

EFFECTS OF MASS TRANSFER AND HYDROGEN PRESSURE ON THE FIXED-BED PYROLYSIS OF SUNFLOWER BAGASSE

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INTRODUCTION

There are a number of waste and biomass sources being considered as potential sources of fuels and chemical feedstocks ⁽¹⁾. The economics for biomass pyrolysis are generally considered to be most favourable for (i) plants which grow abundantly and require little cultivation in arid lands and (ii) wastes available in relatively large quantities from agricultural plants, for example, sunflower and hazel nuts. For the former, one such group of plants is *Euphorbiaceae* which are characterised by their ability to produce a milky latex, an emulsion of about 30% w/w terpenoids in water. One species in the family, *Euphorbia Rigida* from Southwestern Anatolia, Turkey is cultivated in close proximity to the sunflower growing regions and their oil extraction plants. The Turkish sunflower oil industry generates 800,000 tons of extraction residue (bagasse) per annum. Thus, both sunflower wastes and latex-producing plants are being considered as feedstocks for a future thermochemical demonstration unit in Turkey. It was demonstrated previously ⁽²⁾ that much higher oil yields can be obtained from *Euphorbia Rigida* by static retorting than by the traditional method of low temperature solvent extraction (18 cf. 10% daf basis). However, it is well known from studies on coals and oil shales (see, for example, references 3 and 4) that oil yields are severely limited under static retorting conditions and, as a consequence, flash pyrolysis processes, particularly fluidised-beds, have received considerable attention for converting biomass to liquid products ^(5,6). In contrast, pyrolysis at relatively high hydrogen pressures (hydrolypyrolysis) has not been widely investigated for biomass. A potential advantage of hydrolypyrolysis is the ability to upgrade tar vapours over hydroprocessing catalysts ⁽⁷⁾.

For *Euphorbia Rigida*, it was reported previously that an oil yield of ca 40% could be attained by hydrolypyrolysis at 150 bar pressure in a well-swept fixed-bed reactor ⁽⁸⁾. However, the main effect of raising the hydrogen pressure was to decrease the oxygen content of the resultant oil and, thus, on a carbon basis, increase the fraction converted to oil ⁽⁹⁾. This study extends the previous investigation on *Euphorbia Rigida* to sunflower bagasse to ascertain the most appropriate pyrolysis regime for attaining oils in high yield with low oxygen contents.

Fixed-bed pyrolysis (atmospheric pressure) and hydrolypyrolysis experiments at temperatures in the range, 400-700°C have been conducted on sunflower bagasse to assess the effects of mass transfer and hydrogen pressure on oil yield and quality. NMR characterisation of the liquid products and chars has been used to assess the extent of aromatisation of the cellulosic structure during pyrolysis.

EXPERIMENTAL

Pyrolysis experiments have been carried out on sunflower bagasse samples obtained from both pressing and solvent extraction. For the pressed sample, a number of particle sizes and gas sweep velocities were used in a Heinze retort (40 g sample) with a heating rate of 7°C min⁻¹. A faster heating rate of 300°C min⁻¹

was employed for atmospheric pressure pyrolysis experiments in a well-swept resistively-heated fixed-bed reactor (5 g sample) ⁽¹⁰⁾ which was also used for tests with hydrogen pressures of 50, 100 and 150 bar on all the samples investigated.

The product oils have been characterised by elemental and ¹H NMR analyses and column chromatographic separations. Solid state ¹³C NMR analysis was conducted on the bagasse samples and a selection of the chars. Cross-polarisation-magic-angle spinning (CP-MAS) spectra were obtained using a Bruker MSL100 spectrometer with a contact time of 1 ms.

RESULTS AND DISCUSSION

Pyrolysis Figures 1 and 2 indicate that in the Heinze retort, overall conversions (100 - %char), oil and water yields are fairly independent of both particle size and the sweep gas flow rate for the pressed bagasse sample. As the flow rate is reduced from 600 to 100 cm³, the oil yield decreases by no more than 5% from the maximum value of close to 40% (daf basis). Similarly, the smallest (0.4 mm) and largest (>1.8 mm) particle sizes used give only *ca* 3% less oil than the intermediate sizes (Figure 2). Indeed, the overall conversions of nearly 80% achieved in the Heinze retort are the same as those in the resistively-heated fixed-bed reactor (Figure 3) where the gas velocity is an order of magnitude greater. The conversions are somewhat lower for the extracted bagasse than for the

