

Chapter 10

Hydrothermal Liquefaction to Convert Biomass into Crude Oil

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Abstract

All fossil fuels found in nature—petroleum, natural gas, and coal, based on biogenic hypothesis—are formed through processes of thermochemical conversion (TCC) from biomass buried beneath the ground and subjected to millions of years of high temperature and pressure. In particular, existing theories attribute that petroleum is from diatoms (algae) and deceased creatures and coal is from deposited plants.

TCC is a chemical reforming process of biomass in a heated and usually pressurized, oxygen deprived enclosure, where long-chain organic compounds (solid biomass) break into short-chain hydrocarbons such as syngas or oil. TCC is a broad term that includes gasification, including the Fisher-Tropsch process, direct liquefaction, hydrothermal liquefaction, and pyrolysis. Gasification of biomass produces a mixture of hydrogen and carbon monoxide, commonly called syngas. The syngas is then reformed into liquid oil with the presence of a catalyst. Pyrolysis is a heating process of dried biomass to directly produce syngas and oil. Both gasification and pyrolysis require dried biomass as feedstock, and the processes occur in an environment higher than 600°C. The hydrothermal liquefaction (HTL) involves direct liquefaction of biomass, with the presence of water and perhaps some catalysts, to directly convert biomass into liquid oil, with a reacting temperature of lower than 400°C.

This chapter only covers the topic of HTL of biomass. Biomass feedstocks include biowaste (manure and food processing waste), lignocellulose (crop residue), and algae. The chapter is in two parts. The first part covers HTL fundamentals based on the current knowledge, and the second part is a summary of state-of-the-art knowledge of HTL for various feedstocks. The author has attempted to organize this chapter for a variety of readers who are interested in the topic of HTL, including students and professionals.

Fundamentals of HTL

HTL, also called hydrous pyrolysis, is a process for the reduction of complex organic materials such as bio-waste or biomass into crude oil and other chemicals. It mimics the natural geological processes thought to be involved in the production of fossil fuels. HTL is one of the processes of a general term of TCC which includes gasification, liquefaction, HTL, and pyrolysis. There is a general consensus that all fossil fuels found in nature—petroleum, natural gas, and coal, based on biogenic hypothesis—are formed through processes of TCC from biomass buried beneath the ground and subjected to millions of years of high temperature and pressure. In particular, existing theories attribute that petroleum is from diatoms (algae) and deceased creatures and coal is from deposited plants. Gasification of biomass produces a mixture of hydrogen and carbon monoxide, commonly called syngas. The syngas is then reformed into liquid oil with the presence of a catalyst. Pyrolysis is a heating process of dried biomass to directly produce syngas and oil. Both gasification and pyrolysis require dried biomass as feedstock, and the processes occur in an environment higher than 600°C. HTL involves direct liquefaction of biomass, with the presence of water and perhaps some catalysts, to directly convert biomass into liquid oil, with a reacting temperature of less than 400°C.

HTL has different pathways for the biomass feedstock. Unlike biological treatment such as anaerobic digestion, HTL converts feedstock into oil rather than gases or alcohol. There are some unique features of the HTL process and its product compared with other biological processes. First, the end product is crude oil which has a much higher energy content than syngas or alcohol. And second, if the feedstock contains a lot of water, HTL does not require drying as gasification or pyrolysis. The drying process typically takes large quantities of energy and time. The energy used to heat up the feedstock in the HTL process could be recovered effectively with the existing technology.

HTL may have two pathways from biomass to biofuel: (1) direct conversion of biomass or (2) pretreatment of biomass and then fermentation. For the biomass with little lignocellulosic fraction—such as waste streams from animal, human, and food processing—it can be directly converted into biofuel thermochemically. Pretreatment is currently a bottleneck in the conversion of cellulosic feedstock. HTL may hold a substantially greater potential to shorten the fermentation time of lignocellulose. Traditionally, acid hydrolysis was commonly used to convert lignocellulosic materials to monosaccharides, but the high concentration of acids used in hydrolysis requires extensive waste treatment or recovery costs.

The Role of Water in HTL

Water plays an essential role in HTL. It is therefore critical to understand the fundamentals of water chemistry when subjected to high temperature conditions. Water is rather benign and will not likely react with organic molecules under standard environmental conditions (20°C and 101,325 kPa). However, when the temperature increases, two properties of water molecules change substantially. First, the relative permittivity (dielectric constant), ϵ_r , of water decreases quickly when the temperature increases. When the thermal energy increases, the shared electron by oxygen and hydrogen atoms tends to circulate more evenly and the electronegativity of the oxygen molecule is reduced (less polar). For example, when temperature increases from 25°C to 300°C, the relative permittivity decreases from 78.85 to 19.66, resulting in water molecules from very polar to fairly nonpolar, in a relative term. This polarity

change makes water more affinitive to the organic hydrocarbons, most of which are nonpolar molecules.

Second, the dissociation of water dramatically increases with the increase of temperature. Water, like any other aqueous solutions, split into H^+ and OH^- ions in hydrolysis or dissociation. This process is reversible and the rate is sufficiently rapid so it can be considered to be in equilibrium at any instant. Based on Arrhenius reaction rate, the equilibrium constant (or the dissociation constant), K_w , affected by the temperature change, can be written as (Benjamin 2002):

$$\frac{K_{w1}}{K_{w2}} = \exp\left[\frac{\Delta E_{Ar}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \quad (1)$$

where K_{w1} and K_{w2} are equilibrium constant at temperatures T_1 and T_2 , respectively; ΔE_{Ar} is the net change in heat content of the molecules in the overall reaction, also called the molar enthalpy of reaction; R is the universal gas constant, and T is the absolute temperature in Kelvin. ΔE_{Ar} is an empirical constant specific to particular reaction and in units of energy per mole.

The effect of temperature on water dissociation is illustrated in Figure 10.1, where the left side vertical axis is in $pK_w = -\log_{10}(K_w)$, and the right side vertical axis is the ratio of K_w to the K_{w0} . K_{w0} is the water dissociation constant at a temperature of 25°C at atmospheric pressure, and is 10^{-14} . From Figure 10.1, water molecules dissociation constant at 300°C is about 500 times higher than that of 25°C at atmospheric pressure. The increase in the dissociation constant will increase the rate of both acid- and base-catalyzed reactions in water far beyond the natural acceleration due to increased temperature.

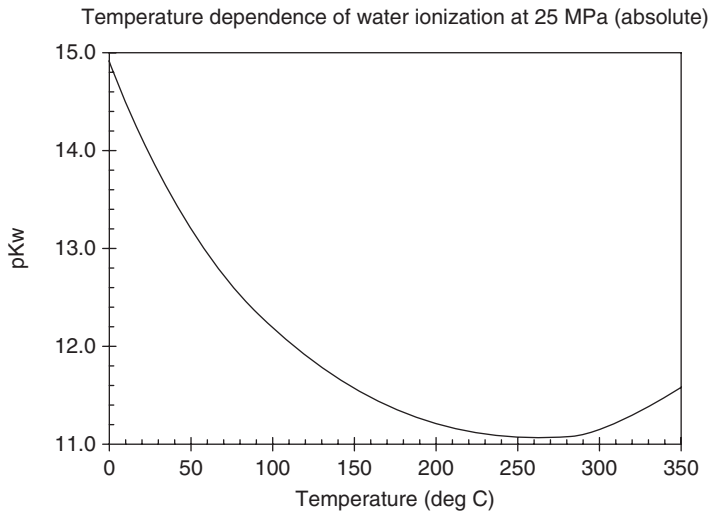


Figure 10.1. Effect of temperature on water dissociation constant at 25 MPa. The dissociation constant K_w is expressed as pK_w , where $pK_w = -\log_{10}(K_w)$. (IAPWS 2004).

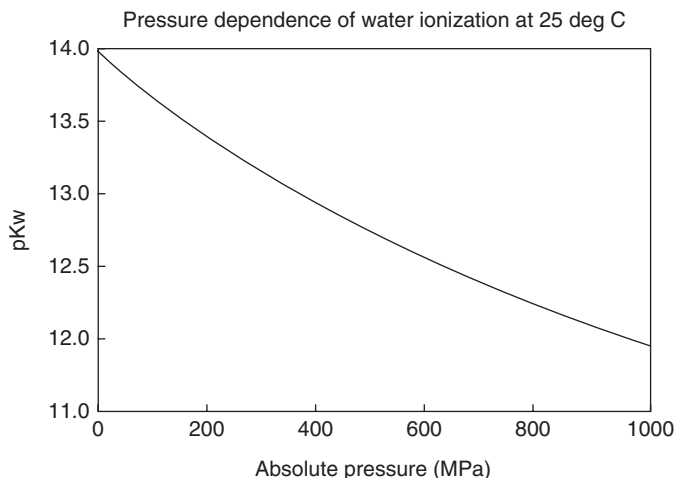


Figure 10.2. Effect of pressure temperature on water dissociation constant K_w at temperature of 25°C. The dissociation constant K_w is expressed as pK_w , where $pK_w = -\log_{10}(K_w)$.

There is also a (usually small) dependence on pressure (ionization increases with increasing pressure). The dependence of the water ionization on temperature and pressure has been fully investigated (Figure 10.2) and a standard formulation exists (IAPWS 2004).

For the above two reasons, water at high temperatures becomes a good solvent for hydrocarbons that are typically nonpolar hydrophobic under standard environmental conditions. These changes in physical properties make the solvent properties of water at 300°C roughly equivalent to those of acetone at 25°C. Ionic reactions of organics should be favored by increased solubility in water. The enhancement of this solubility of hydrocarbons in water will further enhance the possibilities of contact of dissociated H^+ with hydrocarbons, hence accelerate the activities of hydrolysis.

The dramatic changes in the physical and chemical properties of water as temperature increases suggest the possibility of organic chemical reactions to take place (Siskin and Katritzky 1991; Kruse and Gawlik 2003). In addition, water has the ability to carry out condensation, cleavage, and hydrolysis reactions, and to affect selective ionic chemistry, which is not accessible thermally, largely due to changes in its chemical and physical properties, which become more compatible with the reactions of organics as the temperature is increased.

Some classes of organic molecules in biomass proved very susceptible to water's influence. Hot water as a reactant and catalyst likely creates a second pathway for the cascade of molecular transformations that leads to oil. In this pathway, water causes organic material to disintegrate and reform (by adding H^+ to open carbon bond) into fragments that then transform into hydrocarbons. This implies that hot water becomes a catalyst for a series of ionic reactions. The acidic and basic nature of hot water—rather than heat—drives this cascade. For example, water may function first as a base, nibbling away at certain linkages in the organic material. As new molecular fragments build up and modify the reaction environment, water can change its catalytic nature. It can then act as an acid, accelerating different reactions. The resulting products attack parts of the remaining molecules, further speeding the breakdown (Siskin and Katritzky 1991). The above analysis may also help to explain why HTL will more likely directly convert biomass into oil than pyrolysis in which water is not involved.

Feedstocks and Their Primary Compounds

Agricultural biomass and biowaste include crop residues and wood, food processing waste, animal manure, and algae. Crop residues and wood primarily contain lignocellulose, while animal and food processing waste contains lipids, protein, and usually small amounts of lignocellulose (except ruminant animal manure). In this section, the primary compounds and structure in these feedstocks will be summarized and the potential functions in hydrothermal are explored, in the hope that it provides some bases to understand the interaction of carbohydrates with water (H^+ or H^* radicals).

