

Catalytic microwave assisted pyrolysis of aspen

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Abstract: The effect of catalysts on the microwave pyrolysis of aspen pellets was studied. A range of chlorides, nitrates and metal-oxides were added at 2% of the aspen mass (air dry aspen pellet weight basis). Chlorides in particular were found to favor liquid yield, especially the yield of water phase residue. Average liquid yield with added chlorides was 41% mass of the total biomass input, compared to 35% mass without catalyst. Metal-oxides were found to favor pyrolysis heavy oil, and thus total oil yield, since the yield of light oils seemed to be fairly constant. Nitrates were found to favor pyrolysis gas production. Pure light oils and light oils blended with diesel were found to be a potential diesel fuel substitute.

Keywords: Renewable energy, pyrolysis, microwave pyrolysis, pyrolysis liquids, bio-oils, pyrolysis catalysts

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1 Introduction

These days many people see a great hope in bioenergy and biofuels. Recent studies^[1,2] have shown a great deal of variations within different types of bioenergy regarding its effect on the environment. The

use of biomass waste from agriculture and forest industry represents one of the less harmful alternatives, since it does not conflict with food production and supplies or the carbon storage and the virgin value of native vegetation.

Microwave pyrolysis is one of the many ways of converting biomass into higher value products such as oils, gases, charcoal and chemicals. The conversion of

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corn stover^[3] and sewage sludge^[4-6] are among the recent studies in the fields of microwave pyrolysis and bioenergy. Increased process yield, environmental compatibility, savings in process time and low requirements for space and capital equipment are among the advantages reported about microwave processing of materials^[7]. Oils from microwave pyrolysis of sewage sludge is reported to contain no harmful compounds such as heavy polycyclic aromatic hydrocarbons (PAHs), which was the case for oils from conventional pyrolysis of the same feedstock^[5].

Very fine feedstock grinding is required by conventional pyrolysis. Pyrolysis oil and char yields were found to be largely dependent of particle size^[8]. In conventional pyrolysis system, large sized particles are difficult to agitate and process in the fluid bed, as they tend to settle to the bottom of the bed where heat transfer and speed of thermal processing are reduced. This has a negative effect on the efficiency of production of bio-oil, which is increased when the particle size is reduced. Fine particles increase overall heat transfer, but require substantial amount of energy and effort for size reduction, pre-processing and sizing of biomass feed material. Thermochemical conversion reactions can take place rapidly in large-sized biomass materials by using microwave irradiation. Very fine feedstock grinding required by conventional pyrolysis is not necessary for microwave pyrolysis process, resulting in substantial energy savings.

Mobile or decentralized microwave pyrolysis systems are seen as an option for farmers and industry in converting energy crops or biomass waste into higher value, less bulky products. The gases produced can be burned in an engine or turbine on site to produce the electricity required for running the system, or they can be further refined to liquid fuels, for example with the Fischer-Tropsch process. Liquids can be collected and brought to central refineries (modified oil refineries) for upgrading to fuels and valuable chemicals^[9]. The charcoal, containing most of the minerals from the biomass, can be put back out on the fields as a fertilizer, a soil remediation agent and a medium for carbon sequestration. Pyrolysis chars also have the potential for

being sold as activated carbon^[10,11]. Microwave pyrolysis could therefore be a good solution for the complete utilization of biomass and a good option for boosting rural economy. It should also be mentioned that chemical production, reported by Wikipedia to currently require 16% of the world's petroleum extraction, represents a huge future market for biomass refining, independent of which transportation fuel turns out to be the winner.

The objective of this study is to find if certain catalysts and catalyst groups affect the pyrolysis fraction yields and fraction properties when added to biomass that is pyrolysed in a microwave oven. The focus is on obtaining high liquid yields. Catalysts are in this paper used as a very wide term. The effects of the catalysts may include aid in decomposing biomass before (pretreatment) or during the pyrolysis, faster heating rate by enhancing microwave absorption (passive hybrid heating) or reformation of the pyrolysis volatiles.

2 Methods

2.1 Biomass and catalyst characteristics

Pellets of aspen hardwood from Lone Tree Manufacturing at Bagley, Minnesota 56621, were pyrolysed with added chlorides, nitrates, metal-oxides and magnesium sulfate as catalysts. The chlorides tested were sodium chloride, potassium chloride, calcium chloride, magnesium chloride, aluminum chloride, zinc chloride, iron(II) chloride, iron(III) chloride, tin(II) chloride, cobalt(II) chloride and ammonium chloride. The nitrates tested were magnesium nitrate, iron(III) nitrate, copper(II) nitrate, silver nitrate, nickel(II) nitrate, lanthanum(III) nitrate, tellurium(II) nitrate, rhodium(III) nitrate and cobalt(II) nitrate. The metal-oxides tested were manganese dioxide, zirconium dioxide, platinum alumina, aluminum oxide and magnesium oxide. The pyrolysis runs with the last two catalysts mentioned resulted in incomplete pyrolysis, which may be due to the catalyst. The yields from these runs are therefore not part of the reported average results.