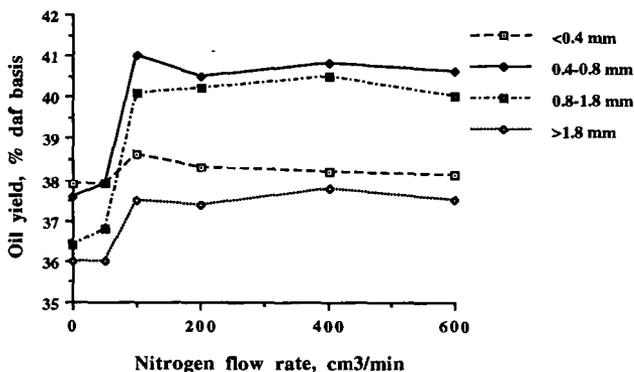


FIGURE 1 EFFECT OF PARTICLE SIZE AND GAS FLOW RATE ON OIL YIELDS IN HEINZE RETORT

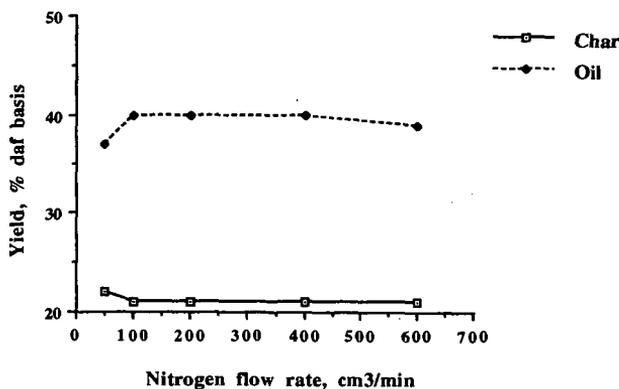


FIGURE 2 EFFECT OF GAS FLOW RATE ON PRODUCT YIELDS IN HEINZE RETORT, 0.8-1.8 mm

pressed sample which contains more residual oil. These results suggest that mass transfer restrictions to volatile evolution are much less marked for the sunflower bagasse compared to coals and oil shales where oil yields are generally reduced significantly by decreases in carrier gas flow rate (3,4), as well as increases in particle size. This major difference is probably attributable to the low bulk density of the bagasse. A rotary kiln would thus suffice to ensure that the maximum oil yields are obtained on a pilot plant scale.

Hydropyrolysis Figure 4 compares the oil yields from the extracted bagasse sample with those obtained from *Euphorbia Rigida* and pure cellulose. Compared to coals and oil shales, the effects of hydrogen pressure on oil yield are seemingly much less pronounced. For the cellulose and *Euphorbia Rigida*, hydrogen pressure hardly affects oil yield which attains a broad maximum between 30 and 40% as the hydrogen pressure is increased from 50 to 150 bar at 520°C (Figure 4). The variation is somewhat more pronounced for the sunflower bagasse sample where the oil yield reaches a maximum at ca 100 bar and then decreases due to water formation (Figure 4). However, in all cases, hydrocarbon gas yields increase monotonically and char yields decrease with temperature. For example, the methane yield increased from 1.2 to 4.8% (daf basis) at 150 bar pressure for the extracted bagasse.