Lignocellulose

Lignocellulosic compounds belong to the carbohydrates group of organic compounds. Carbohydrates are hydroxy aldehydes, hydroxy ketones, or substances derived from them. It is the principal substance that composes plants. The carbohydrates in swine manure come from both digested and undigested feed, and food processing waste contains carbohydrates food and lignocellulosic sources.

Glucose is one of the simplest monosaccharides. The isomers of glucose are shown in Figure 10.3. There are four chiral carbon atoms in the molecule. The carbon atoms at the end of the molecule do not hold four different groups and are not chiral. D-glucose forms a cyclic molecule by an addition reaction involving the carbonyl group and a hydroxyl group. The ring formation produces a new chiral center, and two isomers of D-glucose exist that differ in the orientation of the new OH group (Figure 10.4). Notice the α form of the OH group of the extreme right right-hand carbon atom is on the same side of the ring as the OH group of the adjacent carbon atom. In aqueous solution, α and β forms of the D-glucose exist in equilibrium, together with a low concentration of the open-chain form.

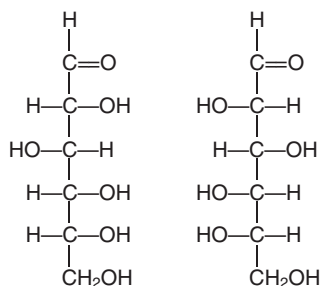


Figure 10.3. Optical isomers of glucose: left—D-glucose and right—L-glucose.

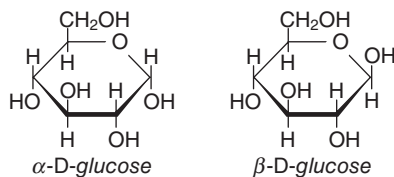


Figure 10.4. Ring forms of glucose.

Cellulose is a polysaccharide that only yields D-glucose upon hydrolysis. The number of D-glucose units in the molecular structures is estimated to be as high as several thousands. The D-glucose units of cellulose are linked in long chains in β combination shown in Figure 10.5. The structure is stabilized by hydrogen bonds between adjacent D-glucose units in the same strand. Cellulose occurs in fibrils brought about by hydrogen bonds among different strands.

Hemicelluloses are polysaccharides that are chemically related to cellulose, having backbones of 1,4- β -linked major sugar units, and being morphologically strongly associated with cellulose in the plant cell walls as well as to lignin in lignified cell walls. These polysaccharides are generally heterogeneous, built up of different hexoses (C6-sugars) and pentoses (C5-sugars), sometimes in addition to uronic acids. They have a lower degree of polymerization than cellulose (100–200 units), are largely soluble in alkali, and also more easily hydrolyzed (Figure 10.6).

The chemical structure of lignin is more complex than cellulose and hemicellulose. It resembles a network of aromatic compounds linked together in a more random fashion. The structure varies depending on source. To illustrate, the structure of a possible lignin molecule is shown in Figure 10.7. Lignin has high carbon content typically more than 60% and about 30% oxygen. Although in smaller amounts than cellulose, lignin represents about half of the available combustible energy in naturally occurring sources (Glasser 1985). Thermal decomposition of lignin occurs above 280°C depending on the source of lignin (Chornet and Overend 1985).

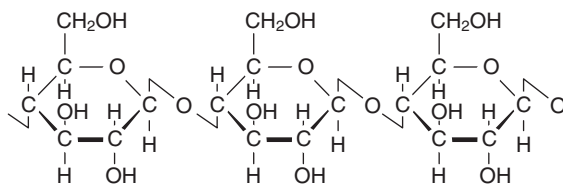


Figure 10.5. Chemical structure of cellulose.

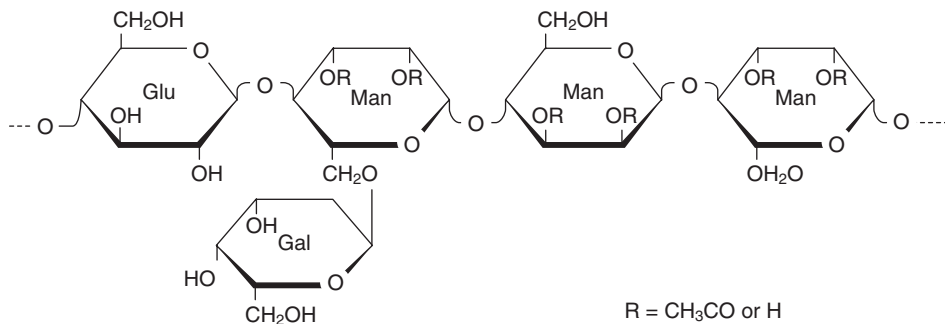


Figure 10.6. Chemical structure of hemicellulose.

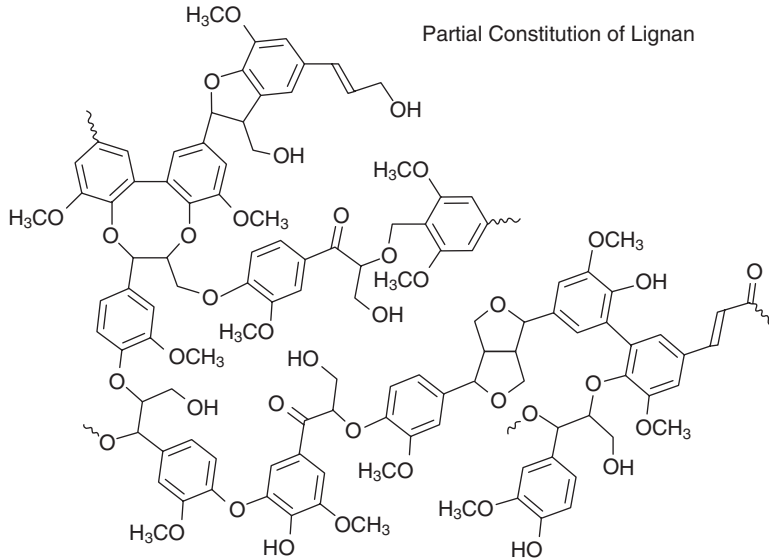


Figure 10.7. An example of chemical structure of lignin.

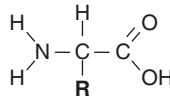


Figure 10.8. General structure of amino acid compounds.

Proteins and Amino Acids

Proteins are macromolecules formed from simpler compounds, α -amino acids. An α -amino acid is a carboxylic acid that has an amino group bonded to the carbon atom next to the carboxyl group. The designation α denotes the position of the amino group. The carbon atom adjacent to the carboxyl group is called the α -carbon atom. The general formula for an amino acid compound is shown in Figure 10.8. In the protein structure, amino acids are linked together by peptide bonds forming the long chains. These bonds are easily broken at high temperatures resulting in the formation of amino acids. Animal manure and food processing waste are rich in protein contents. For example, proteins comprise about 25% of the total solids in swine manure.

The radical, R, in the formula shown in Figure 10.8 differentiates the types of amino acids. The R may be simple hydrocarbons, ring compounds, additional amino or carboxylic groups, or -SH or hydroxyl groups. Alanine, leucine, aspartic acid (aspartate), and glutamic acid (glutamate) account for half of the total amino acids in swine manure (Figure 10.9). Proteins and amino acids are the major sources of organic nitrogen present in swine manure. Organic sulfur is mainly from two particular amino acids, cysteine (R = -CH₂-SH) and methionine (R = -CH₂CH₂-S-CH₃).

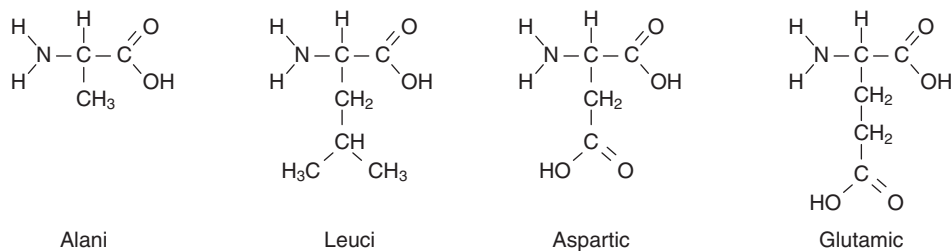


Figure 10.9. Structures of dominant amino acids in swine manure.

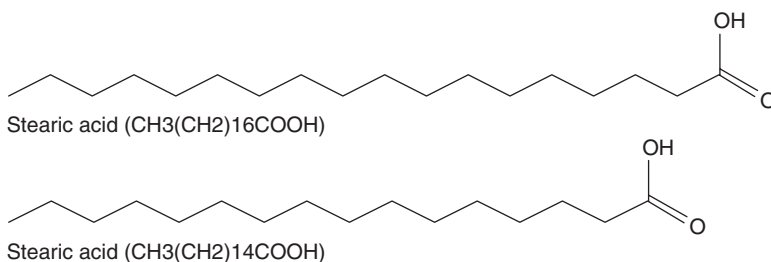


Figure 10.10. Structures of dominant fatty acids in swine manure.

Lipids

Lipids are substances that can be dissolved away from biological material by solvents that are nonpolar or slightly polar. Since the classification is based on solubility, not structure, a wide variety of compounds fall under lipids. Fatty acids are long straight-chain carboxylic acids some of which are saturated and some of which contain one or more double bonds. Almost all fatty acids isolated from natural sources contain an even number of carbon atoms. Among the fatty acids identified in swine manure, stearic acid and palmitic acid are most dominant (Figure 10.10).

Possible Hydrothermal Pathways

HTL is similar to the geological processes that produced the fossil fuels used today, except that the technological process occurs in a time frame measured in minutes instead of geological time. HTL is a chemical reforming process of biomass in a heated and usually pressurized, oxygen deprived enclosure, where long-chain organic compounds (solid biomass) break into short-chain hydrocarbons. All fossil fuels found in nature—petroleum, natural gas, and coal, based on biogenic hypothesis—are formed through HTLs from biomass buried beneath the ground and subjected to high temperature and pressure. Simple heating without water (pyrolysis or anhydrous pyrolysis) has long been considered to take place naturally during the catagenesis of kerogens to form fossil fuels. In recent decades, it has been found that water under pressure causes more efficient breakdown of kerogens at lower temperatures than without it (Siskin and Katritzky 1991; Pennisi 1993). The carbon isotope ratio of natural gas also suggests that hydrogen from water has been added during creation of the gas, in addition to the formation of oil. The state of fossil fuels (solids, liquid, or gaseous) depends

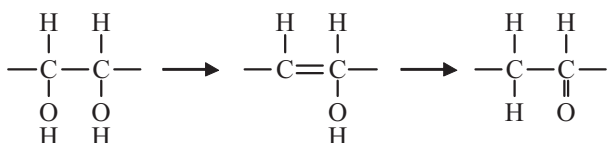
on the composition of feedstocks and environmental conditions, including temperature, pressure, retention time, and presence of particular catalysts.

