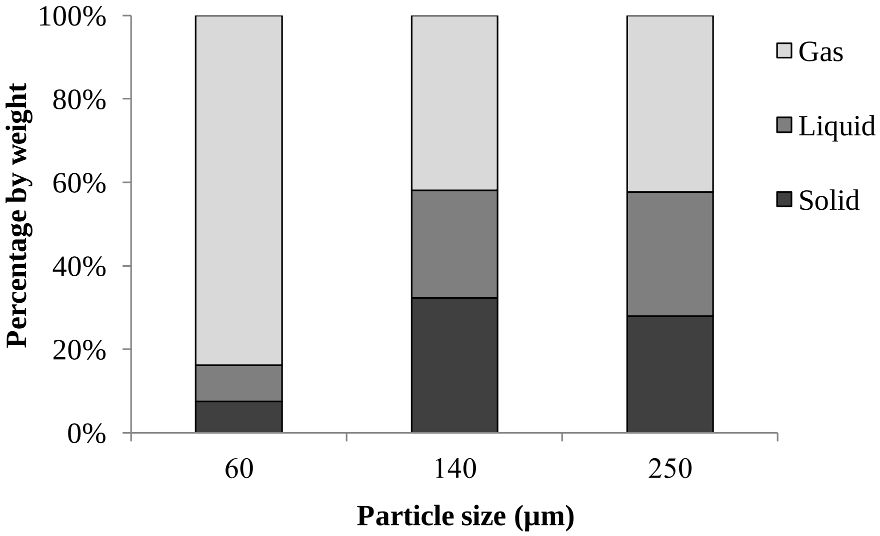

Figure 5.29 the effect of particle size on carbon balance in each phase at temperature 600^{o}C

The experiments investigated the effect of temperature and particle size on the gasification of steamed rice. There were used the equation of Arrhenius rate law for calculation the parameter. The result shows that the rate constant of steamed rice (k_0) was 6.97 x 10^5 s^{-1} and activation energy (E_0) was 1.34 x 10^5 J/mol. Figure 5.30 shows the Arrhenius plot of the reaction rate on steamed rice gasification. Promdej *et al*. studied the gasification of glucose in supercritical water [25]. When compared the gasification efficiency of steamed rice and gasification efficiency of glucose, Glucose was high gasification efficiency. However, the steamed rice has carbohydrate as a major component, it is complicated than the glucose which is polymer of glucose. So, the gasification efficiency of steamed rice would be lower than gasification efficiency of glucose.

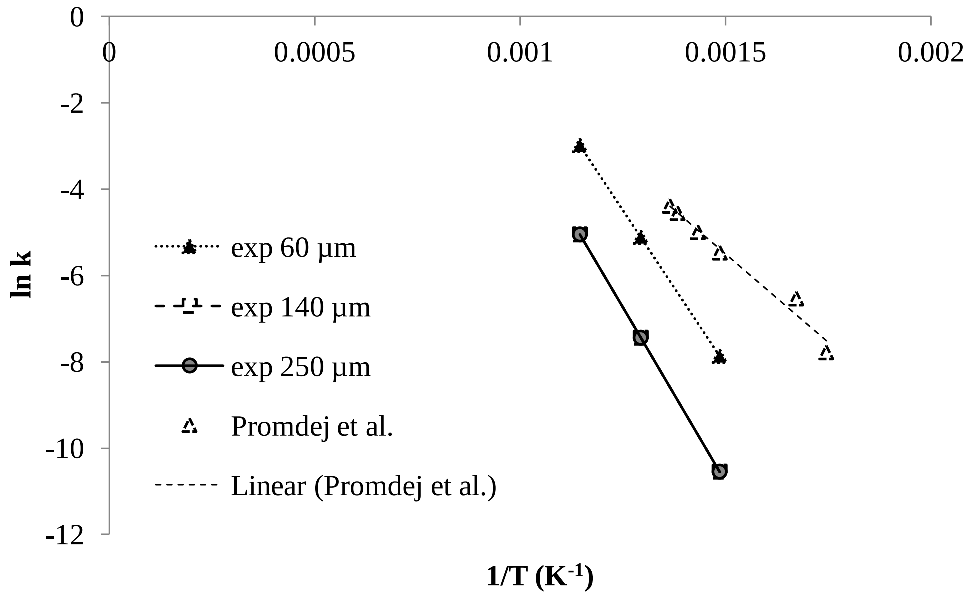

Figure 5.30 Arrhenius plot of the reaction rate on steamed rice gasification

5.2.3 The effect of additive (H_2O_2)

Steamed rice was controlled the particle size in range of 60 to 250 µm and used H_2O_2 as an additive in hydrothermal supercritical water. The effect of temperature and particle size on carbon gasification with H_2O_2 was shown in Figure 5.31. The result shows that the efficiency of gasification increased with increasing temperature. The gasification of steamed rice in each particle size was changed when adding H_2O_2. The experiment that used a largest particle size was reached to 90% when reached temperature at 650°C while the gasification in the experiment which added H_2O_2 with the same particle size was reached to 90% at 500°C. It could be noted that the effect of temperature was the most influence for gasification of carbon and H_2O_2 was enhanced carbon gasification by the oxidation reaction [7 - 12].

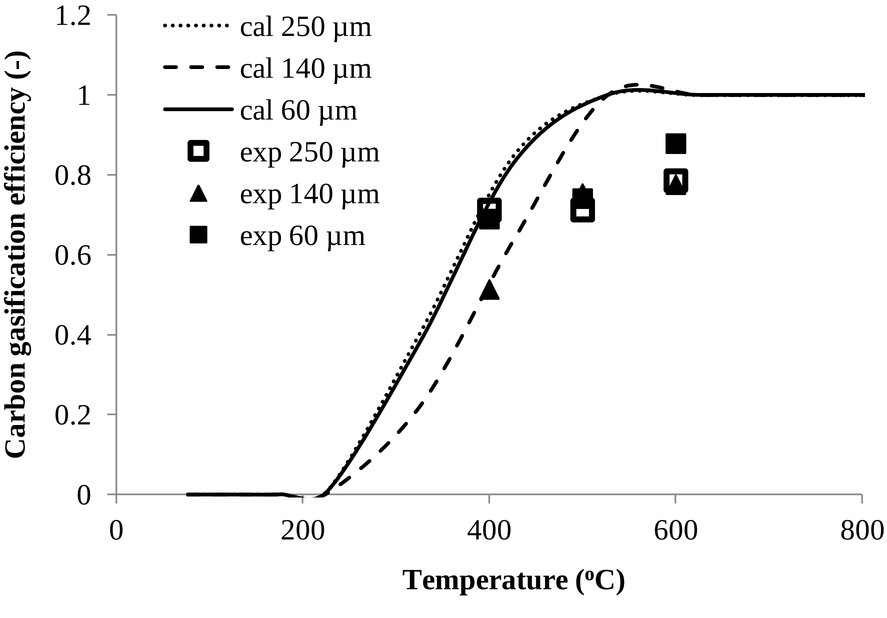

Figure 5.31 Carbon gasification efficiency of steamed rice at difference temperatures in each particle size with H_2O_2 as an additive

Figure 5.32 shows the yield of gas production at difference temperature with particle size 250 µm in a presence of H_2O_2. It shows that the amount of hydrogen and carbon dioxide were the major products. The effect of H_2O_2 was enhanced the amount of carbon dioxide in gas phase at low temperature by oxidation reaction. At high temperature, the amount of hydrogen was increased while the amount of carbon monoxide was decreased because of carbon monoxide was reacted with water in the system to form hydrogen and carbon dioxide by the water gas shift reaction. [7 - 12].