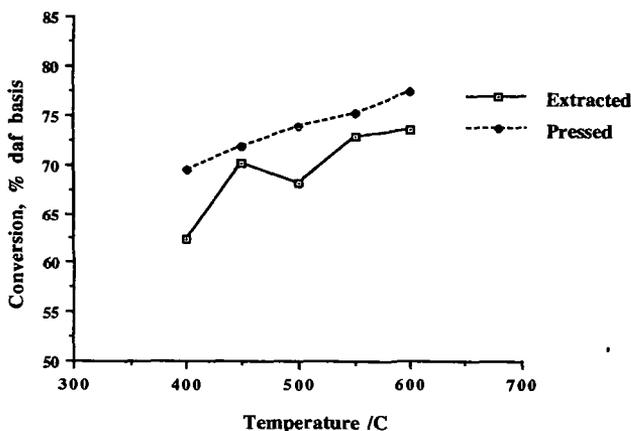


FIGURE 3 EFFECT OF TEMPERATURE ON CONVERSIONS IN FIXED-BED REACTOR

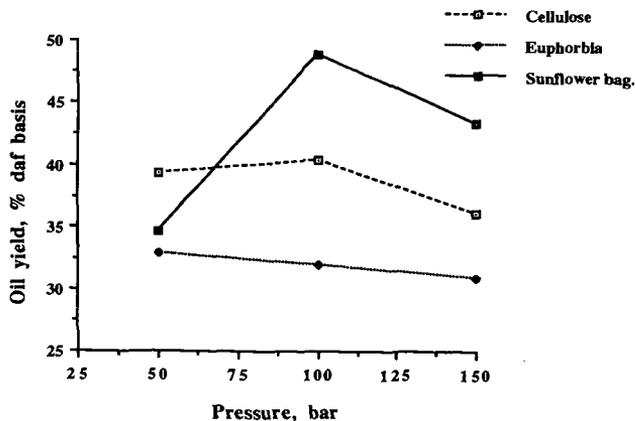


FIGURE 4 EFFECT OF HYDROGEN PRESSURE ON CONVERSIONS IN FIXED-BED REACTOR

Compositional information Table 1 compares the elemental compositions of the pressed bagasse with and an oil obtained from the Heinze retort. The product oil is characterised by a high oxygen content with a somewhat lower H/C ratio than the original bagasse. The typical ^1H NMR spectrum shown in Figure 5 indicates that a significant amount of the aliphatic carbon is still bound to oxygen (peaks in 3.5-5.5 ppm chemical shift range). The fact that most of the aromatic hydrogen intensity occurs in the 6.5-7.0 ppm range indicates that the aromatic species are largely phenolic. In addition to phenols, IR spectroscopy has indicated that carboxylic acids and ketones/aldehydes are also major oxygenates present in the polar fractions from open-column silica gel chromatography. The n-hexane and toluene eluates corresponding to alkanes and neutral aromatics, respectively accounted for 14 and 21% of the n-pentane-solubles. The alkanes and long alkyl moieties which give rise to the characteristic peak at 1.25 ppm in the ^1H NMR spectrum (Figure 5) are probably largely derived from lipids and residual oil in the bagasse. The relatively high nitrogen contents of the sunflower waste-derived oils (Table 1) present the major obstacle to producing hydrocarbon liquid products in two-stage hydrolysis where the tar vapours are passed over a hydroprocessing catalyst.

Figure 6 shows the CP/MAS ^{13}C NMR spectra of the pressed bagasse sample and the pyrolysis and 150 bar hydrolysis chars obtained at 500°C in the fixed-bed reactor. The bagasse still contains an appreciable concentration of lipid material (15-45 ppm) which is the precursor of the alkanes formed during pyrolysis. The lignin aromatic carbons in bagasse account for ca 10 mole%. Both the chars are highly aromatic in character with aromaticities of ca 0.95. However, small peaks at 70 and 180 ppm are evident in the pyrolysis char from residual ether/hydroxyl and carboxyl moieties. From the typical carbon aromaticities of 0.30 and 0.95 for the product oil and char and their respective yields of ca 25 and 35% (Figures 1-3), it is estimated that 40% of the initial carbon has aromatised during pyrolysis at 500°C.

Table 1 Elemental compositions of pressed bagasse, Heinze retort oil and char

	Bagasse (daf basis)	Oil	Char
C	49.6	69.4	77.9
% H	7.4	9.5	2.6
N	4.4	5.1	5.1
O (by difference)	38.5	16.0	14.4
Atomic H/C	1.78	1.63	0.40

