

Part 4. Thermochemical conversion of biomass

4.1 Combustion

4.1.1 General scope

(a) What is combustion?

Combustion is an exothermic chemical reaction accompanied by large heat generation and luminescence, and is a phenomenon in which the reaction is spontaneously continued by the heat generated by the reaction. When using biomass as fuel, the heat-generating oxidation reaction, where carbon, hydrogen, oxygen, combustible sulfur, and nitrogen contained in biomass react with air or oxygen, is known as combustion, industrially. Combustion process proceeds by gas phase reaction, surface reaction, or both, following processes such as fusion, evaporation, and pyrolysis. In actual combustion reaction, complicated phenomena such as evaporation, mixture, diffusion, convection, heat conduction, radiation, and luminescence advance complexly at a very high velocity. Gas fuel burns directly in gas phase as premix combustion or diffuse combustion. Liquid fuel burns as inflammable gas in gas phase after surface evaporation, which is called evaporation combustion., Heavy oil etc. burns in evaporation combustion but decomposition combustion also proceeds, where decomposing the fuel portion occurs by the produced heat.

(b) Forms of combustion

The combustion forms of direct combustion of biomass, which is in solid form, include evaporation combustion, decomposition combustion, surface combustion, and smoldering combustion. In evaporation combustion, the fuel containing simple component and molecular structure with comparatively low fusing point fuses and evaporates by heating, and reacts with oxygen in gas phase and burns. In decomposition combustion, gas produced from thermal decomposition by heating (H_2 , CO , C_mH_n , H_2O , and CO_2) reacts with oxygen in gas phase, forms flame, and burns. Usually, char remains after these forms of combustion and burns by surface combustion. Surface combustion occurs in the case of the component composed of only carbon

containing little volatile portions such as charcoal, and oxygen, CO₂, or steam diffuses to pores existing inside or on solid surface of the component, and burns by surface reaction. Smoldering combustion is the thermal decomposition reaction at temperature lower than the ignition temperature of volatile component of the reactive fuels such as wood. If ignition is forced to smoke or temperature exceeds ignition point, flammable combustion occurs. In industrial direct combustion of biomass, decomposition combustion and surface combustion are the main forms of the combustion.

(c) Combustion method

Industrially, combustion surplus air is supplied in addition to the theoretical amount required for biomass combustion. If surplus air rate is too high, it causes decrease in combustion temperature and thermal efficiency. As the combustion method of biomass, grate combustion (fixed grate and moving grate), fluidized bed combustion, rotary hearth furnace combustion, and burner combustion are used. The features of each combustion method are shown in Table 4.1.1.

Table 4.1.1 Combustion type and feature of biomass

Combustion method	Combustion type	Features
Fixed bed combustion	Horizontal/Inclined grate Water-cooling grate Dumping grate	Grate is level or sloping. Ignites and burns as surface combustion of biomass supplied to grate. Used in small-scale batch furnace for biomass containing little ash.
Moving bed combustion	Forward moving grate Reverse moving grate Step grate Louver grate	Grate moves gradually and is divided into combustion zone and after-combustion zone. Due to continuous ash discharge, grate load is large. The combustion obstruction caused by ash can be avoided. Can be applied to wide range of fuels from chip type to block type.
Fluidized bed combustion	Bubbling fluidized bed combustion Circulation fluidized bed combustion	Uses sand for bed material, keeps fuel and sand in furnace in boiling state with high-pressure combustion air, and burns through thermal storage and heat transmission effect of sand. Suitable for high moisture fuel or low grade fuel.
Rotary hearth furnace combustion	Kiln furnace	Used for combustion of high moisture fuel such as liquid organic sludge and food residue, or large waste etc. Restricted to fuel size on its fluidity.
Burner combustion	Burner	Burns wood powder and fine powder such as bagasse pith by burners, same as that for liquid fuel.

(d) Application

The combustion of biomass is the simplest use of biomass to obtain heat, and is widely used because experiences of fossil fuel technology can be applied, because generation of NO_x, SO_x,

HCl, and dioxin is low, which is the advantage of biomass combustion, and because flammability is excellent. Combustion heat is used for power generation and heat production by recovering heat through heat transfer media such as steam and hot water using boilers and heat exchangers. In district heat supply and in energy centers of industrial complexes, cogeneration fueled by waste wood and agricultural waste is widely used. There are many power plants and heat utilization plants regardless of scale using paddy husk, bagasse, waste wood, oil palm waste and poultry chicken droppings, etc. as fuels.

Further information

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4.1.2 CHP

(a) What is CHP?

Production of electricity and heat from one energy source at the same time is called Combined Heat and Power (CHP). Because the energy efficiencies are higher than the cases to produce only electricity, attention is paid to CHP by the viewpoint of effective use for energy.

(b) Energy conversion in CHP

To generate electricity from biomass, the energy of the biomass is changed into the kinetic energy, the dynamo is turned by it, and the electrical energy is obtained. The main method of changing the energy of the biomass into the kinetic energy is as follows: 1) Steam is made by heat of combustion of the biomass and the steam turbine is turned, 2) The combustible gas is made by pyrolysis or microbial degradation of biomass and the gas engine or the gas turbine is turned using the gas. In any case, the heat obtained by the combustion is converted into the kinetic energy. As all thermal energy cannot be converted into the kinetic energy, a part of the heat is discharged. The energy efficiency of the biomass utilization can be improved if this heat is collected and supplied with the electricity. The CHP has the advantage of raising the energy conversion efficiency in this way.

(c) Possibility of a large-scale plant

CHP can be applied even in a large-scale power plant. The reason for locating a thermal power plant and a nuclear plant near the coast or the big river is to use a large amount of seawater or river water to throw away heat. On the other hand, there is a case to sell the heat that occurs from the power plant to the nearby factories. It would be desirable to consider heat

supply when a large-scale power plant is planned.

(d) Applicability of factories and housing complexes

The CHP facilities can be designed and be set up in a factory or a housing complex according to the demand for the electric power and heat. There are various specifications for the obtained heat from the steam of high temperature and high pressure to the warm water. The collections and supplies of the heat are easier at low temperature and low pressure. The steam and the hot water can also be supplied by combining the CHP facilities with the existing boiler. When the biomass is used as fuel, the generation efficiency decreases when the scale of the facilities gets smaller. In case of the boiler and turbine processes, the scale of 2,000 kW or more in electrical output is necessary and in case of the gasification and gas engine process, the scale of 50 kW or more in electrical output is also necessary.

(e) Examples

An example of the small-scale CHP facility using woody biomass is shown below. In this facility, the wood scrap from the factory is used as fuel, pyrolysis and gasification is performed and electricity, hot air, hot water and cold water are supplied to the factory. The process flow diagram is shown in Fig. 4.1.1.