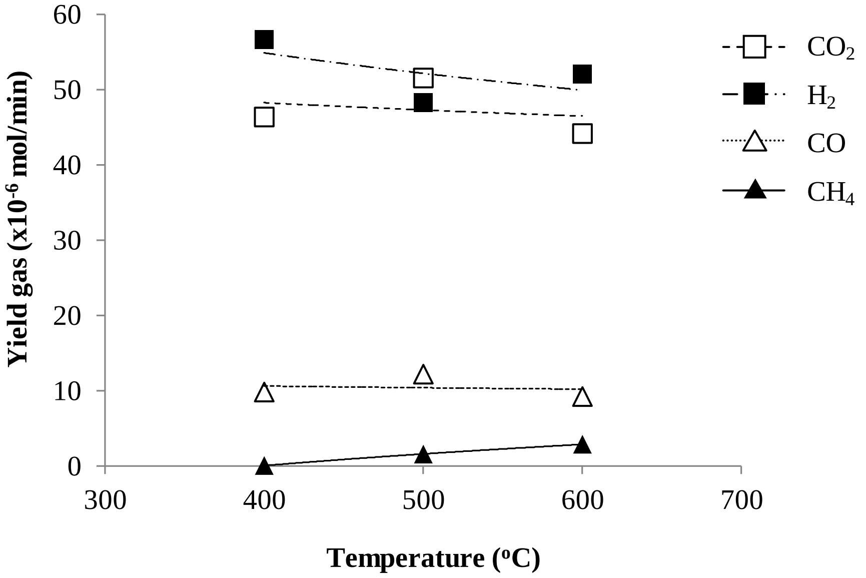

Figure 5.32 The yield of gas production at difference temperatures with particle size 250 µm and H_2O_2 as an additive

The amount of carbon that dissolved in liquid product was analyzed by TOC analyzer. The result shows that the amount of carbon in liquid product was low in every temperature as shown in Figure 5.27. The steamed rice has carbohydrate as a major component that was depolymerized into small sugar with increasing temperature and also H_2O_2 was produced oxygen in the system for oxidization the carbon in liquid and solid phase. The amount of carbon in liquid phase was low because of the gasification efficiency was high as shown in Figure 5.31.

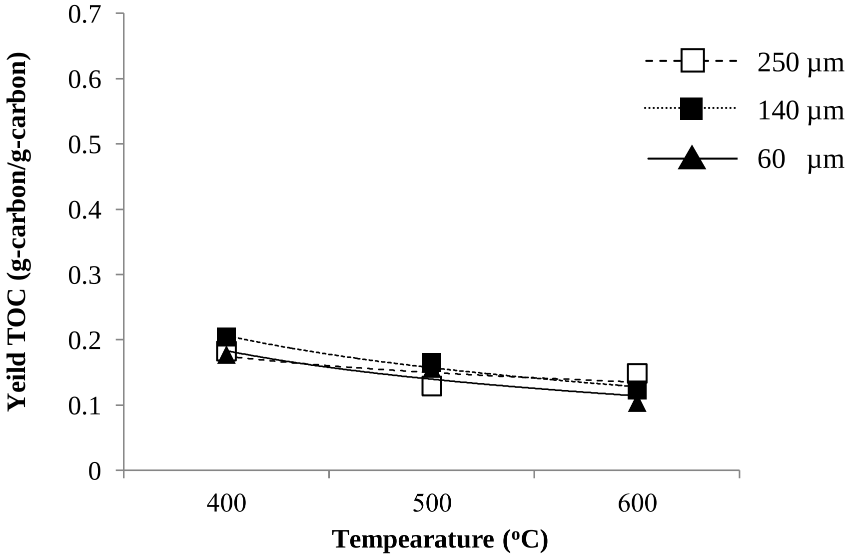

Figure 5.33 The yield of TOC in liquid product at difference temperatures with particle size 250 µm and H_2O_2 as an additive

The carbon balance in each phase at difference temperatures with particle size 250 µm in a presence of H_2O_2 was shown in Figure 5.34. It shows that the amount of carbon in each phase was similar. H_2O_2 was the oxidant for producing oxygen to system and then enhanced carbon gasification in liquid and solid phase. There are confirmed that the effect of H_2O_2 enhanced the gasification of carbon by oxidation reaction as shown in Figure 5.31, Figure 5.32 and Figure 5.33.

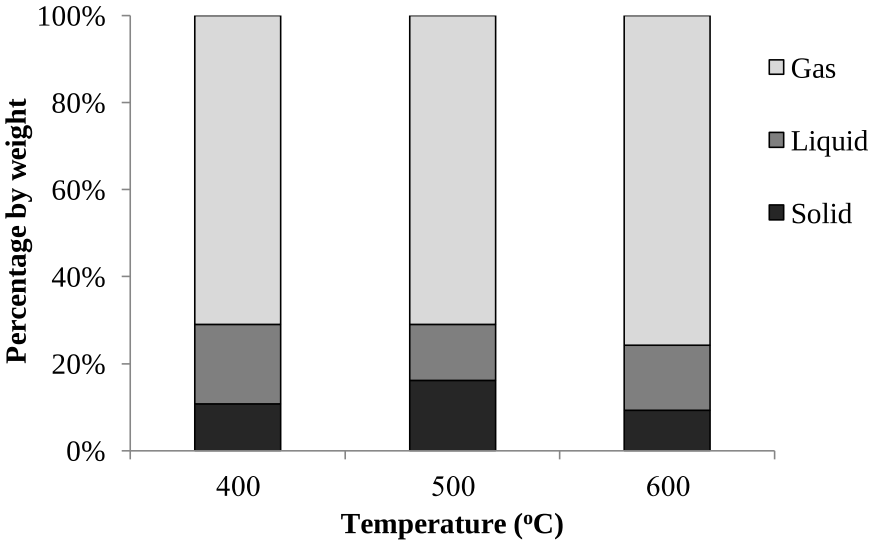

Figure 5.34 Carbon balance in each phase at difference temperatures with particle size 250 µm and H_2O_2 as an additive

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Steamed rice was gasified in the tubular reactor and the tubular flow reactor under sub- and supercritical water condition. The mechanical grinding for the raw material was provided for preparation biomass in each particle size before it was used. The particle size of steamed rice was also employed to improve gas product yield. The effect of temperature on steamed rice, it was experiment on temperature in range of 300, 350 and 400 also at each heating rate which are 8, 10 and 13^{o}C/min. It shows that the maximum yield of hydrogen was produced at the high temperature and high heating rate that was 8.49 x 10^{-6} mol/g reactant. The high temperature and high heating rate would be promoted the conversion of carbohydrate to small sugar and then gasified to gas production. The biomass gasification has hydrogen and carbon dioxide as major products. The carbon monoxide was formed at beginning and then it promoted the water gas shift reaction for converting into hydrogen and carbon dioxide. However, the hydrothermal process at low temperature was observed the carbonaceous product in solid phase.