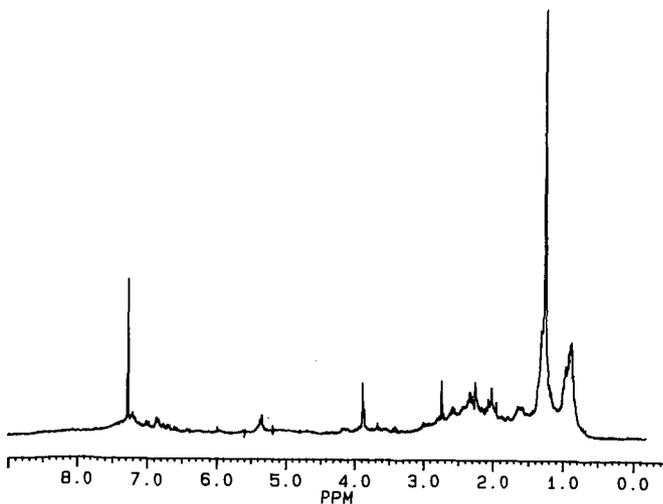


FIGURE 5 ^1H NMR SPECTRUM OF HEINZE RETORT OIL

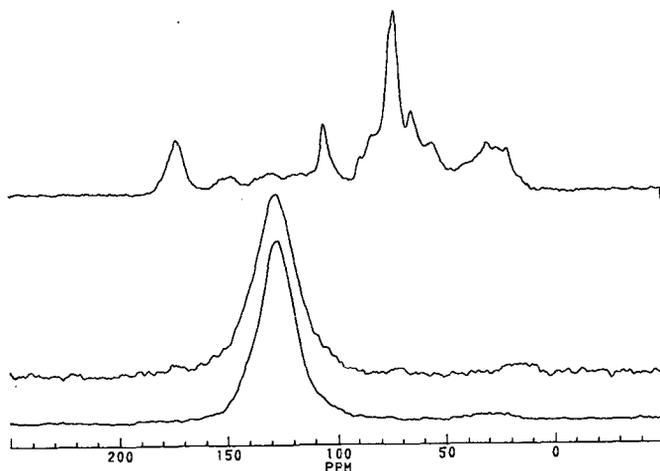


FIGURE 6 ^{13}C NMR SPECTRA OF PRESSED BAGASSE (top), A NITROGEN CHAR (middle) AND A HYDROLYSIS CHAR (bottom)

CONCLUSIONS

In contrast to coals and oil shales, oil yields from the sunflower bagasse were found to be largely independent of particle size (<2 mm) and sweep gas velocity with ca 40% w/w oil (dry basis) being obtained at 450-500°C in both the Heinze retort and fixed-bed reactor. The use of high hydrogen pressures (> 50 bar) increased the oil yields by up to ca 10% w/w but these increases are much greater when expressed on a carbon basis due to the reduced oxygen contents of the oils. Even at low pressure, it has been estimated that ca 40% of the initial carbon aromatised during pyrolysis.

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BIOMASS TO HYDROGEN VIA PYROLYSIS AND REFORMING

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ABSTRACT

Pyrolysis of lignocellulosic biomass and reforming of the pyrolytic oils is being studied as a strategy for the production of hydrogen. New technologies for the rapid pyrolysis of biomass provide compact and efficient systems to transform biomass into vapors which are condensed to oils, with yields as high as 75-80% by weight of the anhydrous biomass. This "biocrude" is a mixture of aldehydes, alcohols, acids, oligomers from the constitutive carbohydrates and lignin, and some water produced during the dehydration reactions. Hydrogen can be produced by reforming the biocrude with steam. A process of this nature has the potential to be cost competitive with conventional means of hydrogen production.

The concept of hydrogen from biomass offers significant opportunities for novel research and development. The use of a renewable resource feedstock is an alternative to conventional means of hydrogen production from petroleum and natural gas. As a consequence, the environmental benefit of zero net carbon dioxide emissions facilitates the approach to a pollution-free energy system.

Two scenarios for the production of hydrogen from pyrolysis oil can be envisioned. One would involve a regionalized system of hydrogen production with small and medium-sized pyrolysis units (<500 Mg/day) providing biocrude to a centralized reforming unit. The alternative is to pyrolyze biomass in a large unit and feed the uncondensed vapors directly to the reforming unit. The first case has the advantage of the availability of cheaper feedstocks, perhaps biomass waste. In the integrated system, however, the costs of condensing the vapors to the oil and transporting them to the hydrogen facility are avoided. The reforming facility can be designed to handle alternate feedstocks, such as natural gas and naphtha, if necessary. Additionally, the biocrude can first be refined to yield valuable oxygenates so that only the residue is used for hydrogen production.

Thermodynamic modelling of the major constituents of the biocrude has shown that reforming is possible within a wide range of steam/compound ratios. Additionally, catalytic reforming of model compounds to hydrogen using a Ni-based catalyst has begun. Existing catalytic data on the reforming of oxygenates has been studied to guide catalyst selection. An initial process diagram for the pyrolysis and reforming operations has been devised, and economic boundary estimates have been calculated.

FAST PYROLYSIS: BIOCRUDE YIELDS AND COMPOSITION

Gasification of solid fuels to yield a mixture of H_2 and CO , followed by shift conversion to produce H_2 and CO_2 , and steam reforming of hydrocarbons are well established processes. Economics of current processes favor the use of hydrocarbons (natural gas, C_2 - C_5 , and naphtha) and inexpensive coal as feedstocks. However, biomass is a potentially cost-competitive feedstock for gasification. An alternative approach to H_2 production begins with fast pyrolysis of biomass.

Recent advances in the understanding of pyrolytic mechanisms and in the technology needed to achieve high heat transfer rates to particles, while controlling secondary cracking reactions responsible for gas and char production, have led to the development of fast pyrolysis routes. These convert biomass materials in high yields (~ 75% wt of dry biomass) into a "pyrolytic oil," or "biocrude." Very little ash and char are present in the biocrude when appropriate filtration technology is used in the pyrolysis process. Results from fluid bed fast pyrolysis (Radlein et al., 1991) have shown that a 76% wt yield of biocrude can be obtained from poplar ($CH_{1.47}O_{0.67}$). The organic fraction of the biocrude represents 85% wt and its elemental composition is $CH_{1.33}O_{0.53}$. Table 1 shows the expected yields of hydrogen from two thermochemical routes (pyrolysis and gasification), compared to the theoretical yield of the reaction between wood and steam using externally supplied heat.