The exact pathways of HTL to produce crude oil from biomass remain unclear, and additional research is needed. The following examples may give some hints of possible pathways of HTL of bio-waste feedstock. In a study by Appell et al. (1975), one of the mechanisms for the conversion of carbohydrates into oil that was consistent with the results they obtained was as follows:

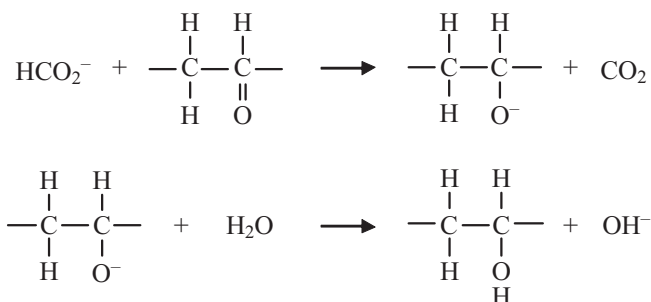
Sodium carbonate reacts with carbon monoxide and water to yield sodium formate:



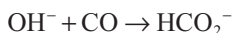
Vicinal hydroxy groups in the carbohydrates undergo dehydration to form an enol followed by isomerization to a ketone:



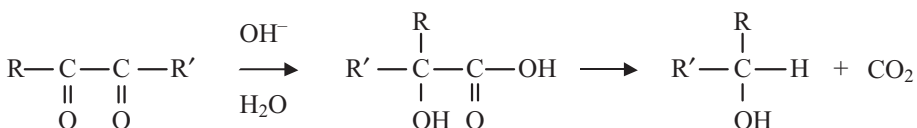
The newly formed carbonyl group is reduced to the corresponding alcohol with formate ion and water:



The hydroxyl ion then reacts with additional carbon monoxide to regenerate the formate ion.



A variety of side reactions may occur and the final product is a complex mixture of compounds. One of the beneficial side reactions occurs in alkaline conditions. Carbonyl groups tend to migrate along the carbon backbone. When two carbonyl groups become vicinal, a benzylic type of rearrangement occurs, yielding a hydroxy acid. The hydroxy acid readily decarboxylates causing a net effect of reducing the remainder of the carbohydrate derived molecule.



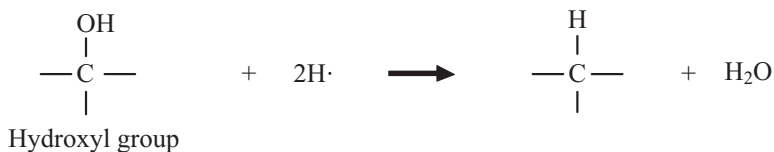
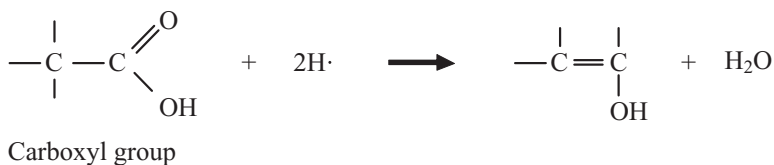
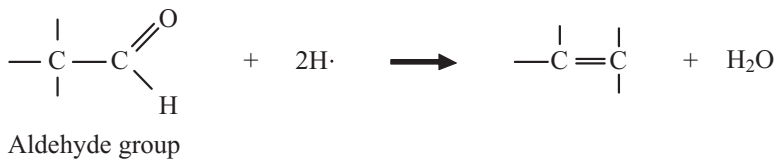
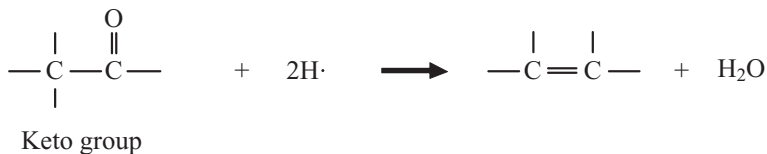
This type of reaction is beneficial to HTL because it leads to the formation of paraffin-type structures, which has less oxygen than the original compounds. In addition, the reaction happens by disproportionation and does not require any additional reducing agent.

Aldol condensation may also be part of the reaction process. Aldol condensation occurs between a carbonyl group on one molecule and two hydrogens on another molecule with the elimination of water. The condensation product is a high-molecular weight compound typically with high viscosity. Condensation reactions become a major pathway in the absence of reducing agents such as carbon monoxide and hydrogen. Reducing agents keep the carbonyl content of the reactant system sufficiently low so that liquid instead of solid products are formed.

In a study by Appell et al. (1980), the authors believed that the free hydrogen radical ($H\cdot$), not the hydrogen molecule (H_2), participates in the chemical conversion reactions. Thus, they concluded that the addition of carbon monoxide (CO) to the process was more efficient than the addition of hydrogen gas. Based on the water-gas shift reaction, carbon monoxide reacts with water to form carbon dioxide and two hydrogen radicals.



In the presence of the hydrogen radicals, the oxygen is removed from the compounds containing carbonyl and hydroxyl groups, then form paraffin and water. A possible pathway is described in the following four reactions (He 2000).



The complexity of the chemical reactions involved in HTL can be attributed to the complex composition of feedstocks. According to Chornet and Overend (1985) and Vasilakos

and Austgen (1985), some of the reactions that may be involved in the liquefaction of carbonaceous materials are cracking and reduction of polymers such as lignin and lipids, hydrolysis of cellulose and hemicellulose to glucose and other simple sugars, hydrogenolysis in the presence of hydrogen, reduction of amino acids, reformation reactions via dehydration, decarboxylation, C-O and C-C bond ruptures, and hydrogenation of functional groups.

State of Knowledge of HTL of Biomass

HTL of Biowaste Streams

In this section, two topics are summarized: one is on HTL of different kinds of waste streams, including manure, sewage sludge, urban waste, and agricultural wastes. The other is on the mechanisms study of HTL.

Appell et al. (1970) are among those who first started the study on the HTL process of waste streams. Urban refuse, cellulosic wastes, and sewage sludge were tried as feedstocks in a 500-mL autoclave. Effects of two kinds of initial gases, CO and H₂, were compared. In the research, using CO as initial gas led to higher oil yield in the process. When using municipal refuse as feedstock, at 20 minutes, 380°C, and 1500 psi, the oil yield is 41% versus 18% for CO versus H₂. At 500 psi CO, 1 hour, 250°C, 20% NaHCO₃, oil yields of 37% and 35.5% were obtained from newsprint, pine needles, and twigs, respectively. For sewage sludge, without a catalyst, oil yield was 24.5%. Infrared and mass spectrometric analysis indicated the oils to be paraffinic and cycloparaffinic with the presence of carbonyl and carboxyl groups. High temperature product has a very small amount of aromatic material, probably phenolic, but the oil product at low temperature does not appear to have any aromatic compounds.

With cellulose as feedstock, at 2 hours, 350°C, 1500 psi initial pressure, a much higher benzene-soluble oil yield was obtained when using CO rather than using H₂ as initial process gas, 40% versus 5% solubility, respectively. CO as a process gas also resulted in a lower oxygen content in the oil (8.9% vs. 15.5%). Residue and oil have similar elemental composition but different structures, making them appear differently. Water-soluble fraction resulting from hydrolysis of the cellulose is believed to be a precursor of the oil because it can be converted to oil by recycling the aqueous solution through the process with subsequent charges of refuse.

Fu et al. (1974) conducted the HTL process on bovine manure. Bovine manure was hydrogenated and liquefied with the existence of hydrogen or synthesis gas (H₂:CO = 1:1) at temperatures of 330–425°C and operating pressures of 1500–3000 psi, in the presence of a recycled manure oil (or an alkylnaphthalene oil) and a Co-Mo catalyst. The Co-Mo catalyst could be a good choice for increasing oil yield. At 380°C/425°C, 3000 psi, better oil yield was observed when the Co-Mo catalyst was present. Of all the variables investigated, temperature has the most dramatic effect on properties of the oil product. Although there were no significant improvements for conversion or oil yield, significant improvements in oil product quality were observed, with increased carbon content, decreased oxygen content, and reduced viscosity. High-resolution mass spectrometry analysis of oil produced at 380°C indicates that the main components are alicyclic hydrocarbons, N-containing heterocyclic compounds, and alkyl phenols with carbon numbers ranging from C8-C18. All carbon dioxide was produced before the reaction mixture reached 380°C (before zero time).

Minowa et al. (1995a) applied the HTL process to artificial garbage prepared by mixing cabbage, boiled rice, boiled and dried sardines, butter, and the shell of short-necked clams. Three temperatures (250, 300, and 340°C) and three retention times (0.1, 0.5, and 2 hours) were tested without a catalyst. Oil yield and its properties strongly depended on the catalyst addition and reaction temperature, while retention time showed no significant effect. Highest oil yield of 27.6% on an organic basis was obtained at 340°C, 18 MPa pressure and 0.5 h retention time with a catalyst. The oil had a heating value of 36 MJ/kg and a viscosity of 53,000 mPa·s at 50°C.

Suzuki et al. (1988) investigated optimum starting materials and catalyst loading for conversion of sewage sludge to heavy oil. Various kinds of sewage sludge were liquefied at 300°C, 12 MPa, and a catalyst loading of 0–20 wt %. Of digested sludge, raw waste activated sludge, raw primary sludge, and raw mixed sludge, have higher oil yields averaging 43%. The nature of the sludge had no significant influence on the elemental composition and heating value of oils obtained. Catalyst loading had no significant influence on the properties of oil products. Results showed a nearly linear relationship between crude fat content and the amount of oil fraction in the starting materials. Calcium salts could possibly have some catalytic effect on the liquefaction reactions.

Murakami et al. (1990) converted activated sludge from a cornstarch processing plant into oil with the HTL process. A 100 cm³ autoclave and N₂ initial gas were used, and the working pressure was maintained at the saturated vapor pressure of water at the required temperature plus 3.0 MPa. Effects of temperature, Na₂CO₃ catalyst loading, and holding time were studied. Results showed that maximum oil yield was 30% at 300°C, 60-minute retention time without a catalyst. Oil yield was not significantly affected by catalyst loading. Properties of the oil product were not influenced to any great extent by temperatures between 225–300°C, while the aqueous phase product yield and solid residue decreased as temperature rose. Heavy oil production at temperature as low as 250°C is possible, provided the reaction is carried out with sufficient retention time. According to their energy balance, the liquefaction could be a self-sufficient process under certain conditions.

A demonstration plant with a capacity for processing up to 5 t/d as dewatered sludge was operated at 300°C, 10 MPa, (feedstock, moisture content ~80%, VS ~80%; Itoh et al. 1994). The sludge had been dewatered by belt press dehydrator after adding a polyelectrolyte coagulant. As a result, 48% mass of the organic materials in the sludge were converted into heavy oil, and a quarter of the oil was separated from the reaction mixture by high pressure distillation with a distillate ratio of 0.33. Heating value of the heavy oils distilled were 37–39 MJ/kg, while that left in the bottom was 31–35 MJ/kg. Energy balance was calculated based on the pilot plant data collected. For a plant of 60 t/d dewatered sludge, the sludge is treated without any auxiliary fuel, and 1.5 tons of heavy oil is produced as surplus energy. In conclusion, the treatment of sewage sludge by this method could be sufficiently profitable.