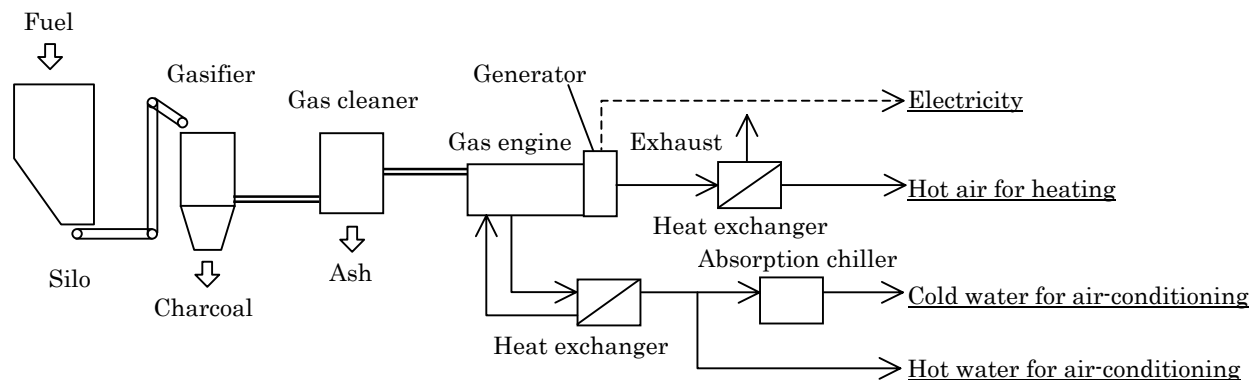


Fig. 4.1.1. Outline flow diagram of a small CHP using woody biomass

Gross power output of electricity is 175 kW and net power output is 157 kW. Heat outputs are 174 kW (150 Mcal/h) as hot air (67°C), 116 kW (100 Mcal/h) as hot water (80°C) and 70 kW (60 Mcal/h) as cold water (7°C). The energy efficiency in the facility can be raised by using heat that is originally thrown away as exhaust and cooling water.

4.1.3 Co-Firing

(a) What is co-firing?

Co-firing refers to the technology whereby biomass is fired with fossil fuels at thermal power stations and so on. The advantage of this technology is that, simply by making some minor revisions to existing equipment to enable biomass treatment, it becomes possible to fire biomass in highly efficient large-scale combustion facilities. Here, an introduction is given to research and development of coal and woody biomass co-firing technology that has been jointly implemented by The Chugoku Electric Power Co., Inc., Hitachi Ltd. and Babcock-Hitachi K.K.

(b) Goals

Upon burning around 5-10% of woody biomass in a coal fired power station (hereafter the proportion of mixed fuel is shown in terms of the calorific base), they aimed to secure stable operation and to clear environmental standards while at the same time minimizing any reduction in generating efficiency. Aiming for generating efficiency equivalent to approximately 40% the level in the existing coal fired power station, they held the reduction in efficiency at the sending end to within 0.5% when the mixed fuel firing rate was 5% (and within 0.8% when the mixed fuel firing rate was 10%).

(c) Feedstock

Based on component analysis of pine, cedar, cypress and bamboo, etc., woody biomass has greater volatile content than coal (bituminous coal), its fuel ratio (ratio of fixed carbon content to volatile matter content) is approximately 1/10 of that of coal, and its ash content is low. Upon conducting tests in a small hammer mill, etc., grinding power consumption for woody biomass was at least 10 times higher than that for the same weight of coal and simultaneous grinding testing of coal and woody biomass revealed that the grindability of coal is reduced a lot when the mixing ratio of wood is increased.

(d) Process flow

Figure 4.1.2 shows the flow diagram of the biomass pretreatment equipment. The woody biomass consisted of thinned timber and bamboo chips procured from the Chugoku region with a size of no more than 50 mm and water content of 50wt%. The chips were crushed to a size suitable for drying (no more than 20 mm) and dried to a water content of 20% or less. Next, two types of pulverizer were combined to regulate the pieces to a top size of 1~5 mm, and the materials were blown into the furnace by fixed quantity feeder. The mixed fuel firing rate was a maximum of 15%. Two types of burner were used: a coaxial coal and biomass mixed burner and a biomass dedicated burner (separately installed).

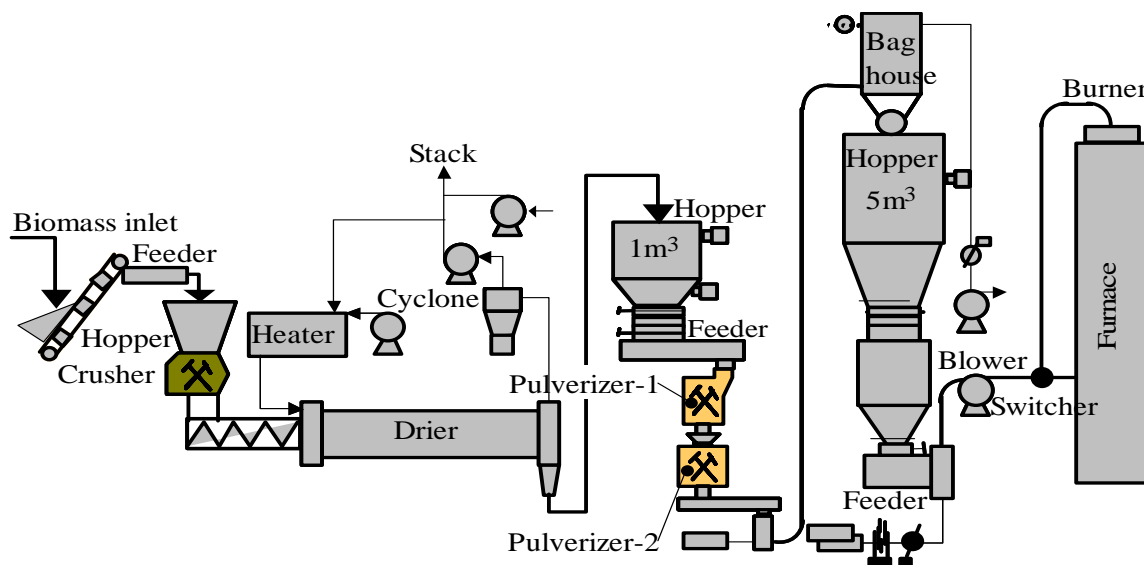


Fig. 4.1.2 Schematic of the Pretreatment Flow

(e) Results

Figure 4.1.3 shows some of the test results. As the proportion of mixed fuel was increased, the unburned matter and relative value of NO_x fell in both the coaxial burner and separately installed burner. The reduction in the unburned matter indicates that mixing of the highly volatile biomass caused the ambient temperature to rise and the combustion efficiency of the fuel itself to increase. The rate of decline in NO_x was lower than the value forecast from the rate of decline in the N content of fuel .