To add the catalysts to the aspen, the catalysts were first dissolved in water and then the catalyst/water solution was mixed with the aspen pellets at 2% of the

aspen mass (air dry aspen pellet weight basis). The mixture was left to dry at room temperature, reaching a final water content of about 5.9% (mass) and a density of 240 kg/m³. The density is lower than that of fresh pellets, since the pellets loosened up when mixed with the catalyst/water solution. For the control tests, the aspen pellets were mixed with pure water and then dried, for better comparison. Samples of (250±15) grams were pyrolysed per batch. Reported results for pyrolysis process and fraction yields are based on the average of three runs for the control samples and the average of two runs with added kalium chloride, nickel(II) nitrate and magnesium sulfate. The reported results for catalyst groups are the averages of one run per catalyst in a group. The ash content of the aspen pellets was measured to be 6.2% (mass).

2.2 Microwave pyrolysis apparatus

A Sineo MAS-II batch microwave oven with a rated power of 1000 W was used at the 800 W power setting. The biomass was placed in a one liter quartz flask inside the microwave oven. Airtight quartz connections, insulated with alumina fibers, lead from the flask to a condenser system with collectors for the liquids. Five parallel bulb condensers, each between one half and one meter long, were used for the condensation. The temperature of the cooling water in the condensers was 0–5°C. During pyrolysis the heavier volatiles are condensed into liquids and the lighter volatiles escape as gases at the end of the condensers, where they are either burned or collected for analysis. Charcoal is left in the quartz flask.

2.3 Separation of pyrolysis liquids

The pyrolytic liquid contains two separate phases: a heavy oil phase and a water phase. A mixed solvent was added to the water phase to extract light oil. The solvent in the extraction fraction was then evaporated at 40°C under vacuum, and recycled. The non-volatile residual, named light oil, was weighed. This light oil fraction has a lighter color and lower density than the heavy oil, and burns easily. Chemicals can be separated from the water phase residue fraction. The heavy oil phase can be further upgraded to light oil or other products.

2.4 Chemical and physical analysis of oils and gases

The water content of the liquids was determined

using a Karl Fischer water titrator (ASTM D 1744, Schott, Mainz, Germany). The pH value was determined using a digital pH meter (Accumet Basic AR-15, Fisher Scientific, Fair Lawn, NJ). The ash content of biomass and oils was determined by heating biomass mass four hours in a Lindberg Hevi-Duty Oven at 600°C. The gas was analyzed using gas chromatography (CP-4900 Micro-GC with MS5A, PPQ, and WAX columns, Varian, Walnut Creek, CA). The heating value and mineral content of samples were determined by the Poultry lab at the University of Arkansas.

The elemental analysis was performed with an elemental analyzer (CE-440, Exeter Analytical Inc., North Chelmsford, Massachusetts). The higher heating value (HHV) which is the enthalpy of complete combustion of a fuel including the condensation enthalpy of formed water, was calculated using the following model, reported to have a standard error of about 2% for dry biomass^[11];

$$HHV=3.55C2-232C-2230H+51.2C\times H+131N+20600 \text{ (kJ/kg)}$$

3 Results and discussion

3.1 Pyrolysis process

The pyrolysis process can be divided into different stages that are reached at certain times depending on the mass of the samples and catalysts. Since the mass does not differ much between the tested samples, time is a good indicator of how the catalysts affect the heating rate and the pyrolysis speed. The first stage is when the first condensation of liquids starts. During the first phase, water is condensed first, and then followed by lighter orange/brown pyrolysis volatiles. The water and these volatiles together form so-called water phase. The second stage is when the condensation of darker pyrolysis volatiles starts. In this stage most of the heavy oils and burnable gases are produced. Finally, when the flame turns significantly small, the pyrolysis process is near its end. The temperature is measured with a thermocouple in the remaining charcoal when the pyrolysis ends. Lower and upper limit of a measured temperature range is reported, since the temperature varies between different spots in the same batch of charcoal.