He et al. (2000a,b; 2001a,b,c) studied HTL for swine manure. The process was evaluated by oil production efficiency and waste reduction efficiency. The oil product was analyzed for its benzene solubility, elemental composition, and heating values. Thermogravimetric properties and viscosity were also measured on selected oil samples. The difference of chemical oxygen demands before and after the HTL process was used as the waste reduction efficiency. The key factors of the HTL process were the operating temperature, the retention time, and the addition of a process gas. The operating temperature effect was studied in the range of 275–350°C. The suggested operating temperatures are between 295°C and 305°C. A process gas addition was necessary to achieve an oil product. Without the process gas, no oil products formed. The process gases investigated include carbon monoxide, hydrogen, nitrogen, carbon

dioxide, and compressed air. Carbon monoxide was the most effective gas for the process. Retention time is another important factor. The necessary retention time to achieve an oil product was largely related to the operating temperatures. When the operating temperatures were 295°C–305°C, the retention time was 15–30 minutes. Based on an average of 135 different oil samples, 62 wt % of the volatile solids were converted to oil. The waste strength was reduced by 60% to 70%. The highest oil production efficiency was 80 wt %. The average carbon and hydrogen contents were as high as 72 wt % and 9 wt %, respectively. The heating values for 80% of the oil products ranged from 32,000 to 36,700 kJ/kg. The results showed that HTL of swine manure to produce oil is technically feasible, and could be a promising technology for waste reduction and renewable energy production.

Since a continuous system is more applicable for scale-up operations, a small-scale continuous HTL (CHTL) reactor system was developed (Ocfemia et al., 2006a) to aid in the evaluation of the technical feasibility and economical viability of a pilot plant that is capable of producing oil from swine manure. The effects of operating conditions, including temperature, pressure, hydraulic residence time, and use of process gas, were evaluated in order to determine the optimal process condition. The composition of the different product streams (i.e., oil, aqueous, and gas) was determined to better understand the mechanics of the reaction process and to provide information for further developments. The CHTL reactor system was composed of a high-pressure slurry feeder, a process gas feeder, a continuous-stirred tank reactor, a products separation vessel, and process controllers. It had a capacity to process up to 48 kg of manure slurry per day. The operating parameters—temperature, pressure, residence time, and the use of CO—were all found to affect oil yield (Ocfemia et al., 2006b). The interaction between operating temperature and pressure was evident. The highest yield of 70% (based on volatile solids content of the manure feedstock) was found to be in the region where temperature was about 300°C and pressure was 10 MPa. Yield was found to increase with hydraulic residence time, but there was a diminishing benefit after 60 minutes. The addition of CO in the process did not improve the oil yield, but produced a more fluid oil product. The heating value of the oil product ranged from 25,176 kJ/kg to 33,065 kJ/kg with the highest value at the operating condition of 305°C, 10.3 MPa, and 80 minutes hydraulic residence time. The energy balance based on oil heating value and energy used for heating the feedstock material to the operating temperature showed that the process was a net energy producer.

Elemental analysis of the crude oil showed that the average (from all tests) carbon and hydrogen content of the oil was $62.7\% \pm 6.4\%$ and $9.6\% \pm 0.4\%$, respectively. The nitrogen content was high with a value of $3.9\% \pm 0.3\%$. The sulfur content of the oil was low with a value of $0.3\% \pm 0.1\%$. The composition of the oil based on SARA analysis showed that the oil was primarily resins (~45%) and asphaltenes (~44%) with small amounts of saturates (~3%) and aromatics (~2%). The boiling point distribution of the oil showed that the majority of the compounds were in the boiling point range of 316–482°C.

In Ocfemia et al.'s study (2006b), the aqueous product was found to contain volatile organic compounds, primarily ketones and benzenyl compounds. Of dominance was acetone, which accounted for 0.7 mg/L of the aqueous product. The total N content was 6.1 ± 1.9 g/L. Phosphorus as phosphate was 1.0 ± 0.3 g/L. The total aqueous K was 1.5 ± 0.8 g/L. The main gas product was CO₂ accounting for ~98% of the total. Carbon monoxide accounted for about ~2%. Hydrocarbons, including methane and ethane, were found to have a combined concentration of 299 ppmv. Very small amounts of aromatic compounds, including benzene, ethylbenzene, toluene, and styrene, were also detected.

Dote et al. (1992) studied the oil samples separated by steam distillation after liquefaction of sewage sludge. Oil was fractionated to strongly acidic, weakly acidic, basic, and neutral fractions by acid–base extraction. The total recovery of fractions was 77%. Each fraction was analyzed by gas chromatography and mass-spectrometry (GC-MS), and 71 types of compounds were identified with reasonable certainty. No strongly acidic fraction was obtained. The weak acidic fraction, comprising 2% of the oil, was exclusively composed of phenolic compounds. The basic fraction, comprising 20% of the oil, was exclusively composed of pyridines, pyrazines, quinolines, amines, and methylphenylacetamide. The neutral fraction, comprising 56% of the oil, was exclusively composed of aliphatic compounds, alicyclic compounds, alcohols, ketones, aromatic compounds, sulfur-containing compounds, nitrogen-containing compounds, and oxygen-containing heterocyclic compounds.

Dote et al. (1996) studied the distribution of nitrogen in the products for direct liquefaction of protein-contained biomass. Albumin from an egg was used as feedstock, and tests were run at 150–340°C, 0.5 hours, and 2 hours, w/o Na₂CO₃ as a catalyst. The maximum oil yield was 10%, much less than that for practical feedstocks (all above 30%). Nitrogen distributed to oil was 5% at most, much less than that for practical feedstocks (30%–45%). Other practical feedstocks contain other elements such as cellulose and lipid, which may increase the amount of oil converted from protein or react with nitrogen-containing compounds produced from protein during the conversion. No distribution of nitrogen to oil occurred below 150°C, and the distribution was completed by 250°C. The majority of the nitrogen in albumin (80%) was distributed to the aqueous phase, and albumin was decomposed to ammonia, not to amino acids. Sodium carbonate seemed to prevent the distribution of nitrogen to oil.

Minowa et al. (2004) used glucose and glycine as model compounds of carbohydrates and proteins, to study the mechanisms of hydrothermal reactions. There were 1.8 g glucose, 0.75 g glycine, and 30 mL distilled water charged into 100 mL autoclave. N₂ was used as initial gas and was added to 3 MPa pressure. Temperatures of 150–350°C were studied. It was concluded that at 150°C, the main reaction was Maillard reaction and melanoidin was formed. At 200°C, produced melanoidin was decomposed to form char, gas, and aqueous-soluble materials. Oil production started at 250°C, and oil yield increased with reaction temperature. It appears that oil is formed through the secondary decomposition of the decomposed products in the aqueous phase and not directly formed from melanoidin. Char was formed in the low reaction temperature range from 150°C to 200°C, and char yield was almost the same over 200°C. No pathway from oil to char is significant. Produced ammonia could inhibit the char formation from oil.

It appears that fatty acid and lipid are the main reactants of HTL. The predominant HTL reaction below 300°C is considered to be distillation of aliphatic compounds. The existence of considerable straight chain compounds (C13–C22) suggests that the aliphatic compound is the main resource of derived oil. A large quantity of nitrogenous compounds (mainly composed of amide and cyanide) in the oil suggests that protein is widely involved in the HTL reaction, possibly by peptide bond splitting and amino acid conversion dehydration. Within 300–450°C, the protein conversion reaction intensifies, and its principal structural bond (peptide bond) begins to react. Saccharide reaction mainly belongs to the splitting of branched chain and group transfer while considerable dehydration and cyclization of the main chain still appears not to be dominant. A simplified reaction model of HTL for sewage sludge consists of two serial competitive reactions—producing volatile matter and char, respectively. Estimated Arrhenius kinetic parameters of the reaction model based on Thermogrametric testing results were introduced.

It is worth mentioning that Huber et al. (2006) conducted a comprehensive review on biofuel producing methods, including gasification, liquefaction, and pyrolysis. Some chemical reaction mechanisms, oil synthesis, and upgrading methods were also included in that review.

HTL of Lignocellulose

The presence of liquid water is essential in the HTL of lignocellulose feedstock, even more important than for other types of biomass (manure and algae, for example). Aside from its role as a vehicle and catalyst carrier for the feedstock, water also serves as a solvent and reactant. The use of water as the solvent for HTL presents several advantages over other solvents. Water is simple to use, is relatively low cost, and is environmentally benign.

Water is an excellent medium for the intermediate hydrolysis of cellulose and other high-molecular weight carbohydrates to water-soluble sugars. The primary reaction in the conversion to oil likely involves the formation of low-molecular weight, water-soluble compounds such as glucose. Hydrogenation of sugars at mild temperatures produces polyols (hexitols and xylitol), which undergo further transformation into mixtures of glycerol, ethylene glycol, and propylene glycol (Chornet and Overend 1985). In another account, monomers such as glucose are further reduced with the presence of reducing compounds (Houminer and Patai, 1969). The sugar is de-oxygenated producing high carbon-hydrogen compounds.

Most organic compounds do not react with water under normal conditions. However, at temperatures between 250°C and 350°C, molecules in liquid water undergo chemical reactions. Previously, these reactions were only expected to occur in the presence of strong acid or base, but recent research indicates otherwise (Siskin and Katritzky 1991). Siskin and Katritzky (1991) have shown the geochemistry of the reactivity of organic molecules in hot water. Ester groups, which are bound in to the network of resource structures and serve as crosslinks, although thermally unreactive, are easily cleaved in water at 250–350°C (Siskin et al. 1990a). Similarly, benzyl aryl ethers were found to be more susceptible to cleavage under aqueous thermal conditions at 250°C. Cyclohexyl phenyl compounds with oxygen, sulfur, and nitrogen links are relatively unreactive thermally, but they readily cleave in water at 250°C to form methylcyclopentene together with phenol, thiophenol, or aniline, respectively (Siskin et al. 1990b). Benzonitriles, pyridinecarbonitriles, benzamides, and pyridinecarboxamides are almost unaffected by thermolysis, but are rapidly hydrolyzed in water at 250°C to the corresponding ammonium carboxylates (the nitriles via the amides). The ammonia formed autocatalyzes these hydrolysates and the subsequent decarboxylations (Katritzky et al. 1990). In the formation and depolymerization of resource materials, autocatalysis appears to be a major mechanistic pathway. During the diagenesis of kerogens, oxygen functionalities such as carboxylic acids, aldehydes, and alcohols are lost directly by cleavage and indirectly by condensation reactions that form methylene-bridged, ether, and ester cross-links. The cleavage reactions release water-soluble products such as carbon dioxide, formic acid, and formaldehyde.

HTL can convert lignocellulose into oil, but the yield is relatively low when no catalyst or solvent is used. Wang et al. (2008) compared the oil produced from different biomass—including legume straw, corn stalk, cotton stalk, and wheat straw—under hydrothermal conditions of temperature 350°C, residence time 2–3 hours, solid content 15% (dry mass), and pressure 10–13 MPa without using any catalyst. Hydrothermal experiments were carried out with 5.0 g biomass in a stainless tubular reactor which is 100 mm length by 10 mm internal diameter. The heating rate of reactor is about 10°C/min. The oil product was separated from

reaction mixture by distillation at 101–405°C and atmospheric pressure. Water and oil automatically separated into two phases in their study. Experimental results showed that oil yield is in the range of 5.2%–10.5% and both char and gas yield are more than 35% as the total biomass was almost completely converted. In addition to CO₂, gas products contained about 4.4%–8% H₂ and 5.5%–13.3% CO. Analysis of the oil product indicated that oil mainly consists of alkanes, cycloalkanes, and aromatic hydrocarbons. Based on these results, they concluded that the component of starting material had little effect on oil composition.