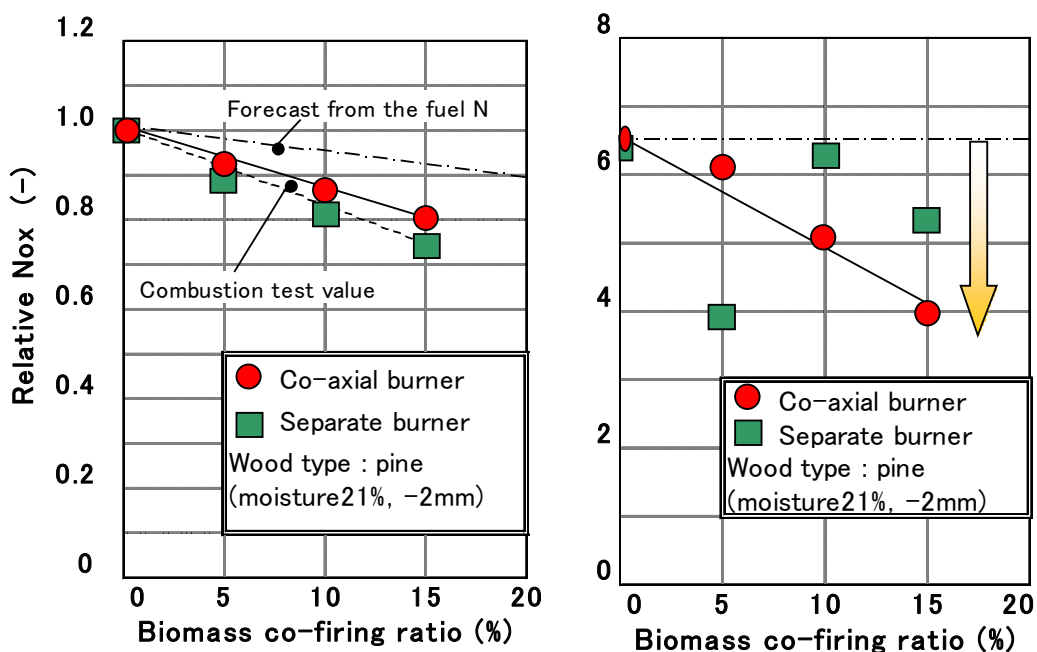


Fig. 4.1.3 Mixed Fuel Firing Test Results

(f) Efficiency

Based on the results of the combustion tests, the basic equipment and system composition in the case of application to the existing coal fired power station (selecting three units of 75-500 MW) was examined and the power generating efficiency and generating cost were assessed. Factors that cause the mixed fuel firing to affect power generating efficiency are thought to be changes in boiler efficiency and auxiliary power. In the case where thinned wood chips having water content of 30% and chip size of 50 mm or less following natural drying of the forest land, etc. are introduced to the power station, this wood is converted to crushed biomass of 20% water content and 2-mm particle size following pulverization and conveyance, and this is combusted in the boiler, whereas the unburned matter of ash is lower than in the case of firing only coal, the boiler efficiency drops slightly due to the water content of the woody biomass. As for auxiliary power of the plant, from the pilot test findings and based on estimation of the crushing power in the case where a two-stage shock crusher is used, the drop in overall sending end efficiency is 0.44% and 0.77% when the proportion of mixed fuel is 5% and 10% respectively, and these values are within the respective targets of 0.5% and 0.8%. Furthermore, upon comparing costs between woody biomass-only firing (10 MW) and mixed fuel firing, since the mixed fuel firing was less expensive than dedicated firing (11.3 yen/kWh), the superiority of mixed fuel firing was confirmed.

4.2 Gasification

4.2.1 Definition

The process to convert biomass solid raw material into fuel gas or chemical feedstock gas (syngas) is called gasification or thermochemical gasification.

4.2.2 Classification of gasification method

Gasification methods are classified according to combinations of conditional factors shown in Table 4.2.1..

Table 4.2.1 Classification of Gasification Method

Classification	Conditional factor
Gasification pressure	Normal pressure (0.1-0.12 MPa), High pressure (0.5-2.5 MPa)
Gasification temperature	Low temperature (700°C and below), High temperature (700 °C and above), High temperature decomposition (ash fusion point and above)
Gasification agent	Air, oxygen, steam and combination of them, carbon dioxide for particular time
Heating (Temperature zone formation)	Direct gasification (heat generation from reaction of partial gasification raw material and oxygen) Indirect gasification (heating raw material and gasification agent by external heat)
Gasifier types	Fixed bed, flow bed, circulating flow bed, entrained bed, mixing bed, rotary kiln, twin tower, molten furnace

4.2.3 Examination of biomass material properties

Examination of biomass material properties is necessary before planning gasification.

(a) Element analysis

Carbon (C), hydrogen (H), oxygen (O), sulfur (S), nitrogen (N) and chlorine (Cl) are observed through element analysis (HCN coder etc.). Excessive sulfur and/or chlorine can cause corrosion of plant equipment. The abbreviated molecular formula $C_nH_mO_p$ can be determined by obtaining the mol ratios for carbon (C), hydrogen (H) and oxygen (O). For biomass consisting of grass and wood, $n=1.2-1.5$ and $p=0.8-1.0$ when $m=2$.

(b) Ash composition and fusion point

The ash softening point, fusion point and flow point are to be measured in both oxidizing and reducing atmospheres. Problems with plant equipment occur more easily when the fusion point temperature is low.

(c) Technical analysis

Technical analysis is to be performed on raw material biomass to determine surface moisture, inherent moisture, volatile matter content, fixed carbon content and ash content, as well as high and low calorific content. These material property values are essential for gasification analysis.

4.2.4 Gasification agent

In order to convert solid biomass into inflammable gas, a substance to promote the chemical reaction is necessary. This substance is called the gasification agent, and mainly air (N_2 , O_2), oxygen (O_2), H_2O , or CO_2 are applied as an appropriate mixture. Air (only O_2 reacts) and O_2

generate heat by oxidation, and increased O₂ decreases the effective amount of inflammable gas.

4.2.5 Fundamental phenomenon of biomass gasification

Fundamental gasification processes are as follows:

(a) Evaporation of surface moisture

Surface moisture evaporates from the raw material at the water boiling point (depends on pressure). Inner moisture remains when the raw material is large.

(b) Evaporation of inherent moisture

Following surface moisture evaporation, inherent moisture evaporates at 110-120°C.

(c) Volatilization

Thermal decomposition of biomass begins at 200-300°C, and CO, CO₂, H₂ and H₂O are vaporized as gas. Thermal decomposition is a heat generating reaction which is a characteristic phenomenon of biomass (C_nH_mO_p).

(d) Volatilization and gasification reaction

The temperature is raised further during volatilization, and the volatile matter of the lightweight hydrocarbons (C_xH_y; where *x* and *y* are integers of at least 1; a low value of *x* indicates lightness and a high value of *x* indicates heaviness) is transformed into heavy C_xH_y with a high boiling point. Subsequently, the C_xH_y reacts with the gasifying agent for conversion to lightweight molecule clean gas, although tar and soot can form when diffusion of the gasifying agent is slow and the C_xH_y condenses.

(e) Char gasification

Following volatilization of the volatile content in the raw material biomass, the fixed carbon and ash become char, and the char is heated to the surrounding temperature. The subsequent reaction with the gasifying agent transforms the carbon into CO and CO₂. However, in cases where the gasifying agent contains excess steam and the surrounding temperature is over 750°C, a wet gas reaction occurs (C+H₂O (CO+H₂) producing gas composed mainly of CO, CO₂ and H₂.

(f) Char residue

The reaction rate of the wet gas reaction is slow, and char residue can easily form. The formation of tar, soot and char tends to reduce efficiency, as well causing equipment trouble.

4.2.6 Characteristics of gasification product gas

Gasification generally adopts the direct gasification method with partial combustion of raw material to raise the temperature. Raw materials are mainly wood chips and corn stalks. Most gasification furnaces use normal pressure and a direct gasification process. To keep the reaction temperature at 800°C and above for direct gasification, air, oxygen and steam (as appropriate) are required for the gasification agent. For this purpose, approximately 1/3 of the oxygen required for complete combustion (known as the oxygen ratio) is supplied, with partial combustion (partial oxidation) causing gasification. The calorific value of product gas depends on the percentage of inflammable gas (CO, H₂, C_xH_y) contained. Generally, gas can be divided into low calorie gas (4-12 MJ/m³), medium calorie gas (12-28 MJ/m³) and high calorie gas (above 28 MJ/m³). For the most part, direct gasification of biomass yields low calorie gas. Fig. 4.2.1 presents composition of the product gas from rice straw when steam and oxygen is employed as gasifying agent. The ratio between the calorific content of the biomass and that of the product gas (at room temperature) is called cold gas efficiency.