As shown in Table 1, different catalyst groups could affect the pyrolysis process. Chlorides seem to speed up the process more than the other catalysts tested. Chlorides also give the highest liquid yields, as shown in Figure 1. Generally in pyrolysis, faster heating rate favors high liquid yields^[13] whereas high temperature favors high gas yields, due to gasification and secondary cracking reactions of the pyrolysis vapors^{[6].}

Table 1 Average pyrolysis process times and final temperatures for runs with different catalyst groups added to the aspen pellets

Catalyst groups	Pyrolysis start /min	Pyrolysis second Stage/min	Pyrolysis end /min	Final temperature /°C
Chlorides	4	13	28	560–610
Nitrates	5	17	34	590–630
Metal-oxides	7	15	31	580–620
No catalyst	6	17	33	580–620

3.2 Fraction yields

Figure 1 shows the pyrolysis fraction yields from the different runs. The yields of heavy oil, light oil and water phase residue combined give the total pyrolysis liquid yields. The following percentages are in mass(%) of total biomass input. Chloride catalysts gave the highest average liquid yield of about 41%, compared to 35% without catalysts. Most of the increase is in water phase residue. Aluminum chloride, iron(III) chloride, ammonium chloride and zinc chloride are reported in literature to reduce hemicellulose decomposition and accelerate cellulose decomposition through the dehydration reaction^[10]. It is reported that during a solid to liquid phase transfer catalysis, the equilibrium exchange between ion pairs and tetra alkyl ammonium salts results in the formation of loose ion pairs, much more prone to strong microwave interaction^{[14].}

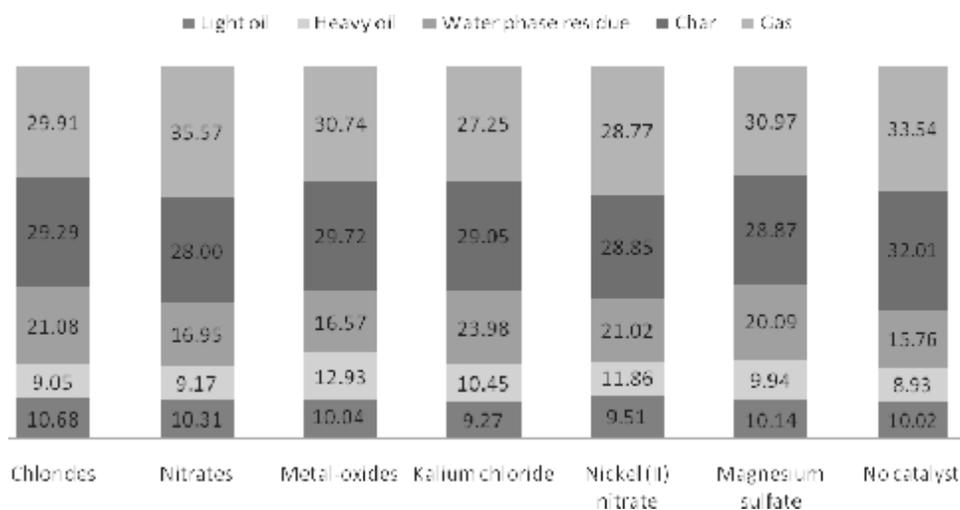


Figure 1 Pyrolysis fraction yields (mass% of total biomass input) from runs with different catalysts and catalyst groups added to the aspen pellets

Metal-oxides gave the highest oil yield. The sum of light oils and heavy oils averaged 23%, compared to 19% with no catalyst added. The heavy oils make up most of the increase. Heavy oil yield is about 13% average for metal-oxides compared to about 9% heavy oil yield with no catalyst added. 20%-30% of the heavy oil mass is a lighter colored waxy fraction that can be separated out with the same solvent as used for the light oil separation. Light oil yields were fairly constant around 10%.

Most catalysts seem to decrease the char yield.

Average char yield was about 29% for catalyst assisted pyrolysis, without much variation between different catalysts. Nitrates gave about 36% gas yield, which is significantly higher than that of other catalyst groups, and also higher than that of the control samples. Silver nitrate gave the highest gas yield, which was about 40%.

3.3 Analysis of pyrolytic liquids

Table 2 shows elemental analysis and calculated (HHV-c) and measured (HHV-m) heating values of aspen pellets, light oils, and heavy oils from the microwave

pyrolysis of aspen. The elemental results of the aspen pellets are based on dry biomass. The oxygen value is calculated by difference after subtracting ash content.

Reported data for bio-oils are shown for comparison purpose^[15,16].

