Laboratory Studies of a Hydrothermal Pretreatment Process for Municipal Solid Waste

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Objectives

The objective of the bench-scale laboratory work has been to establish operating conditions for a hydrothermal pre-processing scheme for municipal solid waste (MSW) that produce a good slurry product for conversion in a Texaco gasifier. "Good" in this context means a slurry that can be pumped and atomized in the gasifier feed injectors, and that has a high Btu content leading to a high yield of hydrogen relative to the CO₂ byproduct. Pumpability and Btu content for raw MSW are contradictory requirements; high water content favors pumpability, i.e. lowers the viscosity of the slurry but also lowers the Btu content. However, hydrothermal treatment (Khan, 1993) results in partial dissolution of the solid and leaves an altered solid product that is more carbon-like in nature, and less water absorbing due to an altered pore structure. Both dissolution and reduced porosity lead to a lower viscosity of a slurry of given MSW content.

A more specific objective of the bench-scale work has been to study the kinetics of the hydrothermal reaction, i.e. the hydrolysis of the MSW, for the purpose of guiding the 1 ton/day pilot plant work. This work has mostly been carried out with model components of the MSW, namely several types of paper, wood and paper/plastic mixtures. The kinetics work encompasses yield determinations for the three products, solubles, solids and gas, as well as rheological characterization of slurry products as a function of organic content.

Experimental Approach

The bench-scale work was carried out in batch autoclaves of three different sizes-140 ml, 300 ml and 1000 ml. The procedure was to load the reactor with the solid and aqueous-phase charge, heat the reactor externally in an electrically-heated oven, cool down the reactor and unload the batch for chemical analysis. Internal reactor temperature and pressure were recorded during the heating, reaction and cool-down phases. The goal was isothermal experiments with preset reaction times. However, isothermal conditions were obtained only approximately because of the slow heat transfer between the oven atmosphere and the reactor wall. The 140 ml reactors that were used for the kinetics work had a time constant of approximately 30 minutes implying that a 30 minute reaction time

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was far from a square pulse for the time/temperature relationship. To standardize the procedure, reaction times were counted from the time the internal temperature reached a temperature within 10°C of the desired temperature. The larger reactors showed even longer time constants, but they were mostly used for other purposes. The 300 ml reactors were built with blow-down valves for the purpose of blowing down a hot mixture to atmospheric pressure in a receiving vessel, and the 1000 ml reactor was used for mixing the reacting charge by means of a steel ball made to rock back and forth inside the reactor.

Gas yield was determined by allowing the product gas to fill an evacuated 1-liter volume at room temperature and recording the final pressure (at ambient temperature). Gas composition was determined by mass spectrometry. The water-soluble organic yield was determined by organic carbon analysis of a water sample and assuming that the composite soluble material had the same stoichiometry as the starting material. Some detailed GC analyses were performed identifying components such as formic and acidic acids, several aldehydes and alcohols. However, a complete breakdown of the components has not been carried out as of yet. The solid yield was determined by filtering the solids and drying the filter cake in a vacuum oven (at ambient temperature) to constant weight.

Slurries were prepared from either the wet filter cake (containing water and solubles) or from the dried cake by adding back the separated water, and shearing the resulting mixture in a food processor (Quisinart). Shearing of the product proved to be very important in that a cake appearing as a dry solid re-fluidized as a result of the shearing. Several minutes in the food processor was believed to bring about a constant-viscosity product but no measurements were made to prove this observation. Slurry rheograms were determined on a Haake RV30 viscometer at Texaco's Montebello Research Laboratory. This viscometer uses a rotating spindle with a narrow gap between the spindle and the stationary wall. Some samples, particularly "thin" slurries, showed thixotropic behavior, i.e. thinning of the sample during the measurement. In this case apparent viscosity was based on the average between the shear rate increase and shear rate decrease curves. "Thick" samples showed separation upon loading the sample and could therefore not be run at all. Apparent viscosity, defined by a forced Newtonian model at a shear rate of 100 1/s, in the range of about 50-500 mPa·s was the ideal viscosity range for the measurements.