4.2.7 Gasification equipment and a practical example

Here is shown a fixed bed gasifier, based on the combustion or gasification of solid fuel, and featuring a comparatively simple structure and low equipment cost. Fig. 4.2.2 shows a concept diagram of the gasifier. Wood chips of about 2.5-5 cm are generally used as the raw material. They are supplied from the upper feed port, and layered in the furnace. The gasifying agent (air, oxygen, steam or a mixture thereof) is supplied from the bottom in a rising flow (some systems

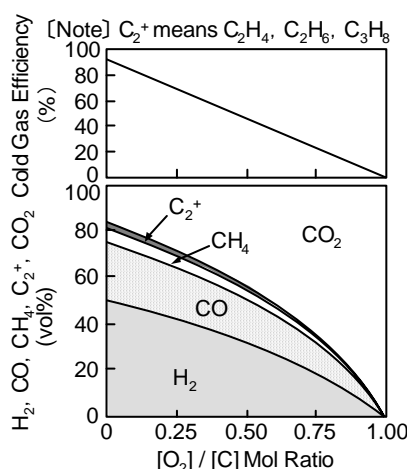


Fig. 4.2.1 Changes in product gas composition due to oxygen ratio

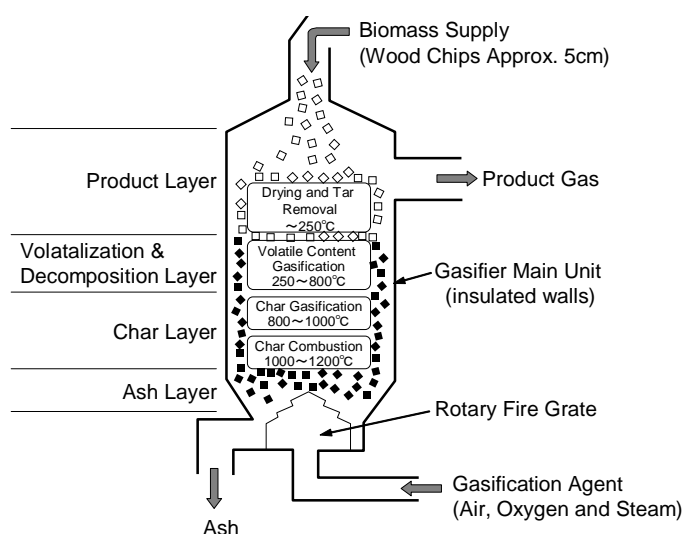


Fig. 4.2.2 Concept diagram of a fixed bed gasifier

use a descending flow). The gasification reaction proceeds from the bottom towards the top. From the bottom upward, individual layers are formed due to the changes accompanying gasification of the raw material, in the order of ash, char, volatilized and decomposed material, and product. The product gas is obtained at the top.

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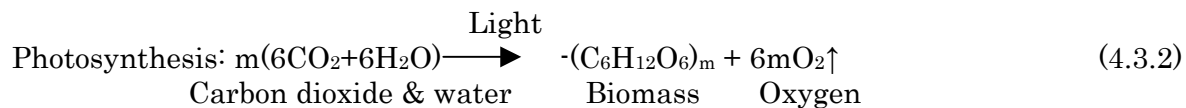
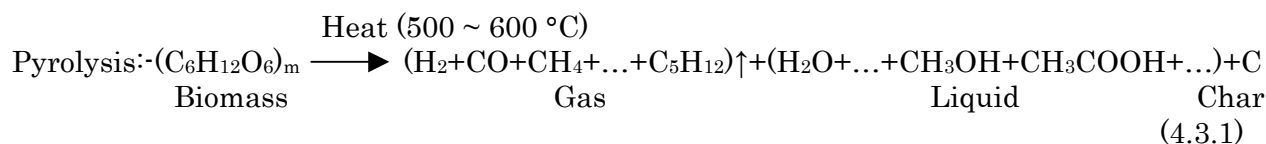
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4.3 Pyrolysis

4.3.1 What is pyrolysis?

Biomass is consisted mainly of carbon, hydrogen and oxygen. The photosynthesis and pyrolysis can be simply described as the following formulas,



The main chemical components of biomass are cellulose, hemicellulose and lignin. Fig. 4.3.1 shows the composition changing during pyrolysis. The cellulose, hemicellulose and lignin are decomposed with temperature increase. Solid residue is char in the yield of 10 to 25%.

4.3.2 Characteristics of pyrolysis

During pyrolysis, moisture evaporates at first ($\sim 110^\circ\text{C}$), and then hemicellulose is decomposed ($200\text{--}260^\circ\text{C}$), followed by cellulose ($240\text{--}340^\circ\text{C}$) and lignin ($280\text{--}500^\circ\text{C}$). When temperature

reaches 500°C , the reactions of pyrolysis are almost finished. Therefore, at the heating rate of 10°C/s , the pyrolysis finishes in 1 min, while it finishes in 5 s at 100°C/s . Higher heating rate results in the more rapid generation of vapor product, increasing pressure, shorter residence time of vapor product in the reactor, and higher liquid yield; named fast pyrolysis or flash pyrolysis. Dynamotive (Canada) and BTG (Netherlands) have developed fast pyrolysis reactors, which show high liquid yield of 60 to 80%. Since heat conductance of wood is $0.12\text{--}0.42\text{ W/(m K)}$, which is around $1/1000$ of copper, heat transfer is important for fast pyrolysis, and the milling to small particles is required.

4.3.3 Reactors at laboratory scale

Thermobalance is most commonly used at laboratory for the fundamental study. Very small amount of sample, around a few mg to 10s mg, is heated up from room temperature to the desired temperature at the desired heating rate to measure the weight changing. However, it is difficult to recover the products.

A few g to 10s g of sample is used at laboratory scale reactor to recover the products. Sand bath or molten salt bath are used as the heater for the batch type reactor. Infrared rays heater is usually used for the continuous reactor. At these reactors, mass balance and product analysis are studied.

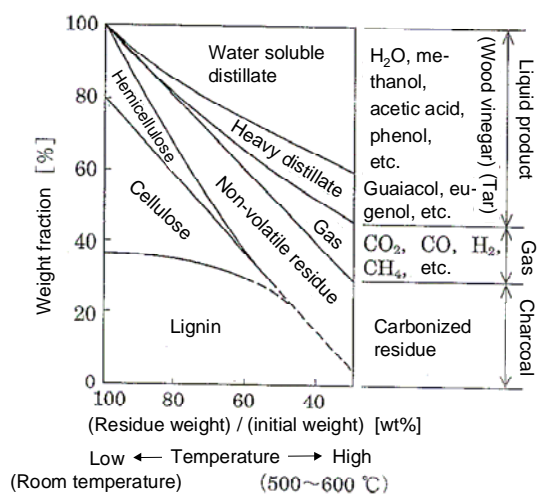


Fig. 4.3.1 Composition changing during pyrolysis.