Table 2 Elemental analysis and heating values of aspen and some pyrolysis fractions

\Element Sample	C (mass%)	H (mass%)	N (mass%)	S (mass%)	O (mass%)	HHV-c/MJ · kg ⁻¹	HHV-m/ MJ · kg ⁻¹
Aspen	45.4	4.8	0.5	0.0	43.1	17.9	18.8
Aspen heavy oil	49.3	6.6	0.5	0.0	43.6	19.8	19.3
Aspen light oil	52.9	8.1	0.7	0.0	38.3	22.3	-
Corn stover bio-oil ^[14]	60.7	7.7	2.0	0.2	-	-	17.5
General bio-oils ^[15]	32-48	7-8.5	<0.4	<0.05	44-60	-	17

Table 3 shows the mineral contents of aspen and some pyrolysis fractions of aspen, and also the mineral content of bio-oils from the microwave pyrolysis of corn stover^[15] for comparison. Aspen generally has higher mineral content than the bio-oils, which implicates that

most minerals stay with the char. The high value of zinc in the water phase residue can be attributed to zinc chloride added in the separation process. Aspen liquids seem to have an overall higher mineral content than corn stover liquids, except for the contents of iron and copper.

Table 3 Mineral content of aspen and some pyrolysis fractions

\ Mineral Sample	mg/kg									
	K	Ca	Mg	S	Na	Fe	Mn	Zn	Cu	Al
Aspen	2279	12390	1192	405	43.0	833	91.9	89.4	5.18	244
Aspen light oil	69.5	9.87	3.15	73.4	41.0	1.33	5.44	860	0.08	9.94
Aspen heavy oil	15.3	12.3	7.20	184	4.93	1.02	14.8	4.28	0.25	-
Aspen water phase residue	34.2	9.13	2.49	56.7	5.67	0.68	0.66	11481	0.06	0.82
Corn stover bio-oil ^[14]	3.13	6.83	1.86	-	1.82	7.59	0.03	0.79	0.40	4.92

Ash content of the light oils, heavy oils and the water phase residue was found to be 0.03%, 0.15% and 0.98%, respectively. Most of the ash stays with the char. The water content of the water phase residue from the control tests without catalysts was found to be 67%, which gives 30% total water content of the pyrolysis liquids. This is higher than reported in other literature, which is 22% for hardwood pyrolysis liquids^[15], 15.2% for corn stover microwave pyrolysis liquids^[16] and 15%-30% for wood pyrolysis liquids in general^[17]. The water is both from the original water content of the biomass and from the dehydration in the pyrolysis process^[18].

There was no significant difference in the pH values of the light oils from the different catalyst groups, with values in the range of 0.5–1.5. In comparison, reported values for pyrolysis liquids are 2–3^[16]. The possible reason for low pH values is the formation of acetic and formic acid during the pyrolysis reactions^[18].

The miscibility of light oils with diesel was tested. A mixture of approximate volume fractions of 25% light oil, 10% n-butanol and 65% diesel gave a clear blend with no phase separation. The n-butanol works as a necessary co-solvent. Pure light oils with added cetane improver were tested as fuel in a 2-cylinder, indirect injection, 478 cm³ Kubota Z482 diesel engine. The engine ran without a problem when the light oils were mixed with 4% octyl nitrate compounds, which improve the cetane number and thereby the ignition quality of the fuel. Typical cetane number for pyrolysis liquids is reported to be 13–14, compared to 48 for petroleum diesel^[16]. These preliminary tests indicate that light oils could be a valuable renewable diesel substitute.

3.4 Gases

Gas was sampled during the first three minutes of the second pyrolysis stage, where the main gasification occurred. The volume yields of hydrogen and carbon

monoxide were found to be 25% and 44%, respectively, giving 69% synthesis gas of the total pyrolysis gas volume. Methane was found to be 18% of the volume. It is reported in literature a synthesis gas content of up to 66% from the microwave pyrolysis of sewage sludge, which is higher than conventional pyrolysis^[6]. Estimating 1 kg/m³ total gas density and assuming that the gas sample represents all the gas, give a HHV of 14 MJ/kg, with contributions only from methane, hydrogen and carbon monoxide. Heating values of pyrolysis gases are reported^[13] to be 3.9–15.7 MJ/kg.

4 Conclusions

Metal-oxides, magnesium sulfate and in particular chlorides increased the liquid yield in the pyrolysis of aspen pellets. Metal-oxides favored heavy oil yield, while magnesium sulfate and chlorides favored water phase residue yield. Nitrates were found to favor gas production. Pure or blended light oils are potential diesel fuel substitutes.

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