The result in batch reactor shows that the gasification process was endothermic reaction. The experiments were conducted in high temperature by using the tubular flow reactor with the steamed rice as a feed stock for investigation the effect of temperature in range of 400, 500 and 600^{o}C and particle size in range of 60, 140 and 250 µm. The result shows that the small particle size and high temperature would be enhanced the gas products. The carbon gasification efficiency was enhanced with increasing temperature and decreasing particle size of material for converting the carbon dioxide and hydrogen while the selectivity of gas formation at high temperature and small particle size would be enhanced the amount of methane instead of formation hydrogen. The result shows that steamed rice could not be the same efficiency of gasification in glucose because of the steamed rice is polymer of glucose that would be hardly complete the hydrolysis reaction with supercritical water in a short time. When using the H_2O_2, H_2O_2 promoted carbon gasification efficiency in all experiment. H_2O_2 was promoted oxidation process on the steamed rice in supercritical state and then the carbon gasification efficiency was increased. This research is noted that the amount of gas production from supercritical state was used high energy for increasing the temperature of water to supercritical water. It shows that used high energy and it is not relate on economics.

Recommendations

Systematic investigation on gasification of steamed rice materials would be beneficial to Thailand and Southeastern Asian countries because of their abundance in this region. The experiment investigated the gasification of steamed rice due to steamed rice was simulated from food waste. It could make more benefit. This research was studied the effect of temperature in range of 300, 350 and 400 at heating rate 8, 10 and 13^{o}C/m in the batch reactor. The continuous system investigated on the effect of temperature in range of 400, 500 and 600^{o}C with particle size in range of 60, 140 and 250 µm. It shows that the amount of carbon was formed into the carbonaceous solid at low temperature that could be inhibited by using based catalyst or alkaline salt. The experiment in the continuous system, high temperature promoted the formation of methane instead of formation hydrogen. There were proved by using the oxidant for increasing the carbon gasification to carbon dioxide.

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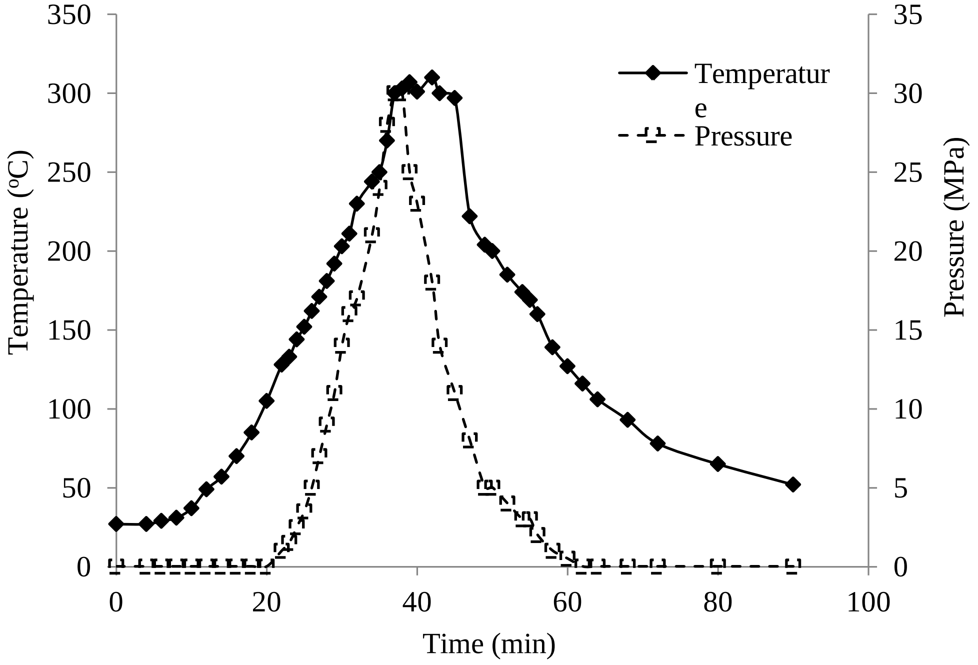
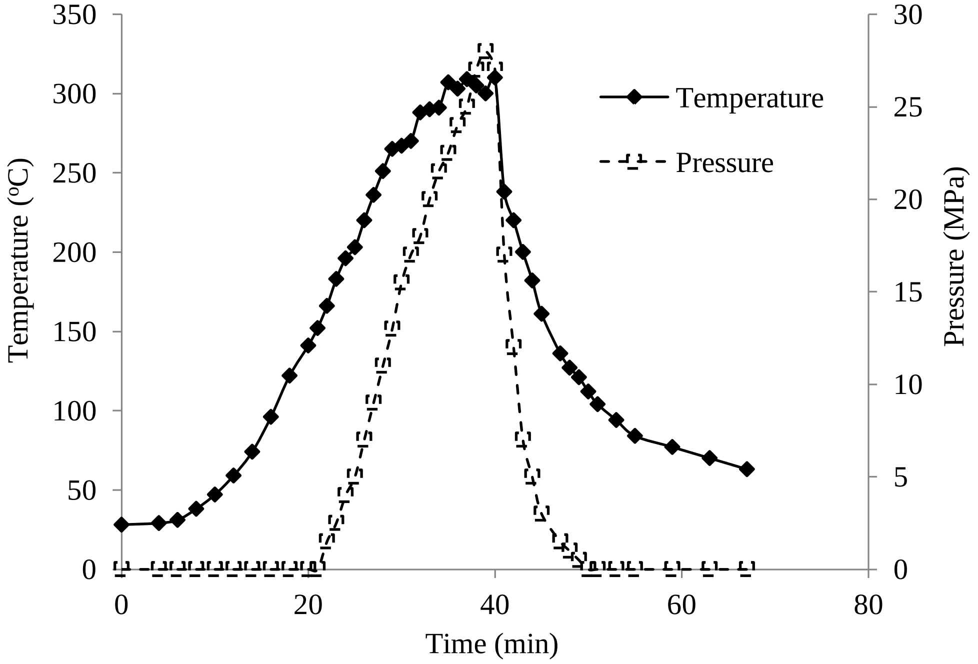
APPENDICES