Yield Results

The yield results are summarized in Table 1 for a newspaper, a coniferous wood and a paper dunnage sample. The source of the newspaper sample was the laboratory bi-weekly newspaper which is printed on high-grade paper while the

paper dunnage, which is composed of tailings from paper mills, came from an industrial packaging company. The wood was in the form of saw dust.

A large fraction of the feed became solubilized in the batch cooks. On the average, 20 wt% of the feed was converted to water-soluble organics. Although this is favorable for making a low-viscosity slurry, the resulting water phase would be a difficult process stream (pH was around 3 and total acidity 0.5 equivalents/liter for a water/feed ratio of 2). This type of water is expected to be very corrosive at the elevated temperatures of the process. With higher water/feed ratios the concentration dropped proportionally resulting in a constant soluble yield for water/feed ratio in the range of 1 to 10. Most experiments in Table 1 were conducted at a water/feed ratio of 2 with the exception of the experiments at 275°C and 2h which were conducted with ratios of 1, 2, 3, 4, and 10 without any significant change in the yield structure (the yield figures in Table 1 for the 275°C, 2h case are averages for the five water ratios). The interpretation of the insensitivity of the conversion results to water ratio is that a one-to-one ratio is sufficient to wet the solid reactant and that any extra water merely acts as a diluent. This is important because a ratio of one produces a relatively thick slurry without any separation of excess water after the reaction. It is, therefore, quite possible that a process can be designed without any excess waste water that would be expensive to treat. It is also noteworthy that no improvement was observed by starting with 0.1N acid instead of pure water. Using a base to make the cooking solution alkaline was deemed to be too expensive for a practical process.

In viscometer tests (discussed below) the paper dunnage was found to produce acceptable slurries at higher concentrations than the newspaper produced. This important result is reflected in a yield difference between the two materials. The paper dunnage produces less solid product and more water. This yield difference is also reflected in the O/C ratio of the solid products. Paper dunnage produced lower O/C ratios which are favorable for making high-concentration slurries. The paper dunnage is believed to be more representative of the paper component of MSW but this postulation needs to be confirmed by detailed feed characterization.

For the paper dunnage feed the solid residue was found to be around 50 % at the higher severity (high temperature and/or long time) and 60 % for the lowest temperature of 260°C. A temperature of 275°C and a time of 30 minutes produce a solid residue of 55 %. The residue drops to 52% when the cooking time is increased to 2 hours. Hence, an increase in cooking time from 30 minutes to 2 hours appears only to have a marginal effect on the yield structure. Contrary to the paper dunnage for which a temperature of 275°C produces acceptable conversion, the high-grade paper shows a solid residue of 67% at 275°C, 2h which is balanced by the low soluble product yield of 10%.

Differences between the newspaper and dunnage feeds are also seen in the O/C ratios of the solid residues. The newspaper-derived solid residue stoichiometry is $\text{CH}_{0.83}\text{O}_{0.21}$ at 320°C whereas the corresponding dunnage-derived stoichiometry is $\text{CH}_{0.83}\text{O}_{0.13}$. The paper dunnage-derived solid residue stoichiometry is reported in Table 1 as $\text{CH}_{1.08}\text{O}_{0.31}$ for the 275°C - 2h cook which appears to have an abnormally high O/C ratio. The cause of this discrepancy is unknown but sample contamination is suspected because the resulting slurry behaved like a product of a higher severity cook, i.e. produced a pumpable slurry at high concentration. Otherwise, the O/C ratio for the paper dunnage-derived residue responded as expected to an increase in the hydrothermal treatment temperature. The ratio declines from 0.26 at 260°C to 0.13 at 320°C . A slight loss of hydrogen accompanies the loss of oxygen which is expected since water dominates over CO_2 as the sink for removed oxygen. Again, an increase in time for the 310°C temperature appears to have a marginal effect on O/C ratio as well as on the product yields.

The solid residue O/C ratios of Table 1 agree well with literature values. A reputable source (Schumacher, Huntjens and van Krevelen, 1960) reports the solid residue stoichiometry $\text{CH}_{0.75}\text{O}_{0.188}$ for hydrothermal treatment of cellulose at 275°C for 3 hours. Also the yields of 47 % residue and 12 % gas are in reasonable agreement with the paper-based results of this work.