4.3.4 Reactors at R&D

NREL, USA, has developed a vortex reactor, in which wood particle slides on the hot reactor wall by the circled hot gas flow. By the revolution, fresh surface is always appeared on the wood particle, and then the flash pyrolysis is realized. BTG, Netherlands, has developed a rotary corn type reactor, in which hot sand is used as the heat transfer medium and the sand fluids by the centrifugal force of the rotated reactor.

Many type of fluidized bed (FB) reactor have been developed by Dynamotive-RTI, Pasquali-ENEL (Italy), Ensyn,(Canada), RedArrow-Ensyn (USA), Union Fenosa-Waterloo (Spain), VTT (Finland), etc. The small particle of wood is introduced in FB with hot gas or hot heat transfer medium, and it is rapidly pyrolyzed for high liquid yield. Since smooth feeding of the wood particle is difficult, tar trouble occurs easily.

AIST, Japan, had developed the pyrolysis using microwave. Microwave can heat wood from inside, and big size wood, log, is directly used. The same result is obtained as the flash pyrolysis of 200°C/s. Bigger size is better for the energy efficiency, and around 1.4 MJ (0.4 kWh) is used for the completed pyrolysis of 1-kg wood. In addition, in this pyrolysis, tar trouble is small.

4.3.5 Products

The liquid, gas and char are obtained by pyrolysis. The liquid has high moisture from original moisture (8-40%) and produced water (14-17%), and it is a mixture of water and polar organics. Its higher heating value is around 12.5-21 MJ/kg. The relationship between the viscosity and heating value of the liquid is shown in Fig. 4.3.2. Higher moisture content results in lower viscosity and lower heating value. In addition, the liquid is unstable, and any improvement is required.

The pyrolysis gas has much CO₂, and CO, H₂, C₁₋₅ hydrocarbon as combustible gas. The char has the higher heating value of 32 MJ/kg, and it is suitable as a feedstock for activated carbon.

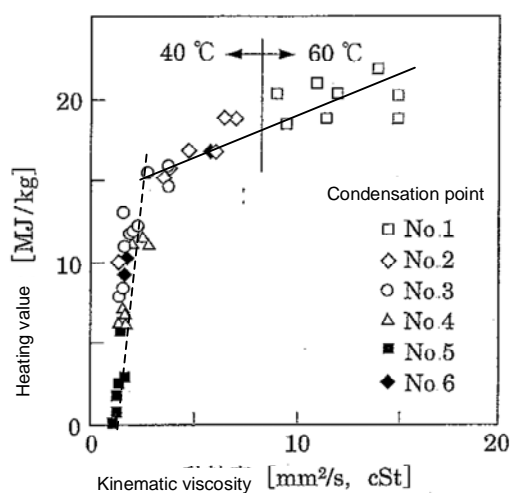


Fig. 4.3.2 The relationship between the viscosity and heating value of pyrolysis liquid.

However, all of the char is usually used as heat resource for the pyrolysis system.

4.3.6 Status of technology

The pyrolysis liquid can not be mixed with the transportation fuel, and any improvement is required. There is tar trouble, but the know-how to operate the reactor is not opened. To get liquid at high yield, rapid heating and cooling are needed, and heat loss and recovery is an important issue. Merit and demerit should be considered.

Further information

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4.4 Carbonization

4.4.1 What is carbonization?

Carbonization is the method or technology to obtain charcoal as the main product by heating such solid biomass as wood, bark, bamboo, rice husks, etc. at 400-600°C in the almost or complete absence of air or oxygen. It can afford tar, pyroligneous acid, and combustible gases as by-products. In case of discrimination from 'dry distillation' aiming at the recovery and utilization of liquid products, 'charcoal making' is used as the terminology. Carbonization customarily means charcoal making, although it is the general term including dry distillation.

4.4.2 Characteristics of carbonization

Carbonization is a classical energy conversion means of biomass, similarly to combustion. While the main objective is increase in the calorific value of the solid product charcoal, it has two sides of liquefaction and gasification. As liquefaction means corresponding to ordinary pyrolysis (see Chapter 4.3), commercial operation was early examined together with high pressure (direct) process (Chapter 4.6). However, the obtained tar (oil) was in a low yield (< 30%) with poor quality (high viscosity, high oxygen content, low heating value, low pH, etc.), so that the process was given up after the appearance of rapid pyrolysis (Chapter 4.3) yielding a

large quantity of oil. As gasification means (Chapter 4.2), it is inferior to current processes in the production of combustible components, due to lower reaction temperature. In the utilization of product gas for generation, a considerable amount of tar must be removed. Nevertheless, carbonization that has industrial advantages of inexpensive apparatus and easy operation is still important for cheaply producing solid fuels with high heating value. The features making a certain proportion of organic carbon stably fixed and the features making the volume of municipal wastes, garbage, sewage sludge, cow dung, etc. effectively reduced contributes to the control of CO₂ emission and serves as a practical measure to dispose of various wastes, respectively.

4.4.3 Reactions in carbonization

Carbonization reactions are basically the same as pyrolytic reactions in an inert gas like nitrogen. For wood, after most water is evaporated at below 200°C, three main constituents of cellulose, hemicellulose, and lignin are decomposed to produce liquid fraction and gaseous fraction, consisting mainly of CO and CO₂, at 200-500°C, thereby occurring a rapid weight decrease. In this region, each wood constituents undergo dehydration and depolymerization to repeat intermolecular and intramolecular fission and re-bonding, and the resulting low molecular weight fragments are cracked into liquid and gaseous products, whereas high molecular weight fragments formed by condensation are charred together with non-decomposed portion. Although the weight loss becomes smaller at above 500°C, polycondensed aromatic carbon increases with the evolution of H₂ to reach about 80% C in char up to 700°C. By further increasing the temperature, the polycondensed carbon structure develops to increase the content of C without prompt production of H₂. The overall scheme of carbonization is represented in Fig. 4.4.1. This signifies that product distribution depends on both steps of the decomposition of 'melt' resulted from wood constituents into gas, liquid, and solid fractions (first stage) and subsequent decomposition of the liquid fraction (second stage), and the ratio of rate constants for first stage to that for second stage. The distribution is also influenced by moisture and size of feed, heating rate, operating temperature, etc. The latter three are particularly important, and the yield of liquid (tar) is increased with decreasing the size and increasing the rate.

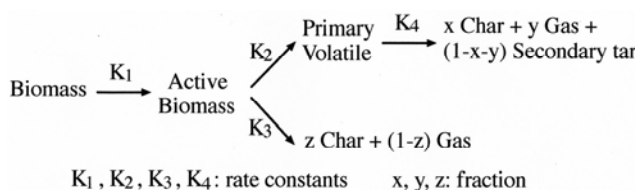


Fig. 4.4.1. Modified Broide-Shafizadeh scheme

Higher temperature makes the yield of charcoal lower and that of tar higher at below 500°C. Pressure is likewise important, and the yield of tar becomes higher at the lower value.