APPENDIX A

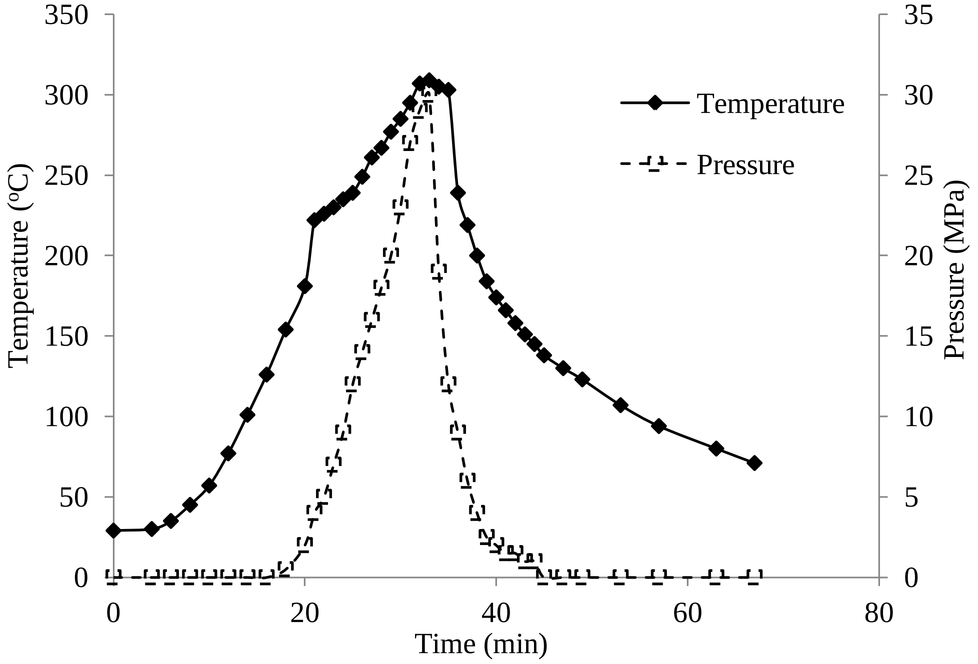
EXPERIMENTAL RESULTS



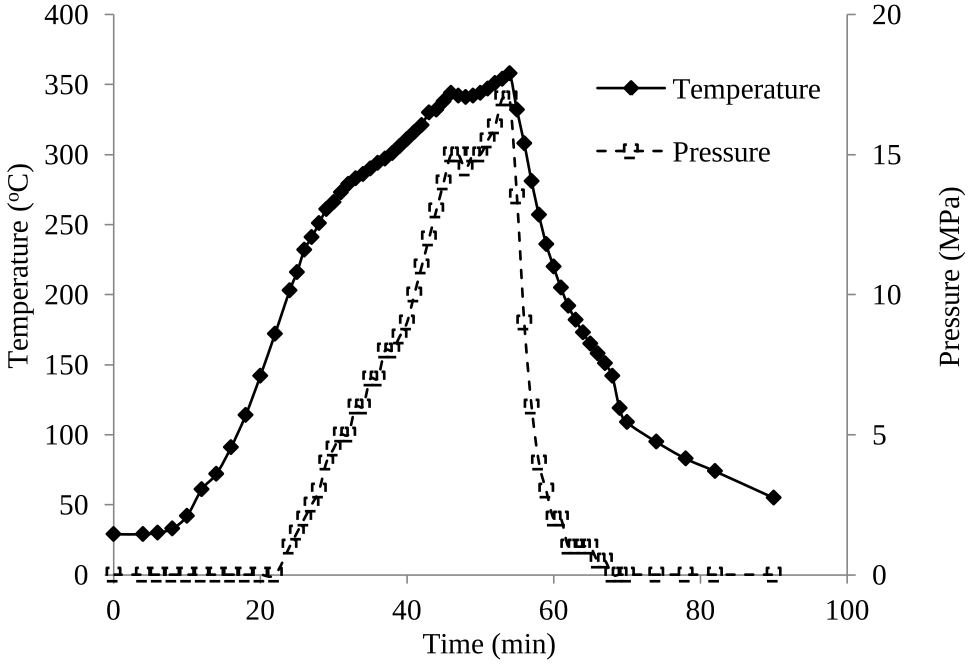
Appendix A1 Temperature history of the tubular reactor at temperature 300^{o}C and heating rate 8^{o}C/min



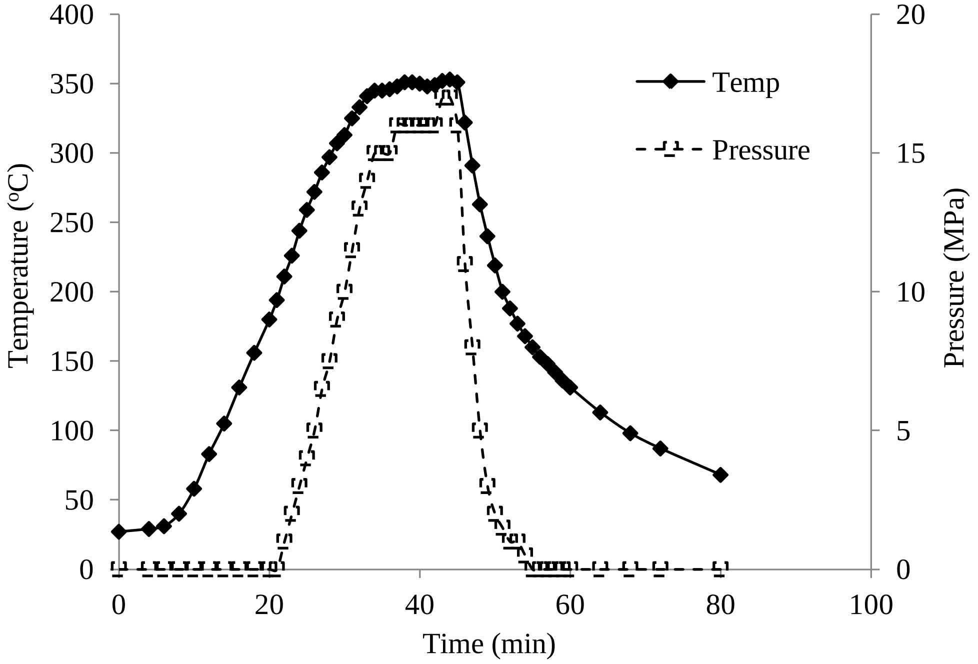
Appendix A2 Temperature history of the tubular reactor at temperature 300^{o}C and heating rate 10^{o}C/min



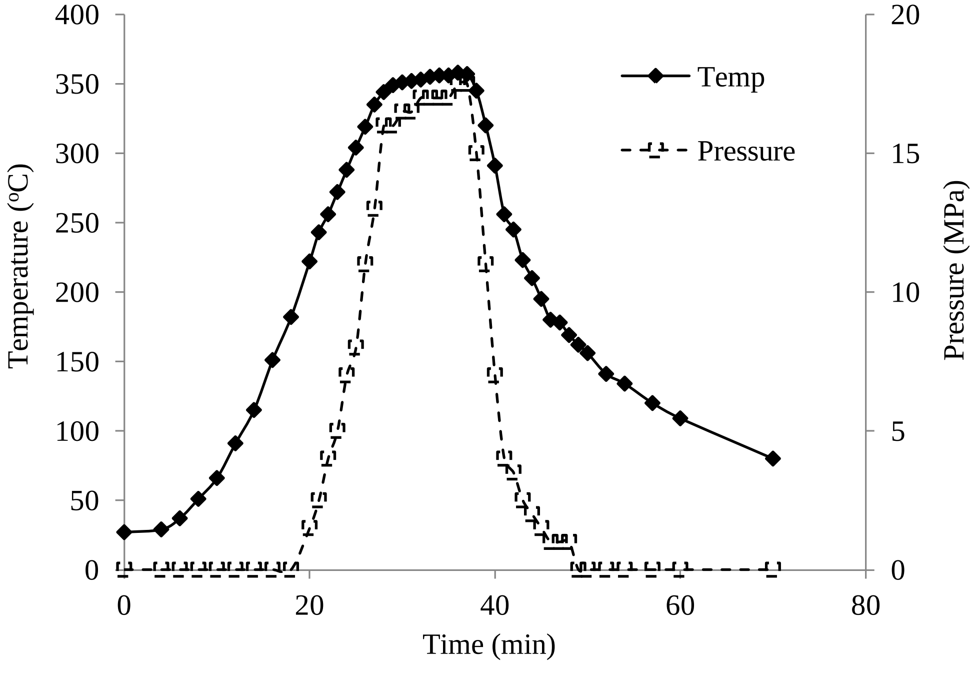
Appendix A3 Temperature history of the tubular reactor at temperature 300°C and heating rate 13°C/min