Tracing the origin of polyphenols, an abundant class of natural compounds, may contribute to awareness of reactions taking place upon high temperature treatment of waste materials. Luijckx et al. (1991) reported on the high yield of 1,2,4-benzenetriol from conversion of aqueous HMF as well as D-fructose. In a heated open tube reactor with 1.43 mm ID × 3.18 mm length, a 0.05 mole of HMF in water was converted 80%–90% with maximum 25% yield of 1,2,4-benzenetriol at about 330–350°C for 250 seconds. At 330°C for 185 seconds the 1,2,4-benzenetriol yield is about 9% from D-fructose. Those observations indicate that 1,2,4-benzenetriol is directly produced from HMF. Other identified compounds are less than 2%, including 4-oxopentanoic acid (levulinic acid), furaldehyde (furfural), and 1,4-benzenediol (hydroquinone).

To understand the formation mechanism of oil-like or tarry compounds, it is logical to start with the chemistry of HTL using model compounds which are present during the reaction. Luijckx et al. (1993) converted model compounds such as HMF derived from biomass to 1,2,4-benzenetriol with a yield of up to 46% at 50% HMF conversion at 290–400°C and 27.5 MPa. Experiments were conducted on a continuous process with a 4.8 mL tube reactor. It was found that 1,2,4-benzenetriol yield increased with residence time as HMF was converted at 290–380°C and that selectivity of 1,2,4-benzenetriol increased to 46% at 50% HMF conversion at 300–350°C followed by a decrease due to decomposition of 1,2,4-benzenetriol at high temperature and long residence time. In addition, distribution of products derived from HMF can be altered by pH changes, although 1,2,4-benzenetriol could be detected in the aqueous phase. It was concluded that HMF was a precursor of hydroxylated aromatics such as 1,2,4-benzenetriol in the HTL of biomass. However, a small amount of tar derived from HMF, which has a very high oxygen content (apparently 30%, and the usual oxygen content of hydrothermal oil products is about 18%) and was unstable due to polymerization. For that reason, HMF may not be considered as a representative compound for simulation of hydrothermal conversion of biomass.

Since the hydroxylated benzenes were identified in the aqueous product from hydrothermolysis of carbohydrates (Suortti 1983), the link between furan and hydroxylated benzenes was examined to further explore chemistry involved in HTL. Luijckx et al. (1994) studied the origin of hydroxylated benzenes from these furan derivatives from biomass under hydrothermal conditions. Hydrothermal conversion of furan derivatives was performed in a continuous tube reactor at 340°C, 27.5 MPa, residence time of 1–33 minutes, and feed concentration 0.01 M or 0.05 M with or without hydrochloric acid. Their results show that furan derivatives such as 2-acetylfuran, 2-propionylfuran, 5-methyl-2-furaldehyde can be directly converted to 1,2-benzenediol, 3-methyl, 1,2-benzenediol, and 1,4-benzenediol, respectively, without experience of smaller molecular fragments since only a few types of hydroxylated benzenes were obtained. Otherwise, a whole range of products would be collected. With catalysis of hydrochloric acid, acetic acid and propionic acids were produced as major products from conversion of furan due to cleavage of the furan ring. However, for 5-methyl-2-furaldehyde (which is found in hydrothermolysis as well as pyrolysis of carbon-hydrolysis of carbohydrates and HMF), 1,4-benzenediol was increased to about 30% due to

the presence of hydrochloric acid. For the conversion of HMF, it was found that it was unlikely to get 1,2,4-benzenetriol via electrocyclic mechanism. The formation of hydroxylated benzenes from furans such as HMF is probably via a hydrolytic furan ring opening followed by an intramolecular aldol condensation which is catalyzed by strong alkaline or sometimes by acid and subsequent dehydration.

With observation of a significant amount of CO_2 formed from HTL, it is interesting to know how CO_2 evolved from biomass under the hydrothermal condition. Luijckx et al. (1995) examined the role of deoxyhexonic acids in the hydrothermal decarboxylation of carbohydrates. Hydrothermal conversion was conducted at 340°C and 27.5 MPa in a continuous tubular reactor for residence times of 1–3 minutes. It was found that the temperature exerted an effect on reaction pathway of hydrothermolysis since almost no 3-deoxy-D-erythrohex-2-ulose was detected at temperatures less than 250°C with the presence of alkaline. Only small amounts of 3-deoxy-d-hexonic acid were observed in hydrothermolysis of a mixture of D-glucose and oligomers. Although 3- and 2-deoxyhexonic acid can decarboxylate, their contribution to CO_2 formation during hydrothermal conversion is limited when small amounts of deoxyhexonic acids formed during hydrothermal conversion of carbohydrates was considered. In addition, it seems that the addition of NaOH increases gas formation of CO but does not favor the formation of CO_2 .

The tar and char formation has been speculated by Chornet and Overend (1985). Chornet and Overend stated that the accessibility to cellulose chains was hindered due to surrounding the compounds. "In a pure pyrolytic context (i.e., carbonization), thermally induced rapid breakdown of the cellulosic chains results in intermediate compounds which are sterically hindered within the rigid lignin-rich structure of the compound, middle lamella, since lignin decomposes at higher temperatures than cellulose (Beall and Eickner 1970). The net effect is the random recombination of the intermediate compounds leading to tar and char formation" (Chornet and Overend 1985).

In the presence of a solvent, catalyst, and hydrogen, the oil yield from hydrothermal conversion of biomass could increase significantly. Kaufman et al. (1974) studied the conversion of cellulosic feed materials to liquid hydrocarbon fuels with newspaper as feedstock and nickel hydroxide as catalyst. The 20 wt % of powdered newspaper in mineral oil was processed in a 1-L continuous stirred tank reactor (CSTR) at $400\text{--}455^\circ\text{C}$, hydrogen pressure 34–102 atm with the presence of 0.2 wt % of $\text{Ni}(\text{OH})_2$ catalyst. Results show that decrease in temperature can lower both the carbon conversion and oil yield, while an increase of hydrogen pressure from 36.7 to 70.8 atm promotes oil yield from 5.2% to 46.1% at 453°C and 17.5 minutes space time and carbon conversion is constant (69.4% vs. 74.1%). The oil product would decompose to gas if exposed to $452\text{--}463^\circ\text{C}$ more than 20 minute space time.

Complete liquefaction and gasification of biomass can be achieved with a catalyst present in water and the degree of gasification changed with the catalyst to biomass ratios (Boocock et al. 1979). Boocock et al. (1980b) hydrothermally liquefied 150 g of air-dried poplar with particle size of a 0.5 mm mesh and 750 mL water in a 2-L magne-drive packless autoclave under catalyst effect. Catalyst (20 g) causes the complete liquefaction and gasification of wood with 33.8% oil yield at 350°C , holding time 1–2 hours, and H_2 initial pressure 10.7 MPa. The catalyst obviously increased the consumption of H_2 and formation of CH_4 , but inhibited CO_2 , which implies that Raney Ni could catalyze formation of CH_4 from CO_2 and H_2 . With the decrease of activity of the Raney Ni catalyst, CO_2 selectivity increased while CH_4 formation decreased and biomass was completely converted. Results suggest that the catalyst was modified during the liquefaction process and that the spent catalyst did not promote the formation of methane, but enhanced the formation of carbon dioxide. It was thought that the oil

product was responsible for catalyst modification and found that reaction was not influenced by water to oil ratio. The spent (modified) catalyst retained its activity as there were no signs of solid residue in the autoclave. In addition, using a lower H₂ pressure slightly increases CO₂ formation. Without H₂, the spent catalyst can also completely convert wood to viscous liquid at 350°C and 2 hours, which is flowable at room temperature except for a much lower hydrogen content in the oil product. The oil product shows viscosities from 700–8000 mPa.s at room temperature, oxygen content about 10%–13%, specific gravity of 1.1, heating value about 35.3 MJ/kg, 97% benzene solubility, 55% diesel solubility, and 33% aromatic carbon content. The residence time was reduced to 30 minutes or less, and the catalyst was upgraded from Raney nickel to nickel from nickel salts.

Raney nickel catalyst can be substituted by a less exotic and hence less expensive, nickel catalyst. Boocock et al. (1982) investigated and reported the effectiveness of the Raney catalyst in detail. Wood (7-year-old hybrid poplar) was thermohydrolyzed in a 2-L packless magedrive autoclave with Raney catalyst at 340°C for 2 hours. As temperature was more than 375°C, excessive char formation was noted. In a typical experiment 150 g dry wood and 20 g Raney catalyst were used with 750 mL water pressured under 1.7–8.3 MPa H₂. The oil product tends to be more viscous, darker, and denser with the stabilization of a fresh catalyst taking place. Their results imply that fresh Raney Ni seems not able to catalyze the conversion of CO₂ and H₂ to CH₄ in the aqueous phase because the change in H₂ consumption is not significant. Therefore, CO₂ may be catalytically produced and CH₄ is probably formed directly by cracking processes in the presence of a catalyst. Raney Ni does oxidize and move to the aqueous phase, presumably to produce H₂, but the amount is not large. Higher initial H₂ pressures favor hydrogen consumption and most of H₂ is consumed in methane formation. H₂ consumption increases with stirring rate (1300–1750 rpm) as initial pressure increases from 1.7 to 8.3 MPa (25–1200 psi). At 2300 rpm, oil viscosity can be lowered without a significant increase in H₂ usage. At the same time, H₂ uptake reduces the viscosity of oil and oil yield (separated by centrifuge and acetone) varies from 36.5% to 41%. The lower pH modified the Raney Ni and favored the CO₂ formation. In general C, H, and O content of the oil product were 73%, 8%, and 17.5%, respectively. Heating value of oil production was about 34 MJ/kg. The H/C is lightly lower in the oil than in the wood. Only 10% H appeared in methane and using H₂ is not theoretically required; its major function is to prevent the nickel from being oxidized and passing to the aqueous phase. With nickel carbonate as the catalyst, promising results of 80% C remained in the oil product and 55% wood H was retained in the oil. Nickel carbonate was reduced *in situ* to finely divided nickel, which presumably functioned as the catalyst (Boocock et al. 1980a). However, commercially available nickel powders did not appear to be as effective as Raney nickel or nickel produced *in situ* (Boocock et al. 1980a).

A recent study has also shown that a modified catalyst theoretically contributed to selectivity of catalyst that potentially makes conversion of biomass to biofuel more efficient in the presence of a catalyst (Teschner et al. 2008). Although heterogeneous catalytic conversion is a surface process, there is accumulating evidence, particularly from experiments applying *in situ* functional analysis, that the bulk and especially the subsurface region (the few layers below the surface) can play a key role in surface events. Reaction conditions (such as temperature and the ambient reactive gas) may not only reconstruct the top surface layer, but also may create added rows and valleys of atoms or even massively change the whole morphology of the catalytic particles (Teschner et al. 2008). Atoms that are part of the catalytic feed can dissolve in metallic particles, and can change the electronic structure of the surface, and dissolved species can even participate in the reaction; for example, alkyne hydrogenation on palladium.

Pd itself is usually even more active in hydrogenating the corresponding alkene to alkane (Teschner et al. 2008). The typical explanation (a thermodynamic view) is that the difference in the heat of adsorption of the feed alkyne and of the partial hydrogenation product alkene forces the intermediate product alkene to desorb and become replaced by the incoming alkyne of the feed (Teschner et al. 2008). A contrary example, ethylene could be adsorbed on a catalyst of Pd supported on silica while acetylene was present in the gas phase. This is possibly because the surface of catalysts is usually heterogeneous and can have discrete sites that facilitate selective adsorption (Teschner et al. 2008). Another fact is that carbonaceous deposits formed during reaction might substantially affect selectivity (Teschner et al. 2008). In addition, alkyne hydrogenation usually goes through an activation period, which strongly suggests that the catalyst is not identical to its “as-introduced” form. It was found that selectively hydrogenate 1-pentyne, the active state of Pd is a Pd-C surface phase (PdC), approximately three Pd layers thick (Teschner et al. 2008).