4.4.4 Energy efficiency of carbonization

Continuous carbonization of a mixture of pine bark and sawdust by Tech-Air pyrolysis system (Fig. 4.4.2) is described as an example. This is an internal heat supply process with a vertical fixed bed reactor. The raw material is fed at the top of the reactor after reducing the initial moisture of 25-55% to 4-7%. Heat for carbonization is provided by partial combustion of the feed with air introduced from the bottom of the reactor. Charcoal produced is drawn out with a screw from another bottom section, while the product vapor passes through a cyclone where fine solid particles are removed to enter a condenser for tar (oil) recovery. The non-condensable gas is then combusted in a burner, and the discharged gas (204-316°C) is used for drying the raw material. The reactor temperature that is

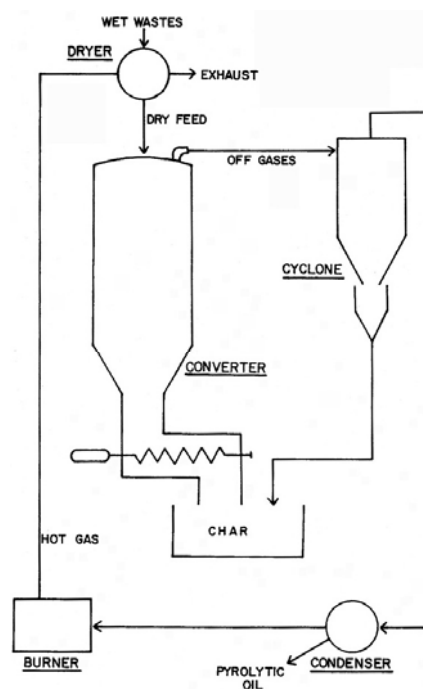


Fig. 4.4.2. Tech-Air pyrolysis system

variable from 430° to 760°C is so controlled as to allow the heating value of the pyrolytic gas to have the energy necessary for drying the feed. Table 4.4.1 summarizes product distribution and two process efficiencies, which are defined as Net Thermal Efficiency (NTE, %) calculated as $[\{\text{heating value of products} - \text{heat of process (gas for drying)}\} / \text{heating value of raw material}] \times 100$, and Energy Benefit Ratio (EBR, %) obtained as $[\text{energy of products} / \text{energy consumed}] \times$

Table 4.4.1. Product energy yields and process efficiency

Case	Feed [GJ]	Char [GJ]	Available Gas ^d [GJ]	Oil [GJ]	Dryer Gas [GJ]	NTE [%]	EBR [-]
Maximum char	9.18	4.54	1.72	0.63	1.85	75.0	3.71
Maximum oil	9.18	2.85	1.84	2.21	1.85	75.2	3.72
Maximum gas	9.18	3.48	2.16	1.26	1.85	75.1	3.72

^d (Total gas produced) – (Dryer gas)

100, respectively, in terms of energy for the maximum yield of each product. Because of no great difference for all of the operations, the optimal conditions are decided by quality, use, cost, and so on for charcoal and oil.

4.4.5 Products of carbonization

In Japan, charcoal is widely used as soil improver, fodder, moisture conditioner, etc. by making use of the adsorption capacity (so-called 'charcoal for new uses'), in addition to solid fuel for cooking and heating. For liquid products, low boiling point fraction, pyrolygneous acid, is on the market as agricultural materials, deodorant, etc. In contrast, high boiling point fraction, tar, has a limited practical utilization, like creosote as medicine. In a laboratory scale, the production of phenolic resin adhesive, the recovery of wood preservatives, conversion into electroconductive carbon, etc. has been reported. The use of gas fraction is a supplementary fuel for process.

4.4.6 Status-quo of the technology

A variety of reactors in scale and shape are developed in response of the diversification of material, and they are commercially operated, although the current system does not greatly differ from the earlier one. Nickel-catalyzed carbonization of wood at 900°C, which was conducted in a laboratory scale to obtain a functional carbon with conductivity and liquid phase adsorption in concurrence with hydrogen-rich gas, has attracted considerable attention.

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4.5 Hydrothermal Gasification

4.5.1 What is hydrothermal gasification?

Hydrothermal gasification is treatment of biomass in hot compressed water, usually above 350°C and above 20 MPa to obtain combustible gas. Figure 4.5.1 shows phase diagram of water, where gas-liquid equilibrium line starts from the triple point and ends at the critical point. Hydrothermal condition is located around the critical point. When both temperature and pressure is higher than

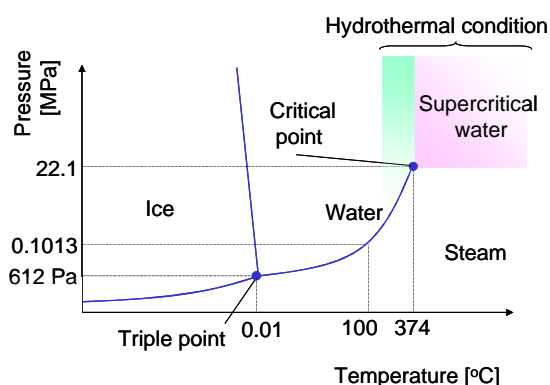


Fig. 4.5.1. Phase diagram of water

critical temperature and critical pressure, respectively, the state is called supercritical water, and gasification in supercritical water is called “supercritical water gasification”. This hot compressed water enjoys high reactivity, and when biomass is placed in this water, it is gasified by hydrolysis and pyrolysis reactions.

4.5.2 Characteristics of hydrothermal gasification

Hydrothermal gasification is suitable for wet biomass treatment. When wet biomass is to be gasified, usual thermochemical gasification is not employed due to its high moisture content. Hydrothermal gasification, on the other hand, uses water as reaction medium, and thus wet biomass can be treated without costly, energy-consuming drying pretreatment. Since reactivity of water is high under these conditions, hydrothermal gasification enables quick and almost complete gasification of biomass. Biomethanation is employed to obtain methane gas from wet biomass, but usually it takes a few weeks for the reaction to complete, and treatment of unreacted fermentation sludge and waste water can be a large problem. Reaction time as long as a few weeks results in bulky reactor. Fermentation sludge can be converted to compost, but when sufficient land is not available for the use of the compost, it is just a waste to be treated. In hydrothermal gasification, reaction is completed in a few minutes at longest, and almost complete gasification is possible when reaction condition is properly adjusted. Sometimes, addition of catalysts such as alkali, metal, or carbon catalysts enhances the reaction.

4.5.3 Reactors for hydrothermal gasification

To investigate the reactions taking place in hydrothermal gasification, tube-bomb reactors of the volume of several mL and autoclaves are often used. However, when you want to develop a commercial plant, a continuous reactor such as is shown in Fig. 4.5.2 is a must. Biomass is fed to the reactor at a high pressure, and then heated to the reaction temperature. In the reactor, biomass is gasified under hydrothermal condition, and the effluent is cooled down to the room temperature. Heat released at this time is recovered by the heat exchanger, and used to heat up the feedstock. After reaching the room temperature, the effluent is depressurized to atmospheric pressure, and the product gas is recovered. The continuous reactor is needed because of the large amount of heat needed to attain the hydrothermal condition. This heat sometimes matches the heat of combustion of the biomass to be gasified, and thus heat recovery using a heat exchanger is needed. Only flow reactors allow this heat recovery. In Fig. 4.5.2, heat balance for the ideal case is also shown. Combustion heat of biomass is maintained in the product gas while heat required to attain hydrothermal condition is recovered so that no heat is added from outside during gasification operation. In practice, the efficiency of the heat exchanger cannot be unity, and endothermic reaction results in necessity of additional heat supply to the reactor.