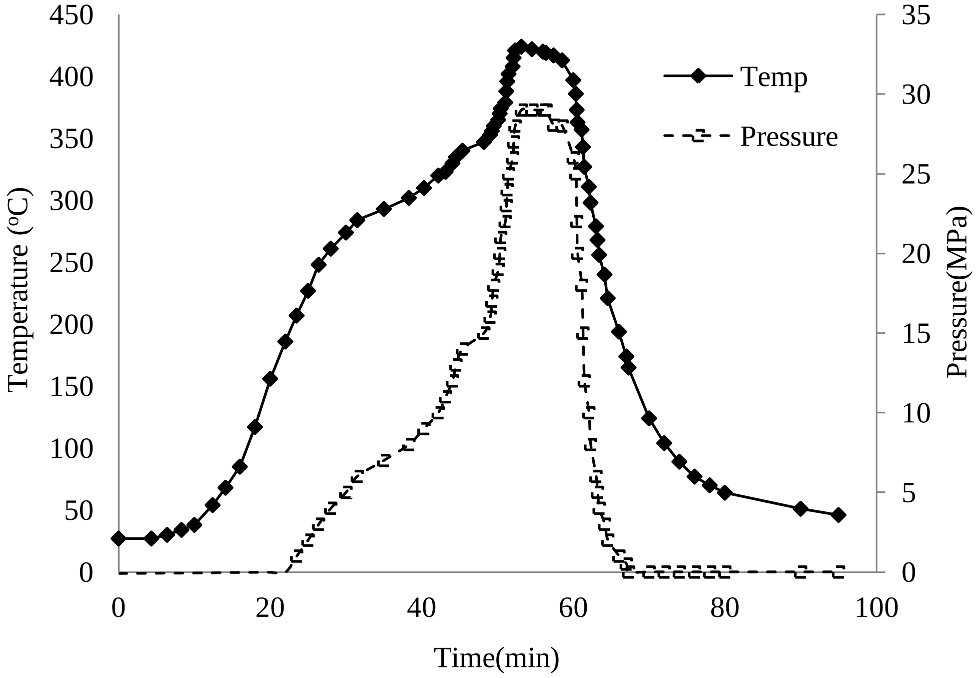
Appendix A4 Temperature history of the tubular reactor at temperature 350°C and heating rate 8°C/min



Appendix A5 Temperature history of the tubular reactor at temperature 350°C and heating rate 10°C/min



Appendix A6 Temperature history of the tubular reactor at temperature 350°C and heating rate 13°C/min



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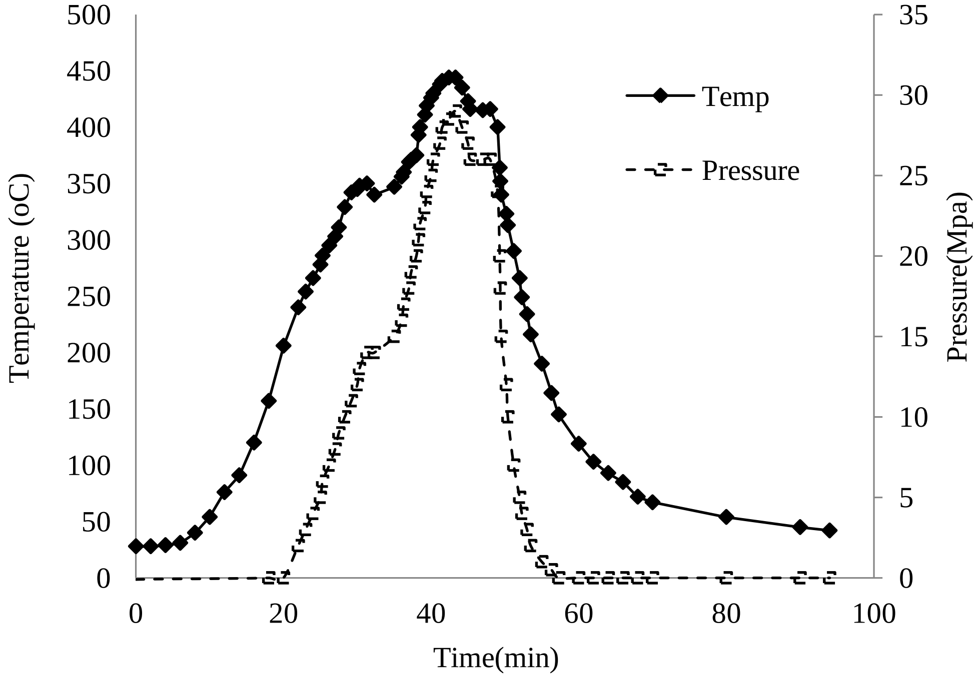
Appendix A7 Temperature history of the tubular reactor at temperature 400°C and heating rate 8°C/min



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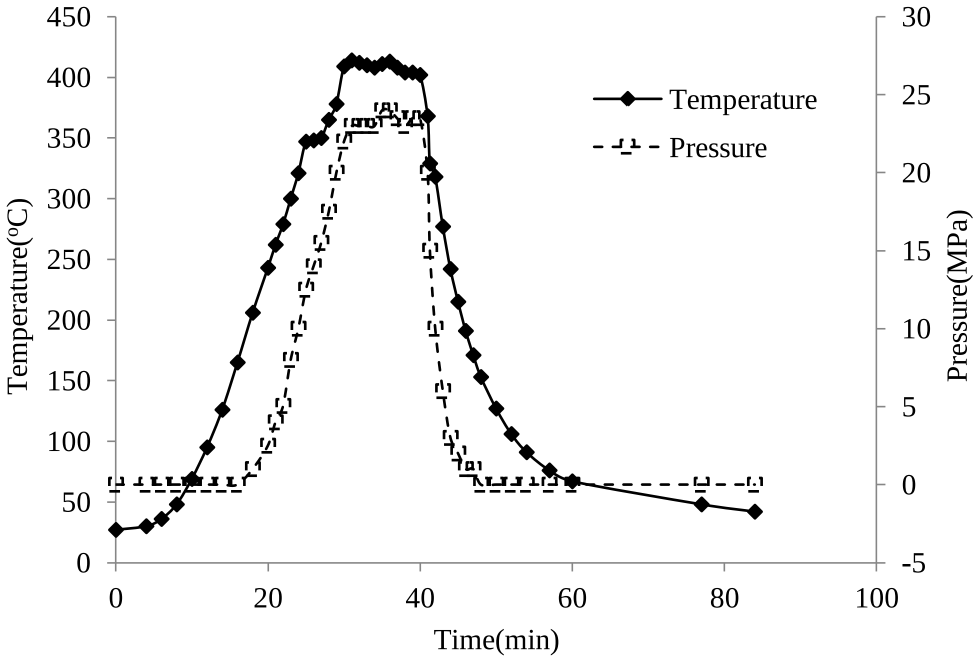
Appendix A8 Temperature history of the tubular reactor at temperature 400°C and heating rate 10°C/min



Appendix A9 Temperature history of the tubular reactor at temperature 400°C and heating rate 13°C/min

Calculation of the hydrogen yield
(For batch system)

Steamed rice content 10%wt

The slurry is 40 g

Particle size is 250 µm

Temperature of reaction 400°C

Heating rate 13°C/min

Injection with 0.2mL

Volume of reactor 175 mL

Gas analysis

Air 0.06572364 mL → there are gas sample = 0.2 - 0.6572364

= 0.13427636 mL

H_2 0.00100679 mL → 0.007498

CH_4 0.02313741 mL →0.172312

CO_2 0.08331766 mL → 0.620494

The amount of hydrogen inside reactor is 0.007498 x 175 = 1.31213354 mL

Yield of hydrogen (mL-H_2/g-reactant) is 1.31213354 divided by 4 gram of reactant

= 0.328 mL-H_2/g-reactant

Calculation of carbon gasification efficiency
(For continuous process)