The *in situ* X-ray photoelectron spectroscopic measurement and *in situ* prompt gamma activation analysis (PGAA) were used to observe the hydrogenation process (Teschner et al. 2008). The amount of C incorporated within the top layers was 35–45 atomic % based on XPS investigation (Teschner et al. 2008). PGAA experiments show that the surface properties are necessarily decoupled from the bulk. The high concentration of dissolved carbon excludes H from populating the subsurface region and hence prevents total hydrogenation of alkynes. They are aware that many other factors, such as promoters in the form of a second metal or selective poison, can strongly modify the hydrogenation selectivity (Teschner et al. 2008). Their aim was to shed some light on the importance of subsurface chemistry in hydrogenation processes. They believed that a critical level of understanding of both surface and subsurface dynamics in these and other complex processes of heterogeneous catalysis is required. Although gas-phase alkynes hydrogenation on palladium catalysts is a surface process, they have shown that the population of the subsurface region by either C or H will determine the surface events.

Nickel catalyst has been shown to be helpful in stabilizing the liquid products and preventing charring. A relative cheaper catalyst, nickel carbonate, was examined. Beckman and Boocock (1983) used an 8-mL tubular reactor with adequate mixing and rapid heat-up rate to convert seven-year-old hybrid poplar in the presence of NiCO_3 . Results indicate that the oil yield was highest at a short residence time. At the same time, oxygen content of oil decreases from 25% to 17% during this period. The pH of the aqueous phase dropped due to carboxylic acids and phenolic compounds followed by an increase. The addition of nickel carbonate is deleterious to the liquefaction process under rapid heat-up in terms of C and H percentages in the wood that is retained oil. NiCO_3 and H_2 may not have a significant effect on oil yield, oil compositions, and pH of the aqueous phase. Degradation of wood begins at 230°C and 267°C because no oil was produced at 230°C. The results were interpreted that as slow heat-up proceeds, the wood is converted from a solid to a viscous tarry which is in turn liquefied in the presence of Ni or carbonized in the absence of Ni. At fast heat-up, wood is liquefied directly.

Besides nickel, other commercially available catalysts with different active sites such as Pd, Fe_2O_3 , NiO, and MoO_3 were used to convert lignin to oil in the presence of hydrogen. Meier et al. (1992) directly hydrogenated lignin in the aqueous phase over to a catalyst without using any solvents and pasting oil. In their experiments, 40 g of dry lignin with 3.5 g moisture inside mixed with 15 g of catalyst in a 250 mL autoclave under hydrogen pressure and stirring rate 1500 rpm. An oil product was extracted with dichloromethane in a Soxhlet apparatus. Screening tests show that Fe_2O_3 has a negligible effect on oil yield and zeolitic support is unsuitable for hydrogenation of lignin because its channel system makes lignin

difficult to access the active site. Pd/C exhibits highest activity among Ni/Mo/Al₂O₃/SiO₂ > Raney Ni, = NiO/MoO₃/Al₂O₃/SiO₂ in terms of oil yield. The composition of oil depends on the catalyst. Mo catalyst mainly gives monophenols while Pd/C produced ethylcyclohexanones and catechols, and so on. Ni/Mo was found possessing a high demethoxylating power, and Pd or noncatalyst tests showed demethylation to catechols. It was also noted that sulfided NiMo was more active than the oxidized form when much higher oil yield was observed with kraft lignin than that from organocell lignin. The acetyl group in acetosolv lignin lowered the oil yield due to blockage phenomena. Surprisingly, oil composition from different types of lignin shows no difference.

Iron compounds (FeS or FeSO₄) used in coal liquefaction were also examined for HTL of biomass to oil. Xu and Etcheverry (2008) treated 1 g of Jack pine wood with particle size smaller than 20 mesh (~0.8 mm) in a 14-mL reactor with 5 wt % catalyst and 13 mL ethanol in the presence of 2.0–10.0 MPa hydrogen. Generally, oil yield (15%–35%) increases with reaction time of 15–60 minutes, temperature of 200–260°C, and initial H₂ pressure of 2.0–10.0 MPa without a catalyst. At the supercritical condition of ethanol, 45% oil yield can be obtained at 350°C, but more char formed at a temperature more than 300°C. In the presence of 5% FeS or FeSO₄, the oil yield shows no significant improvement. It was noted that ethanol consumption and contribution to oil were considered.

An organic solvent layer may extract oil molecules from the aqueous phase during HTL in a two-layer reaction system. Miller and Fellows (1981) reported that wood or cellulose can be almost totally converted to liquids or gases at 350°C in pressurized phenol and water with catalyst. In a typical reaction, 2 g biomass mixed with 2 g phenol, 2.5 g water and 0.5 g catalyst was heated to 350°C for a few minutes to several hours in a pressurized glass vessel. The phenol in a two-layer reaction system, which can be produced from lignin and recycled, intends to provide a solvent to slow down the higher order solid state condensation reaction. The recovered yield of neutral product was 0.55–0.76 g per 2.5 g dry aspen. About 3% aromatic hydrocarbons, including toluene, ethyl benzene, and xylene were found in nonphenolic products when zinc chloride and nickel were used with hydrogen. In addition, the observed recoveries showed that a net phenol could be produced.

Except for phenol, other organic solvents such as acetone, methyl ethyl ketone, 1-, and 2-propanol, and 1-butanol were used for biofuel production with marked effect on the direct formation of a fluidized product. Ogi et al. (1990) examined the role of butanol solvent in direct liquefaction of wood. The wood chips in 80 mesh were heated with water, sodium carbonate, and organic solvent in an autoclave under nitrogen pressure. They observed that there were three phases, that is, butanol layer, water layer, and tar-like product on the reactor wall when butanol was used as a solvent. (It is interesting to know that t-butanol is different from 1-, 2-, and i-butanol, which mixes with water freely.) Blank tests indicated that butanol, especially t-butanol, degraded under experimental conditions of 270°C, 90 atm, and 60 minutes retention time. They found that isomers of butanol have no effect on oil yield as high as 45%–55% assuming that no isomer was converted to oil. The function of sodium carbonate was thought to be an agent inhibiting hydrolysis of biomass. The use of hydrogen donors is believed to be one of the most efficient ways to reduce these undesirable reactions. They clarified that butanol did not function as a hydrogen donor solvent, but only acted as an extraction solvent/stabilizer, in which undesirable reactions such as repolymerization were retarded.

Instead of direct TCC of biomass to oil in one reactor, a two-stage HTL was employed to produce the alternative oil product from lignocellulosic biomass. Román-Leshkov et al. (2007) developed a process to produce dimethylfuran for liquid fuels from biomass-derived

carbohydrates. The sugar solution was converted to HMF in high yield by the acid-catalyzed dehydration of fructose in a biphasic reactor using a low boiling point solvent (e.g., butanol) that continuously extracts the HMF product with NaCl presented in the aqueous phase. The extracting solvent containing HMF was then purified in an evaporator at low temperature (e.g., 89.9°C). Next, HMF is converted to dimethylformamide (DMF) over a copper-based catalyst such as CuCrO₄ or CuRu/C by hydrogenolysis. Finally, DMF was separated from the solvent and intermediates via a distillation process. Sugar dehydrates at 180°C for 3 minutes with ~75% conversion and 5 wt % HMF can be converted to DMF with 61%–71% yield over CuRu/C catalyst in a flow reactor at 220°C, 6.8 bar hydrogen, and feed rate of 0.2 cm³/min.

Minowa et al. (1998) applied the HTL process to 18 kinds of agricultural and forest residues in Indonesia. Tests were run in a 300 mL stainless steel autoclave with a magnetic mixing, at 300°C, and 30 minutes retention time. N₂ was used as the initial gas and added to 3 MPa at the beginning. Five wt % Na₂CO₃ was used as the catalyst and acetone was used to extract the oil product. Oil yields were in the range of 21%–36%, depending on the species and parts of feedstock. All oils had almost the same elemental properties, C ~70%, H ~7%, N <1%, O~20%. Heating values were around 30 kJ/g and viscosity was greater than 105 mPa.s. Gas yields were around 20%, consisting mainly of CO₂ with a range of 78–86 mol %. Other gases included CO (11–19 mol %) and H₂ (~2 mol %). More than 35% of the energy in raw materials was recovered in the form of oil, and for some materials, this number was as high or more than 50%. Residue also had energy content, indicating it is possible to use residue as a process energy source, especially for coconut husk and oil-palm shell.

A high correlation between lignin and residue was observed (Minowa et al. 1998). The phenoxy radicals could be formed from the lignin under high temperatures, and a higher lignin content resulted in a higher residue yield by condensation and repolymerization.

The correlation between lignin and residue was also studied by Demirbas (2000) and a similar conclusion was drawn. In his study, nine species of biomass with different lignin contents were thermohydrolyzed in an autoclave with and without a KOH catalyst (20 wt %). All tests were performed in a 250 mL cylindrical autoclave. Tests were run at 575K over 30 minutes, using N₂ as the initial gas. There was a strong correlation between lignin content and oil yield. With increasing lignin content, the oil yield decreased and the char yield increased.

Nelson et al. (1984) studied the mechanisms of direct liquefaction of cellulose. At 250–400°C, a pressure up to 20.7 MPa, and with the presence of Na₂CO₃, pure cellulose was converted in a 300-mL autoclave, to a mixture of phenols, cyclopentanones, and hydroquinones as well as other components. At 300°C for 1 hour, most of the oil components are present in amounts of 0.1 wt % or less in the oil, which makes it very complicated to analyze the oil product. Phenolic products have been observed as products of the alkali treatment of saccharides. Biacetyl and acetoin are precursors for aromatic components during cellulose liquefaction. A scheme of the formation of biacetyl and acetoin from cellulose was discussed. Faster heating rates would be useful to reduce the inevitable degradation and recombination of the initial products. The use of alkaline catalysts at 300°C was shown to shift the mechanism from one involving aqueous pyrolysis (predominant furan formation) to one incorporating aldol and related condensations.

Russell et al. (1983) used selected aldehydes and ketones which might have formed from cellulose degradation as model compounds to study the formation of aromatic compounds during cellulose liquefaction, under the same conditions as those of cellulose liquefaction. Many of the same aromatic compounds were formed from these reactions as were found in

cellulose derived oils. The condensation and cyclisation of aldehydes and ketones is apparently involved in the formation of aromatic compounds in cellulose liquefaction oils. Eight aromatics were identified in both cellulose oils and model compound products. Mechanisms were proposed for five of the eight aromatics.

Maldas and Shiraishi (1997) studied the liquefaction of biomass in the presence of phenol and water, using alkalis and salts as catalysts. A closed pressure-proof tube was used as a reactor at 150–250°C, 0–90 minutes reaction time. A higher temperature was required to reduce residue. A reaction time of 45 minutes was sufficient to maintain low residue and to keep constant other parameters, such as nonreacted phenol, combined phenol, and pH of liquefied mixtures. Aqueous alkali was more effective than water for the liquefaction of biomass in phenol. The ultimate pH of liquefaction was always acidic whether the starting pH was alkaline or acidic. Dissolution of wood varied significantly with the variation of reaction conditions, for example, pH, temperature, and nature of metal ions.