4.5.4 Energy efficiency of hydrothermal gasification

For the ideal process as shown in Fig. 4.5-2, the energy efficiency of hydrothermal gasification is unity. This is to be noted since misunderstanding that energy efficiency of hydrothermal gasification is low due to the large amount of heat required to attain hydrothermal condition. When heat recovery is properly made, a high energy efficiency is possible.

Energy efficiencies higher than 70% including electricity and heat loss at the heat exchangers have been shown by a detail process calculation.

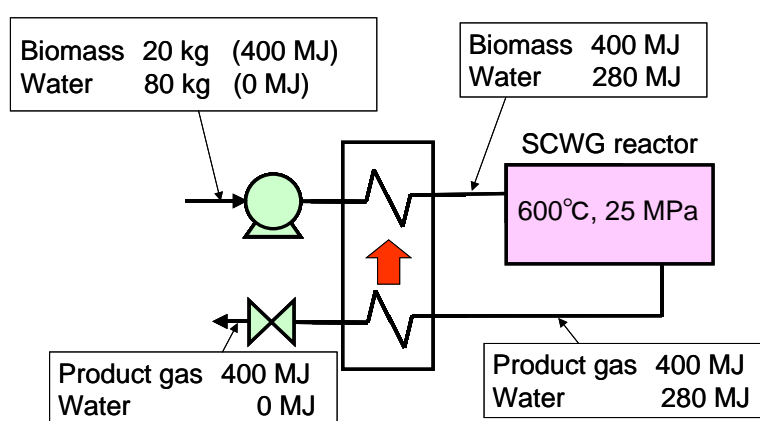


Fig. 4.5.2. Heat balance of hydrothermal gasification.

4.5.5 Products of hydrothermal gasification

The product gas is automatically separated from liquid phase when the reactor effluent is cooled down to the room temperature. Tar free gas is available, which is a benefit over usual thermochemical gasification of biomass. The main component is hydrogen, carbon dioxide, and methane. Due to the water-shift gas reaction the yield of carbon monoxide is negligible. The high temperature, low pressure, and dilute feedstock favors high hydrogen content. The heating value of the product gas depends on reaction condition, and usually varies from 12 to 18 MJ/m³-N.

4.5.6 Status-quo of the technology

Many reports on experiment with laboratory scale reactors exist. There are three pilot plants in operation: Energia Co. plant in Japan; VERENA Plant in Germany; and TEES Process in USA. The capacity ranges from 1 to 2.4 t-wet/d. Feedstocks tested are many including chicken manure, corn silage, and cheese whey. No commercial plants have been built mainly due to the high plant cost at present.

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4.6 Hydrothermal Liquefaction

4.6.1 What is hydrothermal liquefaction?

Hydrothermal liquefaction is pyrolysis in hot compressed water of around 300°C and 10 MPa. Biomass is converted into gas, liquid and solid, like common pyrolysis in gas phase. The light tar fraction, such as pyroligneous, can be dissolved in water, and the heavy tar fraction can be obtained in the mixing with char. That is, products are gas, aqueous, and oily material.

4.6.2 Characteristics of hydrothermal liquefaction

Since hydrothermal liquefaction proceeds in water, drying process of feedstock is not needed. Therefore, it is suitable for high moisture content biomass, such as aquatic biomass, garbage, organic sludge, and so on. In addition, many kinds of reaction can occur at different reaction temperatures, and many application is possible. Fig. 4.6.1 shows the reactions which occur in the hot compressed water. At around 100°C,

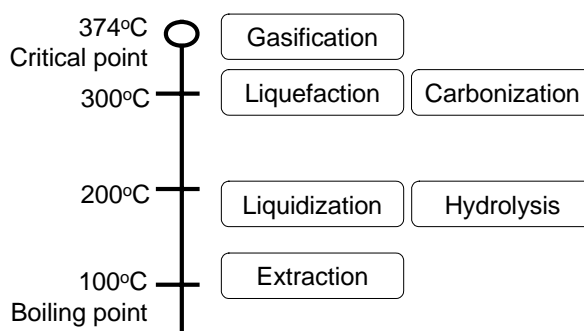


Fig. 4.6.1. Reactions which occur in the hot-compressed water

aqueous soluble fraction is dissolved, and extraction is applicable. At above 150°C, hydrolysis occurs, and biomass polymers, such as cellulose, hemicellulose, protein, and so on, are degraded into monomer. At around 200°C and 1 MPa, solid like biomass is changed to slurry (liquidization), and oily product, however, is not obtained. At severer condition of 300°C and 10 MPa, liquefaction occur, and oily product is obtained. When reaction condition is changed such as reaction time or catalyst, main product can be changed to char (hydrothermal carbonization). At around critical point and with catalyst, biomass can be gasified (see Chapter 4.5).

4.6.3 Reaction scheme of hydrothermal liquefaction

Fundamentally, hydrothermal liquefaction is pyrolysis, and therefore degradation and polymerization occur. Simple reaction scheme is shown in Fig. 4.6.2. At first step, biomass can be degraded into water-dissolved materials. Then the water-dissolved materials are

polymerized to form oil. When reaction is prolonged, the formed oil is polymerized into char.

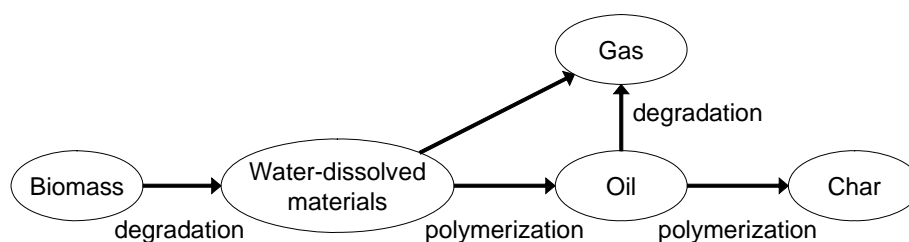


Fig. 4.6.2. Simple reaction scheme of liquefaction

4.6.4 Product oil from hydrothermal liquefaction

Properties of obtained oil by liquefaction are shown in Table 4.6.1. The reaction was conducted without reducing gas, such as hydrogen and carbon monoxide, and with alkali catalyst for wood and without catalyst for sewage sludge. The obtained oil has oxygen content of around 20 wt%, and therefore, its higher heating value is lower than that (around 42 MJ/kg)

of heavy oil from petroleum. In addition, its viscosity is very high. The obtained oil from wood has much amount of acid fraction, and it can corrode and polymerize during storage. On the other hand, the obtained oil from sewage sludge has nitrogen originated from protein, and NO_x treatment is needed at its combustion. As chemical fraction, pyridine derivative, pyrazine derivative, and amid compounds are detected. If they can be separate, they might be used as chemicals.

Table 4.6.1. Properties of obtained oil by liquefaction

Biomass	Wood	Sewage sludge
Elemental composition [wt%]		
Carbon	72	71
Hydrogen	6	9
Nitrogen	-	6
Oxygen	22	16
H/C	1.00	1.52
Higher heating value [MJ/kg]	29 - 30	33 - 34
Viscosity [mPa.s]	> 10 ⁶	10 ³ - 10 ⁴

4.6.5 Energy efficiency of hydrothermal liquefaction

The energy yield (= calorie in the obtained oil / calorie in the feedstock biomass) is around 70%. As for energy efficiency of hydrothermal liquefaction process, the effective calorie of the obtained oil almost balances or is surplus a little with the required heating energy of feedstock biomass from room temperature to reaction temperature. The moisture content affects it strongly, and at below around 85% of moisture content, it is calculated that the process can

produce energy.