Steamed rice 0.127%wt 600^{o}C

Water flow rate: 2.0 mL/min

Gas generation rate: 3.563319 mL/min

IC: 84.51 mg-C/L

Room temperature: 12^{o}C

Room pressure: 987 hPa

Carbon contain in steamed rice: 43.6%

Steamed rice 1 g. contain with 0.436 g-C

Steamed rice 0.127%wt → (0.436)(0.00127) = 0.000556 g-C

And flow with water at 2.0 mL/min → (2)(0.000556) = 0.001112 g-C/min

(0.001112 g-C/min)/(12 g/mol) = 4.633 x 10-5 mol/min → 0.04633 mmol/min

Gas sample injection is 0.3 mL

Contain with: Air	0.1263 mL	→ there are gas sample → 0.3 – 0.1263 = 0.1736
Methane	0.01159 mL	→ (0.01159/0.1736) = 0.0667
Ethylene	0.00095 mL	→ (0.00095/0.1736) = 0.0055
Ethane	0.00204 mL	→ (0.00204/0.1736) = 0.0117
CO	0.00035 mL	→ (0.00035/0.1736) = 0.0020
CO_2	0.02945 mL	→ (0.02945/0.1736) = 0.1696
H_2	0.12830 mL	→ (0.12830/0.1736) = 0.7390

{(1 mol)(0.08206 L.atm/mol.K)(12+273.15 K)[(1013.25 hPa/atm)/987hPa]}

= 24.021 L/mol = 24021 ml/mol

{[0.0667 + (0.0055x2) + (0.0117x2) + 0.0020 + 0.1696] x 3.563319}/24021

= $4.0509x10^{-5}$ mol/min = 0.0405 mmol/min

Then, Carbon Gasification Efficiency (CGE) is {[0.0405 + (84.51x2/1000)]/0.04633} = 0.5890

Calculation of carbon gasification efficiency

(For continuous process)

Assume: A → B, first order reaction

$$\frac{d[A]}{dt} = r_A = -k_A[A]$$

$$\int_{A_0}^{A} \frac{1}{[A]} d[A] = \int -k_A dt$$

$$ln\frac{[A]}{[A_0]} = -k_A t$$

$$[A] = [A_0]e^{-k_A t} \qquad (1)$$

Carbon conversion (X)

$$[A_0] = [A] + [Gas]$$

$$1 = \frac{[A]}{[A_0]} + \frac{[Gas]}{[A_0]}$$

When $\frac{[Gas]}{[A_0]} = X$

$$[A] = [A_0] - [A_0]X \qquad (2)$$

Substituted (1) into (2)

$$[A_0]e^{-k_A t} = [A_0] - [A_0]X$$

$$e^{-k_A t} = 1 - X \qquad (3)$$

Arrhenius equation

$$k = A_0 e^{-\frac{E_a}{RT}} \qquad (4)$$

Substituted (4) into (3)

$$X = 1 - e^{-A_0 e^{-\frac{E_a}{RT}} t}$$

Trial and error for finding A_0 and E_a then plot the Arrhenius equation

Experimental condition

Condition

Study the effect of temperature and particle size

Feedstock	Steamed rice
Reaction temperature [^{o}C]	600
Reaction pressure [MPa]	25
Concentration [wt%]	0.3
Particle size[μm]	250
H_2O_2 concentration [wt%]	-
Flow rate [g/min]	2.0
Room temperature [^{o}C]	12
Atmosphere [hPa]	987

Experimental result

Gas fraction

CO [%]	CO_2 [%]	CH_4 [%]	C_2H_4 [%]	C_2H_6 [%]	H_2 [%]
0.20	16.96	6.67	0.55	1.17	73.90

Carbon gas efficiency

Temperature [^{o}C]	Residence time [s]	Product Yield [kg-C/kg-C]		CGE [%]
		TOC	Gas	
600	94.32	0.29	0.10	42.31

Experimental condition

Condition

Study the effect of temperature and particle size

Feedstock	Steamed rice
Reaction temperature [^oC]	500
Reaction pressure [MPa]	25
Concentration [wt%]	0.3
Particle size[μm]	250
H_2O_2 concentration [wt%]	-
Flow rate [g/min]	2.0
Room temperature [^oC]	13
Atmosphere [hPa]	991

Experimental result

Gas fraction

CO [%]	CO_2 [%]	CH_4 [%]	C_2H_4 [%]	C_2H_6 [%]	H_2 [%]
7.09	5.67	1.67	0.11	0.19	80.40

Carbon gas efficiency

Temperature [^oC]	Residence time [s]	Product Yield [kg-C/kg-C]		CGE [%]
		TOC	Gas	
500	119.71	0.63	0.09	15.59

Experimental condition

Condition

Study the effect of temperature and particle size

Feedstock	Steamed rice
Reaction temperature [^{o}C]	400
Reaction pressure [MPa]	25
Concentration [wt%]	0.3
Particle size[µm]	250
H_2O_2 concentration [wt%]	-
Flow rate [g/min]	2.0
Room temperature [^{o}C]	12
Atmosphere [hPa]	990

Experimental result

Gas fraction

CO [%]	CO_2 [%]	CH_4 [%]	C_2H_4 [%]	C_2H_6 [%]	H_2 [%]
26.91	33.37	0.61	1.53	0.16	35.76

Carbon gas efficiency

Temperature [^{o}C]	Residence time [s]	Product Yield [kg-C/kg-C]		CGE [%]
		TOC	Gas	
400	222.12	0.50	0.04	23.55

Experimental condition

Condition

Study the effect of temperature and particle size

Feedstock	Steamed rice
Reaction temperature [^oC]	600
Reaction pressure [MPa]	25
Concentration [wt%]	0.3
Particle size[μm]	140
H_2O_2 concentration [wt%]	-
Flow rate [g/min]	2.0
Room temperature [^oC]	12
Atmosphere [hPa]	987

Experimental result

Gas fraction

CO [%]	CO_2 [%]	CH_4 [%]	C_2H_4 [%]	C_2H_6 [%]	H_2 [%]
2.66	6.91	2.84	0.22	0.20	84.65

Carbon gas efficiency

Temperature [^oC]	Residence time [s]	Product Yield [kg-C/kg-C]		CGE [%]
		TOC	Gas	
600	94.32	0.25	0.32	41.99

Experimental condition

Condition

Study the effect of temperature and particle size

Feedstock	Steamed rice
Reaction temperature [^oC]	500
Reaction pressure [MPa]	25
Concentration [wt%]	0.3
Particle size[μm]	140
H_2O_2 concentration [wt%]	-
Flow rate [g/min]	2.0
Room temperature [^oC]	12
Atmosphere [hPa]	990

Experimental result

Gas fraction

CO [%]	CO_2 [%]	CH_4 [%]	C_2H_4 [%]	C_2H_6 [%]	H_2 [%]
3.85	4.15	0.73	0.06	0.05	80.69

Carbon gas efficiency

Temperature [^oC]	Residence time [s]	Product Yield [kg-C/kg-C]		CGE [%]
		TOC	Gas	
500	119.71	0.53	0.16	21.19

Experimental condition

Condition

Study the effect of temperature and particle size

Feedstock	Steamed rice
Reaction temperature [^oC]	400
Reaction pressure [MPa]	25
Concentration [wt%]	0.3
Particle size[µm]	140
H_2O_2 concentration [wt%]	-
Flow rate [g/min]	2.0
Room temperature [^oC]	12
Atmosphere [hPa]	991