Inoue et al. (1999) used ammonia and cellulose as feedstock to study the effect of nitrogen/carbon ratio in the feedstock on the oil production. Ammonia water of 25 wt % and microcrystalline cellulose were charged into 500 mL autoclave, and liquefied at 300°C, 2 MPa N₂ initial pressure, and 1 hour retention time. Alkali acted as a catalyst for hydrolysis of cellulose into small fragments and for prevention of undesirable reactions, such as polymerization. Ammonia acted both as reactant and a basic catalyst. The liquefaction process resulted in the creation of C-N bonds. Yield and nitrogen content of the oil increased with increasing N/C ratio. Excess ammonia did not react with cellulose under high N/C ratio. Productive mechanism of nitrogen-containing oil from protein-containing feedstock might be the decomposition of proteins to water-soluble materials, which are then combined and converted into oil. Not only amine and amide were contained in the oil, but also heterocyclic compounds. Oil derived from this liquefaction consists of aldehydes, ketones, and aromatic compounds, containing many unidentified compounds.

Conversion of Algae to Biofuel

If biomass were grown for energy to an amount equal to that consumed during their any given production period, there would be no net buildup of CO₂ in the atmosphere (Gao and Mickinley 1994). Microalgae are particularly promising biomass species because of the high growth rate and high CO₂ fixation ability compared to plants (Tsukahara and Sawayama 2005).

The earliest idea focused on producing methane gas from microalgae. The concept of producing fuel by using microalgae as a source was reported by Meier (1955). Golueke and Oswald (1959) presented the concept of using microalgae as a substrate for anaerobic digestion, and the reuse of the digester effluent as a source of nutrients. They realized these concepts by using a large pond (40 pa) to grow microalgae, then the microalgae was digested to methane gas for producing electricity. The gas production by the digester averaged about 10 ft³ per lb of volatile matter introduced. The methane content of the gas varied from 68% to 74%. The maximal efficiency attained by the algal culture was 3%, whereas the maximal overall efficiency of the entire conversion unit was approximately 2% (Golueke and Oswald 1959). From the 1970s, the National Science Foundation-Research Applied to National Needs Program (NSF-RANN) started to support laboratory studies of microalgae fermentations to methane gas (Uziel et al. 1975). Six microalgae species were studied, approximately 60% of microalgae biomass energy could be converted to methane gas. It was found that the rate of biogenic methane gas production by the marine strain methanogenic bacteria at 50% wet

algal thalli amendment was greater by 33.4% in comparison with results of the freshwater cattle manure strain methanogenic bacteria under similar experimental conditions. The proportion of methane gas content in this biofuel gas was 58%, while the remaining gases are CO₂ (major portion), H₂S, NH₃, N₂, and O₂ (Silvalingam 1982).

Many microalgae, in particular species classified as “green algae,” produce hydrogen after a period of anaerobic conditions in the dark, during which the hydrogenase enzyme was activated and synthesized, and small amounts of hydrogen production were observed (Das and Veziro lu 2001). Green algae are probably better for hydrogen production than cyanobacteria (blue-green algae) whereas the latter uses more energy-intensive enzymes, ATP-requiring nitrogenase for the production of H₂ (Lee and Greenbaum 1997).

Methane production from microalgae became the basis and motivation of the U.S. DOE's program to develop renewable transportation fuels from microalgae, which started in 1978 and ended in 1998. This program mainly focused on the production of biodiesel from high lipid-content microalgae grown in ponds, utilizing waste CO₂ from coal fired power plants. Biodiesel is an alternative fuel produced from triglycerides and fatty acids present in naturally occurring fats and oils. Traditional oil crops such as corn, soybeans, canola, coconut, and oil palm cannot adequately contribute to replacing petroleum derived from liquid fuels in the foreseeable future due to their relatively low oil yield per hectare compared with microalgae. For example, 30% oil (by wt) of microalgae has an oil yield of 58,700 l/ha and 70% oil (by wt) of microalgae has an oil yield of 136,900 l/ha. By comparison, corn and soybeans have only an oil yield of 172 l/ha and 446 l/ha, respectively (Chisti 2007). Hu et al. (2008) reported that based upon the photosynthetic efficiency and growth potential of microalgae, theoretical calculations indicated that annual oil production of larger than 30,000 L or about 200 barrels of algal oil per hectare of land may be achievable in mass culture of oleaginous algae (algal species have been found to grow rapidly and produce substantial amounts of triacylglycerols or oil). This value was 100-fold greater than that of soybeans, a major feedstock currently being used for biodiesel in the United States.

Another unique benefit of using microalgae to produce biodiesel is that it will not compromise production of food, fiber, and other products derived from crops. Xu et al. (2006) used n-hexane to extract large amounts of microalgal oil from *Chlorella*, which the crude lipid content is about 55.2%. Then the microalgal oil was transformed into biodiesel by acidic transesterification. The biodiesel was characterized by a high heating value of 41 MJ/kg, a density of 0.864 kg/L, and a viscosity of 5.2×10^{-4} Pa·s at 40°C (Xu et al. 2006).

Pyrolysis with different solvents and re-agents were conducted on algae-protein (Goldman et al. 1980). The reactions yielded rather low conversions in the presence of water in spite of the existence of carbonates and catalysts, for example, nickel sulfate. The presence of benzene improves the yield and the presence of a mixture of K-Mg-Mn salts was beneficial for such a reaction. The nitrogen content of liquid oil decreased in the presence of carbonates and other catalysts. The maximum amount of protein converted into liquid oil was 27% by weight for algae-proteins containing 5.7 wt % nitrogen.

Lipid content in microalgae was considered as the most important component for yielding biofuel, such as biodiesel and other forms of oil. Peng et al. (2001a) studied the pyrolytic characteristics of *Chlorella protothecoides*. *Chlorella protothecoides* were pyrolyzed at the heating rates of 15, 40, 60, and 80°C/min up to 800°C. The pyrolysis reactions mainly took place between 160–520°C with a volatile yield of about 80%. The devolatilization stage consisted of two main temperature zones (I and II) with a transition at 300–320°C. The researcher found that crude lipid in cells decomposed at Zone II while other main components at Zone I, which might indicate that more energy input for lipid pyrolysis seems needed in

comparison with other main components (Peng et al. 2001b). In another study, two kinds of high protein and lipid contents microalgae, Cyanobacterium *Spirulina platensis* (SP) and green alga *C. protothecoides* (CP) were pyrolyzed at the heating rates of 15, 40, 60, and 80°C/min up to 800°C in the thermogravimetric analyzer to investigate their pyrolytic characteristics. The results showed the value of activation energy for CP pyrolysis was lower than that of SP, and the char in final residue of CP was 2%–3% less than that of SP, which indicated CP was preferable for pyrolysis over SP (Peng et al. 2001).

Fast pyrolysis (a sweep gas [N₂] flow rate of 0.4 m³/h, and a vapor residence time of 2–3 s) was used to treat *C. protothecoides* to produce bio-oil. The highest yield of bio-oil is 57.9%, at an operating temperature of 450°C. This yield is 3.4 times higher than that from autotrophic cells also treated by fast pyrolysis. After reaction, the total liquid products were composed of an aqueous and an oil phase. The oil was fractionated using column liquid chromatography, and separated into n-hexane soluble and n-hexane insoluble compounds. The bio-oil was characterized by a much lower oxygen content, with a higher heating value (41 MJ/kg), a lower density (0.92 kg/L), and lower viscosity (0.02 Pa·s) compared to those of bio-oil from autotrophic cells and wood. These properties are comparable to fossil oil (Miao and Wu 2004).

Algal lipid or even the whole algae could be pyrolyzed to a similar, high-octane, aromatic gasoline product slate when passed over HZSM-5, a medium-pore, shaper-selective, acid catalyst. The first of these results was reported by Milne and Evans (1987). The same authors carried out exploratory studies of the pyrolysis and zeolite conversion of whole algae and their major components. Four species of microalgae were pyrolyzed: *Chaetoceros muelleri* var. subsalsum, *Monoraphidium minutum*, *Naviculus Saprophylla*, and *Nannocloropsis* sp. However, the results of whole algae were ambiguous due to very high mineral matter content (10%–50%) and unknown proportions of water, lipids, and other organic components of the exact sample used (Milne et al. 1990).

One of the shortcomings of using pyrolysis to convert microalgae is due to the high moisture content of microalgae. The large amount of energy consumed to vaporize the water during the pyrolysis process was considered as a negative effect of this method (Minowa et al. 1995a). Dote et al. (1994) performed a liquefaction of *Botryococcus braunii*, with and without sodium carbonate as a catalyst. High-quality oil was obtained, which was more than the content of hydrocarbons in *B. braunii* (50 wt % db), in a yield of 57–64 wt % at 300°C. The oil was equivalent in quality to petroleum oil (Dote et al., 1994). The properties of the oil obtained from *B. braunii* were clarified by the same research group (Inoue et al. 1994). The oil was fractionated into three fractions by silica gel column chromatography and analyzed to determine its composition. The yields of the three fractions based on organics were 5% of lower molecular weight hydrocarbons (MW = 197–281), 27.2% of botryococenes (MW = 438–572), and 22.2% of polar substances (MW = 867–2209). The maximum recovery (78%) of botryococenes in the liquefied oil was achieved at 200°C with the use of a catalyst.

Minowa et al. (1995b) used HTL to convert *Dunaliella tertiolecta* (78.4% moisture content) into oil at around 300°C and 10 MPa. The *D. tertiolecta* was cultured batchwise in an open tank of 10-L capacity at continuous light of 20,000 lux, temperature of 27°C, and bubbling air with 3% CO₂. Then the algal cells grown for HTL were harvested by a centrifugal separator. Some Na₂CO₃ (0–5 wt % of the dry solid in the algal cells) was used as additive. However, the results showed it had no catalytic effect on either the oil yield or its properties. Nitrogen was introduced to purge the residual air in the autoclave. To prevent water from vaporizing, additional nitrogen was added to 3 MPa. Several reaction temperatures were tried: 250, 300, and 340°C. The retention time (holding time) was from 5 minutes to 60 minutes.

The gas phase was primarily CO₂. Besides the gas phase, the reaction mixture consisted of a tar-like material and a water phase. The tar-like material floated on the surface of the water phase in all experiments and was easily separated. The oil was extracted from the reaction mixture by dichloromethane. Then the dichloromethane was evaporated from the extract at 35°C under reduced pressure, yielding a dark-brown viscous material, which was referred to as the oil. The oil was obtained in the range of 31%–44% (average 37%) on an organic basis. The oil yield exceeded the algal cells crude fat content (20.5%). The reaction parameters, including reaction temperature, holding time, and sodium carbonate addition, had no significant effect on the oil yield. However, the author thought the properties of oil strongly depended on the reaction temperature. The viscosity decreased and the heating value increased slightly with a rise in temperature. The carbon and hydrogen content tended to increase with temperature increases. The oil obtained at a reaction temperature of 340°C and holding time of 60 minutes had a viscosity of 150–330 mPa·s and a calorific value of 36 MJ/kg. These values were comparable to those of No. 3 fuel oil in JIS (50–1000 mPa·s, about 40 MJ/kg). The results of the energy consumption ratio (ECR) indicated the liquefaction was a net energy producer (Minowa et al. 1995b).