The gas yield responds to increasing temperature with a slight increase. It is 12% at 260°C and 16% at 320°C . The gas is approximately 90% CO_2 , 5% CO with a balance of minor components such as H_2 , CH_4 , and higher hydrocarbons.

The experiments with wood produced results similar to the newspaper except that the soluble yield reached 30%. This was expected because the lignin present in wood should be largely soluble judging from the behavior of wood in pulp processing. The wood cook produced a slurry product that in appearance was similar to the paper-derived products but no quantitative viscometer tests were performed on the wood-derived slurry.

Viscosity Results

A shear stress/shear rate relationship for a paper dunnage-derived slurry of 50 wt% organic content is shown in Fig.1. The rheogram shows Bingham plastic behavior with a yield stress of 17 Pa and a coefficient of rigidity of 180 mPa·s for the "up" curve. The "down" curve shows shear thinning due to the thixotropic characteristic of the slurry. An apparent viscosity can be obtained from the rheogram by simply drawing a straight line through the origin and the point on the rheogram at 100 1/s and determining the slope. The apparent viscosity as a one-parameter model can then be correlated to slurry properties such as solids content.

Fig. 2 shows the correlation between organic content of the slurry and the apparent viscosity for a bituminous coal, and for two newspaper-derived slurries. The organic content is used rather than solids content because organic content was determined directly by chemical analysis. The solids content is similar to the organic content because the solids contain inorganic ash that partially offsets the soluble organic content of the slurry. It is further argued that the important parameter is the organic content because it determines the heating value (stoichiometry is a second-order effect). Within experimental accuracy, all three materials in Fig.2 obey the same type of exponential relationship between apparent viscosity and organic (solids) content as evidenced by the same slope of the straight lines. The exponent is approximately 0.3 times the organic content implying a rapid increase in apparent viscosity with organic content. The three materials in Fig.2 show widely different pre-exponential factors leading to widely different organic contents at a fixed viscosity. If 1000 mPa·s is taken as the maximum pumpable slurry, the high-grade newspaper produces a slurry of maximum concentration of 34 %, the standard newspaper a slurry of maximum concentration of 43 %, while the coal reaches 61% organic content. Raw paper would be of the order of only a few percent organic content before its slurry viscosity reaches 1000 mPa.s. These effects are attributed to both differences in chemical composition (different O contents) and differences in the structure of the individual particles. These two factors produce different water retention characteristics of the pores. A bituminous coal is ideal in that the internal porosity is low and the physical composition includes few sites for water to absorb on (hydrophobic surface).

Fig. 2 also includes a result obtained by Design Integrated Technology, Inc. using their sharp orifice viscometer on one of the samples. The apparent viscosity calculated from the orifice rheogram agrees well with the result from the Haake viscometer. However, there were differences between the rheograms obtained by the two viscometers that warrant further study. For example, the coefficient of rigidity was much higher for the orifice viscometer translating to higher shear at high rates. This will be studied further with the orifice viscometer that the laboratory has ordered.

Fig. 3 shows the first results on the effects of treatment severity on the paper dunnage that will be used for the pilot plant work. Overall, this particular paper produces slurries of lower apparent viscosity than either of the newspaper samples shown in Fig 2. With severe treatment (310°C or 320°C for 30 minutes , or 275°C for 2 hours) the paper dunnage produces a slurry of 55 % organic content at 1000 mPa·s apparent viscosity. Fig. 3 also shows that the slurry quality degrades quickly as the hydrothermal treatment becomes less severe. Further work will be required to derive kinetic expressions to be used for reactor design calculations. The preliminary finding that, in terms of slurry viscosity, 310°C with a 30 minute residence is equivalent to 275°C with a 2 hour residence time translates to very different reactors because the pressure requirement is very sensitive to operating temperature.