Experimental result

Gas fraction

CO [%]	CO_2 [%]	CH_4 [%]	C_2H_4 [%]	C_2H_6 [%]	H_2 [%]
6.70	9.31	0.30	0.32	0.07	78.29

Carbon gas efficiency

Temperature [^oC]	Residence time [s]	Product Yield [kg-C/kg-C]		CGE [%]
		TOC	Gas	
400	222.12	0.61	0.04	11.97

Experimental condition

Condition

Study the effect of temperature and particle size

Feedstock	Steamed rice
Reaction temperature [^oC]	600
Reaction pressure [MPa]	25
Concentration [wt%]	0.3
Particle size[µm]	60
H_2O_2 concentration [wt%]	-
Flow rate [g/min]	2.0
Room temperature [^oC]	12
Atmosphere [hPa]	987

Experimental result

Gas fraction

CO [%]	CO_2 [%]	CH_4 [%]	C_2H_4 [%]	C_2H_6 [%]	H_2 [%]
2.25	21.79	16.31	0.80	1.69	52.35

Carbon gas efficiency

Temperature [^oC]	Residence time [s]	Product Yield [kg-C/kg-C]		CGE [%]
		TOC	Gas	
600	94.32	0.09	0.17	83.08

Experimental condition

Condition

Study the effect of temperature and particle size

Feedstock	Steamed rice
Reaction temperature [^{o}C]	500
Reaction pressure [MPa]	25
Concentration [wt%]	0.3
Particle size[µm]	60
H_2O_2 concentration [wt%]	-
Flow rate [g/min]	2.0
Room temperature [^{o}C]	12
Atmosphere [hPa]	989

Experimental result

Gas fraction

CO [%]	CO_2 [%]	CH_4 [%]	C_2H_4 [%]	C_2H_6 [%]	H_2 [%]
11.37	9.93	1.41	0.36	0.27	75.54

Carbon gas efficiency

Temperature [^{o}C]	Residence time [s]	Product Yield [kg-C/kg-C]		CGE [%]
		TOC	Gas	
500	119.71	0.22	0.16	50.08

Experimental condition

Condition

Study the effect of temperature and particle size

Feedstock	Steamed rice
Reaction temperature [^oC]	400
Reaction pressure [MPa]	25
Concentration [wt%]	0.3
Particle size[μm]	60
H_2O_2 concentration [wt%]	-
Flow rate [g/min]	2.0
Room temperature [^oC]	11
Atmosphere [hPa]	991

Experimental result

Gas fraction

CO [%]	CO_2 [%]	CH_4 [%]	C_2H_4 [%]	C_2H_6 [%]	H_2 [%]
10.19	17.30	0.65	0.20	0.18	58.88

Carbon gas efficiency

Temperature [^oC]	Residence time [s]	Product Yield [kg-C/kg-C]		CGE [%]
		TOC	Gas	
400	222.12	0.53	0.06	17.24

Experimental condition

Condition

Study the effect of temperature and particle size including catalyst

Feedstock	Steamed rice
Reaction temperature [°C]	600
Reaction pressure [MPa]	25
Concentration [wt%]	0.3
Particle size[μm]	250
H_2O_2 concentration [wt%]	0.3
Flow rate [g/min]	2.0
Room temperature [°C]	11
Atmosphere [hPa]	986

Experimental result

Gas fraction

CO [%]	CO_2 [%]	CH_4 [%]	C_2H_4 [%]	C_2H_6 [%]	H_2 [%]
8.48	40.69	2.64	0.07	0.09	48.01

Carbon gas efficiency

Temperature [°C]	Residence time [s]	Product Yield [kg-C/kg-C]		CGE [%]
		TOC	Gas	
600	94.32	0.14	0.22	78.54

Experimental condition

Condition

Study the effect of temperature and particle size including catalyst

Feedstock	Steamed rice
Reaction temperature [^oC]	500
Reaction pressure [MPa]	25
Concentration [wt%]	0.3
Particle size[µm]	250
H_2O_2 concentration [wt%]	0.3
Flow rate [g/min]	2.0
Room temperature [^oC]	14
Atmosphere [hPa]	986

Experimental result

Gas fraction

CO [%]	CO_2 [%]	CH_4 [%]	C_2H_4 [%]	C_2H_6 [%]	H_2 [%]
10.72	45.37	1.36	0.02	0.02	42.48

Carbon gas efficiency

Temperature [^oC]	Residence time [s]	Product Yield [kg-C/kg-C]		CGE [%]
		TOC	Gas	
500	119.71	0.12	0.21	71.18

Experimental condition

Condition

Study the effect of temperature and particle size including catalyst

Feedstock	Steamed rice
Reaction temperature [^oC]	400
Reaction pressure [MPa]	25
Concentration [wt%]	0.3
Particle size[µm]	250
H_2O_2 concentration [wt%]	0.3
Flow rate [g/min]	2.0
Room temperature [^oC]	12
Atmosphere [hPa]	977

Experimental result

Gas fraction

CO [%]	CO_2 [%]	CH_4 [%]	C_2H_4 [%]	C_2H_6 [%]	H_2 [%]
8.62	40.78	0.03	0.02	0.67	49.84

Carbon gas efficiency

Temperature [^oC]	Residence time [s]	Product Yield [kg-C/kg-C]		CGE [%]
		TOC	Gas	
400	222.12	0.18	0.17	71.19

Experimental condition

Condition

Study the effect of temperature and particle size including catalyst

Feedstock	Steamed rice
Reaction temperature [^oC]	600
Reaction pressure [MPa]	25
Concentration [wt%]	0.3
Particle size[µm]	140
H_2O_2 concentration [wt%]	0.3
Flow rate [g/min]	2.0
Room temperature [^oC]	12
Atmosphere [hPa]	991

Experimental result

Gas fraction

CO [%]	CO_2 [%]	CH_4 [%]	C_2H_4 [%]	C_2H_6 [%]	H_2 [%]
4.25	39.98	3.48	0.16	0.26	51.83

Carbon gas efficiency

Temperature [^oC]	Residence time [s]	Product Yield [kg-C/kg-C]		CGE [%]
		TOC	Gas	
600	94.32	0.12	0.17	77.53

Experimental condition

Condition

Study the effect of temperature and particle size including catalyst

Feedstock	Steamed rice
Reaction temperature [^oC]	500
Reaction pressure [MPa]	25
Concentration [wt%]	0.3
Particle size[µm]	140
H_2O_2 concentration [wt%]	0.3
Flow rate [g/min]	2.0
Room temperature [^oC]	13
Atmosphere [hPa]	992

Experimental result

Gas fraction

CO [%]	CO_2 [%]	CH_4 [%]	C_2H_4 [%]	C_2H_6 [%]	H_2 [%]
16.26	45.97	0.84	0.07	0.04	36.80

Carbon gas efficiency

Temperature [^oC]	Residence time [s]	Product Yield [kg-C/kg-C]		CGE [%]
		TOC	Gas	
500	119.71	0.16	0.14	75.31

Experimental condition

Condition

Study the effect of temperature and particle size including catalyst

Feedstock	Steamed rice
Reaction temperature [^oC]	400
Reaction pressure [MPa]	25
Concentration [wt%]	0.3
Particle size[μm]	140
H_2O_2 concentration [wt%]	0.3
Flow rate [g/min]	2.0
Room temperature [^oC]	14
Atmosphere [hPa]	978

Experimental result

Gas fraction

CO [%]	CO_2 [%]	CH_4 [%]	C_2H_4 [%]	C_2H_6 [%]	H_2 [%]
9.28	26.20	0.08	0.05	0.00	64.36

Carbon gas efficiency

Temperature [^oC]	Residence time [s]	Product Yield [kg-C/kg-C]		CGE [%]
		TOC	Gas	
400	222.12	0.20	0.21	51.30