Metal catalysts had been used in microalgae liquefaction. Matsui et al. (1997) investigated the liquefaction of *Spirulina*, a high-protein microalgae in various organic solvents or water under hydrogen, nitrogen, or carbon monoxide in the temperature range 300–425°C, using Fe(CO)₅-S catalyst. Among the solvents of tetralin, 1-methylnaphthalene, toluene, and water, it seemed more favorable for liquefaction of *Spirulina* to take place in water. After reaction, tetrahydrofuran (THF) was used to extract the production. Then the THF-soluble fraction was further separated into hexane-insoluble and hexane-soluble fractions by precipitation into hexane. The hexane-soluble fraction was denoted as oil in this research. Liquefaction of *Spirulina* at 300–425°C under hydrogen gave more than 90 wt % conversion and 60 wt % oil yield. Addition of the Fe(CO)₅-S catalyst increased the oil yield from 52.3 wt % to 66.9 wt % at 350°C for 60 minutes in tetralin. Liquefaction in water gave an oil yield as high as 78.3 wt % at 350°C even under nitrogen without a catalyst. Liquefaction in toluene gave oil fractions having a heating value of 32–33 MJ/kg, but products obtained in water, containing large amounts of oxygen, were estimated to have a lower heating value of 26 MJ/kg (Matsui et al. 1997).

The microalgae and coal were co-liquefied with the presence of coal liquefaction catalysts (Ikenaga et al. 2001). Dried samples of *Chlorella*, *Spirulina*, and *Littorale* were used as microalgae and Australian Yallourn brown coal and Illinois No. 6 bituminous coal were employed. Commercial iron pentacarbonyl (Fe[CO]₅), trisruthenium dodecacarbonyl (Ru₃[CO]₁₂), and molybdenum hexacarbonyl (Mo[CO]₆) were employed as catalysts. The co-liquefaction was carried out under pressurized H₂ in 1-methylnaphthalene at 350–400°C for 60 minutes. Co-liquefaction of *Chlorella* with Yallourn coal was successfully achieved with excess sulfur to iron (S/Fe = 4). The conversion and the yield of the hexane-soluble fraction were close to the values calculated from the additivity of the product yields of the respective homo reactions. All three catalysts were effective for the co-liquefaction of microalgae with coal. Some 99.8% of conversion and 65.5% of hexane soluble fraction were obtained at 400°C with Fe(CO)₅ at S/Fe = 4, when the 1:1 *Chlorella* and Yallourn coal were co-liquefied. In the co-liquefaction of *Chlorella* with Illinois No. 6 coal, the oil yield was close to the additivity of the respective reaction with Fe(CO)₅-S, even at S/Fe = 2. Mo(CO)₆ catalyst (S/Mo = 4) was the most effective for the respective homo-liquefactions of *Chlorella* and Yallourn coal. When *Littorale* and *Spirulina* were used as microalgae, a similar tendency was observed with the iron catalyst.

Microalgae culturing conditions and the fixation of CO₂ during the microalgae growth were studied in order to find the optimal condition to harvest large amounts of algae. It was also useful to investigate the energy balance and CO₂ mitigating effect of a liquid fuel production process from microalgae using HTL. Kishimoto et al. (1994) studied the CO₂ fixation during the microalgae growth and oil production of microalgae by using thermochemical liquefaction. The green microalga *D. tertiolecta* AHTP 30929, which contained 10% glycerol, was used throughout the study. The effects of saline, light intensity, and CO₂ concentration on microalgae growth were investigated. The details of the liquefaction were not mentioned in this paper, but the authors concluded that the heavy oil yield from the liquefaction was 35.6%. The contents of the chemical elements were as follows: carbon 73%, hydrogen 9%, nitrogen 5%, and oxygen 13%. The heating value of the heavy oil was 34.7 MJ/kg, which was almost the same as C heavy oil. The viscosity of the oil was 860 mPa·s, the same as that of castor oil. The nitrogen content was higher than that of ordinary petroleum.

Continuous culturing of the *B. braunii* Berkeley strain in secondarily treated sewage (STS) was conducted and then liquefied by Sawayama et al. (1995). *B. braunii* grew continuously for a period of over 1 month at a growth rate of 200 mg dry weight per liter water per week and the algal cells fed on STS containing 49% oil as the hexane soluble fraction. Liquefaction of microalgae cells was conducted in a 300 mL autoclave. Wet cells (30 g wet weight, 92% moisture content) were charged to the autoclave with 5 wt % or without sodium carbonate. N₂ was used as the initial gas for preventing water from vaporizing. The autoclave was heated to 200, 300, and 340°C, with a retention time of 1 hour. Oil was extracted with dichloromethane from the reaction mixture. The maximum yield of oil obtained by liquefaction was 64 wt % on a dry basis at 300°C with a sodium carbonate catalyst. The yield of the hexane soluble fraction was 97 wt % compared with that in the feedstock algal cells. The heating value of the liquefied oil obtained from this reaction was 49 MJ/kg and the viscosity was 64 mPa·s at 50°C.

Different microalgae are not the same in producing oil through liquefaction. The data of liquefaction of microalgae *B. braunii* and *D. tertiolecta* were collected and compared, and then the energy balance of the reactions was calculated by Sawayama et al. (1995). Liquefaction was performed using a stainless steel autoclave with 100 or 300 mL capacity using 0–5 wt % and Na₂CO₃ as a catalyst. After purging with nitrogen, the autoclave was charged with nitrogen at 2–3 MPa. The reaction temperature was 300°C. The reaction mixture included a gas mainly composed of CO₂, a tar-like material that sank to the bottom, a water phase, and an oil-like material that floated on the surface of the water phase. Solvent extraction with CH₂Cl₂ or acetone was performed to separate the oil from the reaction mixture. The yield of oil was determined as a percentage by weight of the organics in the original material. Based on the energy calculation and comparison, the yield of liquid fuel produced from *B. braunii* and its lower heating value were high compared with those of *D. tertiolecta*; therefore, the energy inputs for cultivation and separation of *B. braunii* were calculated to be smaller than those of *D. tertiolecta*. The energy input for fertilizers of *B. braunii* was also smaller than that of *D. tertiolecta*. Therefore, the hydrocarbon-rich microalga, *B. braunii*, could be more suitable for liquid fuel production using thermochemical liquefaction compared with *D. tertiolecta*. The authors also concluded: if a 100-MW thermal plant using coal would be replaced by liquid fuel produced from *B. braunii*, the quantity of CO₂ mitigation could be 1.5 × 10⁵ t/yr and 8.4 × 10³ ha of microalgal cultivation area could be necessary (Sawayama et al. 1999).

To find the most suitable operational conditions of HTL of microalgae, Yang et al. (2004) used the *Microcystis viridis* strain as feedstock. The series of experiments were conducted

under the following various conditions: catalyst (Na_2CO_3) loading rate of 0 and 5 wt %; reaction temperature of 300 and 340°C; and holding times of 30 and 60 minutes. The initial operational pressure was designed at 3 MPa of nitrogen, and the maximum pressure of the autoclave was 10–20 MPa in order to decrease water evaporation. The reaction mixture was extracted with chloroform to recover the oil by evaporating chloroform at 40°C. The aqueous phase and insoluble mixture were separated by filtration. The chloroform insoluble fraction remaining on the filter paper was dried at 105°C for one day to obtain a solid residue. The evolved gas was transferred to a sampling bag and composition was determined by gas chromatography. The oil yield was defined as the ratio of the weight of oil products after liquefaction to the weight of organic matter in feedstock. The energy yield was defined as the ratio of the weight of C and H in oil products after liquefaction to the weight of C and H in feedstock. After investigating the effects of the reaction parameters, such as retention time, reaction temperature, and load of the catalyst, the maximum 33% oil yield (energy yield of around 40%) was obtained with the 30-minute holding time, reaction temperature of 340°C, and alkali catalyst dosage of 5 wt %. The heating value of the obtained oil was 31 MJ/kg, less than that of heavy oil (40 MJ/kg). The elemental composition of liquefied oil was composed of 62% carbon, 8% hydrogen, 8% nitrogen, and 2% sulfur. The liquefied oil contained n-alkane of C_{17} – C_{18} hydrocarbon as a main component of the saturated compounds, so typical aromatic compounds of heavy oil, such as n-naphthalene and n-dibenzothiophene were found in liquefied oil, and it was considered that the liquefied oil should be classified as heavy oil. The gas consisted primarily of CO_2 and methane. The total nitrogen in the aqueous phase ranged from 998 to 1157 mg/L, and half of the total nitrogen was detected as ammonia nitrogen. The total phosphate in the aqueous phase ranged from 2.47 to 5.38 mg/l.

After microalgae liquefaction, other forms of biofuel—such as biodiesel—could be obtained by further extraction. Based on the efficiency of biodiesel extraction, Aresta et al. (2005) compared HTL of algae with the extraction using supercritical carbon dioxide (sc- CO_2). Green alga *Chaetomorpha linum* was used as the feedstock. Almost 20 g of fresh, washed thalli of *C. linum* were placed into the glass reactor which was then put into the autoclave. The latter was closed under N_2 atmosphere to purge the residual air and 3.0 MPa of N_2 . The autoclave was then heated to the desired temperature (250, 300, 350, and 395°C) for 1 hour. The reaction mixture was recovered and treated with CH_2Cl_2 . Then an organic and an aqueous/solid suspension were separated. From the organic solution, after evaporation of the solvent under controlled conditions, an amber-yellow oily liquid was obtained. The aqueous solution was separated and a solid was recovered by centrifugation. For the sc- CO_2 extraction, the thalli of alga were dried for 5–8 days at room temperature, 3–5 g of dried algae were milled in liquid nitrogen (5 mL) to break the cellular wall in order to increase the extraction yield. A 0.5–1 mL of methanol was used as a co-solvent to improve the efficiency of the extraction. In both liquefaction and sc- CO_2 extraction, the oils obtained were treated to convert all fatty acid (FA) components into the mono-methyl-esters (Biodiesel). Then the extracted material was analyzed quantitatively by GC and qualitatively by GC-MS. For liquefaction, increasing the temperature for the total amount of oil extracted from the algae increased reaching a plateau between 350–395°C (about 80 mg/g dry wt). Increasing the temperature affected the amount of fatty acid extracted. However, at higher temperatures, some oil decomposed, resulting in a decrease of the recovered amount of extracted fatty acid. After comparing the results from the sc- CO_2 extraction, the authors implied that HTL seemed to be more efficient from the quantitative point of view.

Summary

HTL mimics the natural process of fossil fuel formation from biomass feedstocks. In that sense, it holds great promise as a renewable energy source, especially for liquid fuel. Although great effort has been made since the 1970s, the results have been intermittent due to the low energy price since the 1980s. It is time once again that we need to revisit the science and technology of HTL, together with other renewable technologies.

HTL of biowaste materials into liquid fuel holds several unique advantages. First, it safeguards national security—by using biowaste and producing algae within dispersed local communities, the geopolitical threat from the required importation of petroleum can be neutralized. Second, it has a net-zero carbon emission—bio-waste materials are renewable, typically a product or byproduct of photosynthesis. Third, it does not compete with the food supply—bio-waste is often a negative-cost feedstock. In the event of algae growth within or at nearby waste treatment facilities and animal farms, HTL will not compete with the supply of farmland or food.

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