4.6.6 Status-quo of the technology

There are many reports on laboratory scale and pilot scale, and no commercial plants have been built. About pilot scale R&D, US Bureau of Mines had developed PERC process and US DOE had developed LBL process in 1960 to 1970s, NIRE and Organo Co. in Japan had developed a sewage sludge liquefaction plant in around 1990, and Biofuel Co. and Shell Co. in Netherlands had developed HTU process in around 2000.

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4.7 Biodiesel Production

4.7.1 What is biodiesel production?

Compared with other biomass resources, oils and fats are high in heat capacity, and their majority is liquid at an ambient temperature. Although these characteristics are preferable for automobile fuel, viscoelasticity (>30mm²/s at 40°C) and flash point (>300°C) are so high that it cannot be used without modification. Therefore, by transesterifying triglycerides of the oils and

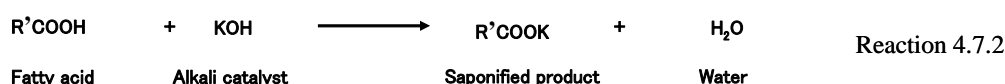
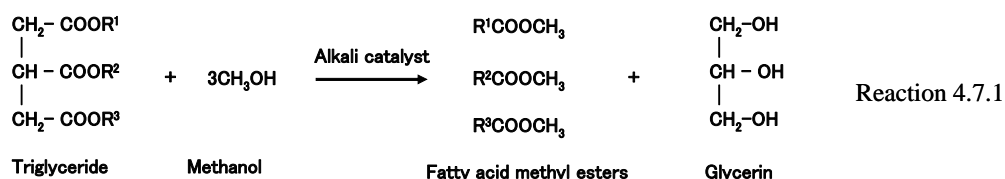
fats, its viscoelasticity and flash point are reduced respectively down to 3~5mm²/s and 160°C which would be appropriate with cetane number of 50-60 to substitute for the diesel fuel. This fatty acid methyl ester is called biodiesel fuel (BDF).

4.7.2 Characteristics of biodiesel production

Biodiesel is low in SO_x, dark smoke and particulate matters, compared with diesel. Therefore, its exhausted emission is relatively clean. Additionally, there exists an advantage to keep carbon balance on the earth due to its biomass-derived product. Furthermore, it contains oxygen as an ester to be 11% low in heat capacity. However, due to its lubricity and less dark smoke emission, biodiesel is almost comparable to diesel in practical engine performance.

4.7.3 Reactors for biodiesel production

For biodiesel production, transesterification is applied for vegetable oils (Reaction 4.7.1) in which triglycerides, the esters of glycerin with fatty acids, and free fatty acids exist. Generally, oils are mixed with methanol using alkali catalyst such as potassium hydroxide or sodium hydroxide, and its mixture is stirred at 60-70°C for 1 h. After the reaction, the lower and upper portions are phase-separated with glycerin in the lower and esterified products in the upper which is washed to be fatty acid methyl esters as biodiesel. Since free fatty acids are contained in the waste oils, they can react with a catalyst to produce saponified products (Reaction 4.7.2), thus reducing the yield of biodiesel.



R¹, R², R³, R⁴; Hydrocarbon residues

Due to such a disadvantage of the alkali catalyst method, it is reported that free fatty acids are first esterified by acid catalyst, followed by alkali catalyst method. As non-catalytic methods, ion-exchanged resin catalyst method, lipase catalyst method and supercritical

methanol method are proposed. In addition, to promote efficiency of esterification, the two-step supercritical methanol method is also proposed by hydrolyzing triglycerides with subcritical water followed by esterification of fatty acids with methanol in its supercritical state (Reactions 4.7.3 and 4.7.4, Fig. 4.7.1). This process is the only one to handle the low-grade waste oils with

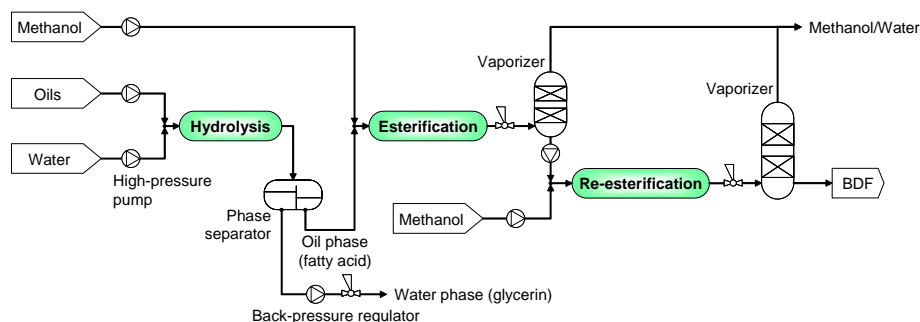
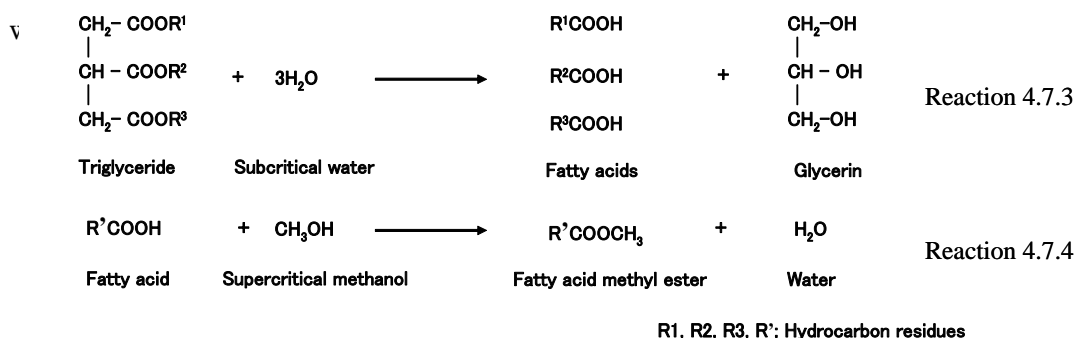


Fig. 4.7.1. Two-Step supercritical methanol process adopting the re-esterification step.

4.7.4 Energy efficiency of biodiesel production

Transesterification of triglycerides and esterification of fatty acids are both exothermic reactions but their heat capacity is small. In alkali catalyst process, energy to increase the system to 60-70°C, energy for a methanol, and energy for the whole reaction process are essential. Furthermore, additional energy is required after the reaction for purifying the glycerin as a by-product. In the biodiesel production with 2.2 kg/s (70,000 t/year) capacity, energy efficiency is reported to be 62% on higher heating value basis.

4.7.5 Status-quo of the technology

Biodiesel production has been commercially developed in Europe and North America, and their production is mainly based on alkali catalyst method. However, for the low-grade waste

oils, a combined process with acid catalyst has been developed with their own non-disclosed technologies. Due to the limited raw materials in Japan, new development of the technology will be expected to handle the low-grade waste oils to be converted into high-quality biodiesel.

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