Experimental condition

Condition

Study the effect of temperature and particle size including catalyst

Feedstock	Steamed rice
Reaction temperature [^{o}C]	600
Reaction pressure [MPa]	25
Concentration [wt%]	0.3
Particle size[µm]	60
H_2O_2 concentration [wt%]	0.3
Flow rate [g/min]	2.0
Room temperature [^{o}C]	13
Atmosphere [hPa]	991

Experimental result

Gas fraction

CO [%]	CO_2 [%]	CH_4 [%]	C_2H_4 [%]	C_2H_6 [%]	H_2 [%]
1.24	42.79	9.50	0.66	1.53	44.25

Carbon gas efficiency

Temperature [^{o}C]	Residence time [s]	Product Yield [kg-C/kg-C]		CGE [%]
		TOC	Gas	
600	94.32	0.13	0.10	87.80

Experimental condition

Condition

Study the effect of temperature and particle size including catalyst

Feedstock	Steamed rice
Reaction temperature [^oC]	500
Reaction pressure [MPa]	25
Concentration [wt%]	0.3
Particle size[µm]	60
H_2O_2 concentration [wt%]	0.3
Flow rate [g/min]	2.0
Room temperature [^oC]	13
Atmosphere [hPa]	991

Experimental result

Gas fraction

CO [%]	CO_2 [%]	CH_4 [%]	C_2H_4 [%]	C_2H_6 [%]	H_2 [%]
13.00	37.73	0.69	0.19	0.10	48.26

Carbon gas efficiency

Temperature [^oC]	Residence time [s]	Product Yield [kg-C/kg-C]		CGE [%]
		TOC	Gas	
500	119.71	0.15	0.18	74.05

Experimental condition

Condition

Study the effect of temperature and particle size including catalyst

Feedstock	Steamed rice
Reaction temperature [^oC]	400
Reaction pressure [MPa]	25
Concentration [wt%]	0.3
Particle size[μm]	60
H_2O_2 concentration [wt%]	0.3
Flow rate [g/min]	2.0
Room temperature [^oC]	14
Atmosphere [hPa]	978

Experimental result

Gas fraction

CO [%]	CO_2 [%]	CH_4 [%]	C_2H_4 [%]	C_2H_6 [%]	H_2 [%]
10.65	30.11	5.23	0.21	0.12	53.66

Carbon gas efficiency

Temperature [^oC]	Residence time [s]	Product Yield [kg-C/kg-C]		CGE [%]
		TOC	Gas	
400	222.12	0.17	0.16	68.91

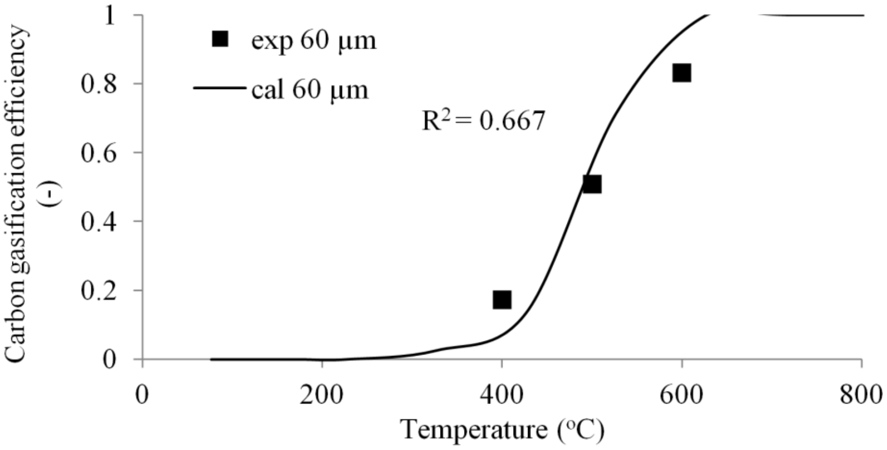


Figure A10 Carbon gasfication efficiency of steamed rice at 60 μm

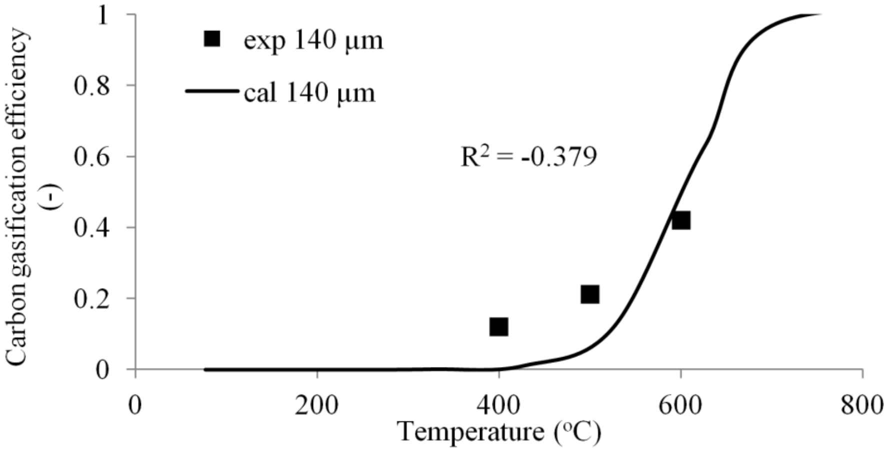


Figure A11 Carbon gasfication efficiency of steamed rice at 140 μm

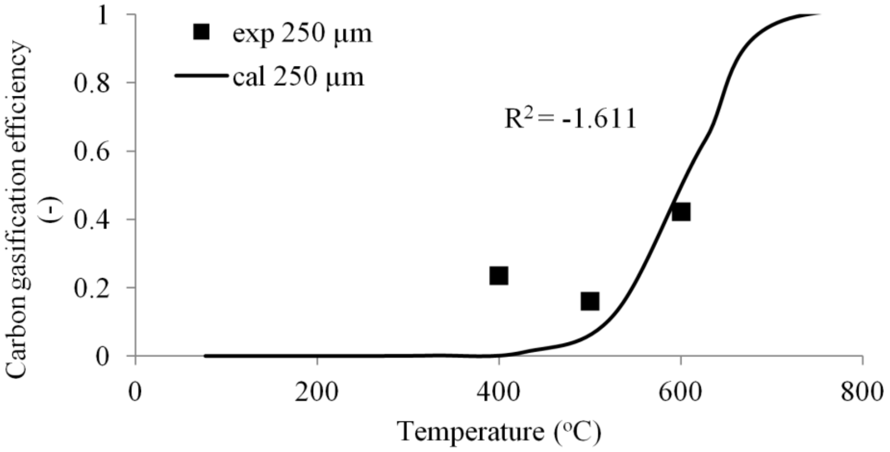


Figure A12 Carbon gasfication efficiency of steamed rice at 250 μm

VITA

Mr. Chatree Asayatamanon was born on April 21, 1988 in Bangkok, Thailand. He stayed in Kampheangphet province. He completed high school at Princess Chulabhorn's college Phitsanulok. In 2010, he received the Bachelor Degree of Engineering (Chemical Engineering) from King Mongkut's University of Technology Thonburi. After that, he continued to study in Master program in Center of Excellence in Particle Technology (CEPT) at Chemical Engineering Department, Faculty of Engineering, Chulalongkorn University with the master thesis entitled "Fuel gas production from steamed rice by hydrothermal treatment in subcritical water".