Results with plastic-containing feed

A breakdown of the plastic components of "typical" MSW was obtained from the San Marcos facility (Bill Worell, North County Resource Recovery Associates, 1994) as follows:

Component	Wt % of total* plastics
Low-density polyethylene	40.0
High-density polyethylene	8.8
Polypropylene	1.4
Polyethylene terephthalate	3.2
Polystyrene	21.7
Polyvinyl chloride	4.7
Other (phenolic resins etc.)	20.2

*Total plastics 5.6 wt% of MSW

Based on these results polyethylene (PE) garbage bags were used in the initial laboratory work as representative of the main plastic component of MSW .

Batch hydrothermal treatment experiments of 90 % paper with 10 % PE have simply shown that the paper produces the usual slurry, whereas the PE component is largely unaltered by the process. PE melts at treatment conditions to a very viscous liquid and then re-solidifies during cooling. A small amount of paper-derived product "sticks" to the plastic pieces in the re-solidification but this is only of the order 10 % of the plastic and therefore negligible in terms of paper loss (paper and other cellulosic material are the main slurry-forming vehicles). However, the plastic pieces remaining after the cook were found to be so resilient that no comminution occurred in food processor. Because of these difficulties in comminuting, several alternatives addressing treatment of plastics were investigated in the bench-scale work.

Real MSW samples containing about 50 % plastics (San Marcos final product after removal of the recyclables) were cooked in the large reactor with a steel ball mixer. However, the results were disappointing; the plastic components agglomerated on the steel ball to a large lump with great resilience to comminution.

Some success was achieved with the 90-10 paper/PE feed in the 300 ml reactor provided with a hot blow-down valve. Although only the water and part of the molten PE flowed through the valve, the plastic component appeared to have been atomized in the process. The valve was apparently too small to allow the paper component to flow through. However, the approach of using a hot blow-

down valve to disperse the plastic component warrants further study on a larger scale.

Conclusions

Slurry viscosity at a given solids content was found to be strongly correlated both with the source material, and with the temperature of the hydrothermal treatment. As expected, more severe conditions yielded better results. Treatment temperature could be lowered by a compensating increase in residence time but quantitative reaction kinetics will require further study. Quite unexpectedly, different paper grades produced different results with low-quality paper forming better slurries than high-quality papers. This finding points to the need for more detailed feed characterization. Polyethylene plastic was not affected favorably by the batch hydrothermal treatment used in the bench-scale work. Hot blow down as part of hydrotreatment is proposed as an enhanced treatment scheme for the plastics. This will be investigated in future work in conjunction with expansion to other types of plastics.

Acknowledgment- This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-Eng-48. The author would like to thank Mr. Harry C. Wiese of Texaco's Montebello Research Laboratory for consultations on slurry rheology.

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Table 1. Product yields (wt% feed)

Feed material	Cooking Conditions	Solid Residue Stoich. (m.a.f.)	Solid Residue (incl. ash)	Soluble Product	Gas Product (mostly CO ₂)	Water by balance
High-grade newspaper, CH _{1.55} O _{0.67} ✓	320°C, 30 minutes	CH _{0.83} O _{0.21}	55	23	12	10
	275°C, 2 hours	CH _{0.98} O _{0.31}	67	10	11	12
Wood (sawdust)	310°C, 30 minutes	---	47	30	11	12
Paper dunnage, CH _{1.66} O _{0.72} ✓ ✓ ✓ ✓ ✓ ✓	260°C, 30 minutes	CH _{1.00} O _{0.26}	61	16	12	11
	275°C, 30 minutes	CH _{0.97} O _{0.23}	55	17	12	16
	310°C, 30 minutes	CH _{0.94} O _{0.17}	48	17	17	18
	320°C, 30 minutes	CH _{0.83} O _{0.13}	50	16	16	18
	275°C, 2 hours*	CH _{1.10} O _{0.32}	52	22	14	12
	310°C, 2 hours	CH _{0.93} O _{0.16}	45	17	17	21

*Average for water/feed ratios of 1, 2, 3, 4, and 10

Fig.1: Rheogram of Typical Paper-Based Slurry

Fig.2: Effect of Slurry Concentration on Viscosity

Fig.3: Effect of Treatment Severity on Slurry Viscosity