Table 1: Comparison of H₂ yields from biomass process routes

Process Routes	Yield of Hydrogen (% wt biomass)	Energy Content (HHV) of H ₂ , Energy Content of Biomass
Pyrolysis + Catalytic Reforming	12.6	91%
Gasification + Shift Conversion	11.5	83%
Biomass + Steam + External Heat (Theoretical Maximum)	17.1	124%

Calculations were made using current yields for non-optimized fast pyrolysis (Radlein et al, 1991) and gasification (Probststein and Hicks, 1982) processes, and the theoretical maximum for the indirectly heated gasification process. The H₂ production potential for these two routes is similar. However, the pyrolysis process is less severe and does not require an oxygen supply as in gasification. Both options require steam for the reforming and shift conversion steps.

Three technologies appear to be capable of achieving high yields of biocrude:

- Fluid beds (Piskorz et al, 1988): 450°C-550°C, < 0.5s
- Entrained beds (Graham and Freel, 1988): ~650°C, < 1.0s
- Ablative reactors, i.e. vortex (Diebold and Scahill, 1988): 450°C-625°C, < 1.0s

In these technologies, 55-70% wt of mf biomass is the organic fraction of the biocrude, and 5-15% wt is water. A fourth, vacuum pyrolysis, has also demonstrated the ability to produce high biocrude yields (Roy et al, 1990); the organic fraction represents 50-60% wt of mf biomass and water 13-16% wt. Reliable values of oil, water, char and gas yields are difficult to obtain because of unclosed and/or unreported material balances. The composition of typical oils from poplar has only been reported in quantitative detail by the University of Waterloo, Canada (Piskorz et al, 1988), and is shown in table 2.

Table 2: Pyrolytic Oil Composition Derived from Poplar (Radlein et al, 1991)

<u>wt % mf wood</u>	
Oil*	65.8 Oil + Water = Biocrude
Water*	12.2
Char	7.7
Gas	10.8
Unaccounted	3.5
<u>Composition of the Oil</u>	
Acetic Acid	5.4
Formic Acid	3.1
Hydroxyacetaldehyde	10.0
Glyoxal	2.2
Methylglyoxal	0.65
Formaldehyde	1.2
Acetol	1.4
Ethylene Glycol	1.05
Levogluconan	3.0
1,6-Anhydroglucofuranose	2.4
Fructose	1.3
Glucose	0.4
Cellobiosan	1.3
Oligosaccharides	0.7
Pyrolytic Lignin	16.2 Material precipitated by addition of water
Unidentified	15.5

Variations in the composition of pyrolysis oil should be expected as a function of raw material, pyrolysis conditions (T, t, and dT/dt), and the use of catalysts during the pyrolytic step. However, the biocrude is essentially a mixture of two major acids, aldehydes and alcohols plus a significant fraction of lignin. Based on the works of Antal (1982), Shafizadeh (1982), and Richards (1987), the unidentified compounds should contain a large number of

carbohydrate-derived components. Monomeric lignin-derived products having alcohol characteristics should also be present (Elliott, 1988).

THERMODYNAMICS

Thermodynamic simulations of the reforming reaction were performed in order to guide experimental design and determine equilibrium constraints. These simulations were performed on ASPEN Plus using a mixture of compounds with the following composition, based on the results obtained by the University of Waterloo and from the vortex reactor at NREL.

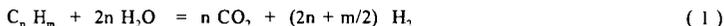
Table 3: Mixture Composition for Thermodynamic Simulations

Compound	Molar Percent	Weight Percent
hydroxyacetaldehyde	38%	33%
acetic acid	27%	23%
acetol	9.3%	9.8%
guaiacol	3.7%	6.6%
syringol	1.4%	3.3%
formic acid	7.5%	4.8%
coniferol	2.6%	6.6%
phenol	2.4%	3.3%
benzene	2.9%	3.3%
toluene	2.5%	3.3%
furfural	2.4%	3.3%

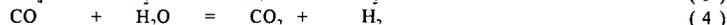
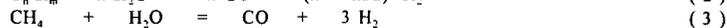
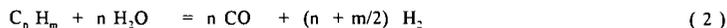
The plots of hydrogen production versus temperature and the molar ratio of steam to carbon content (S/C_1), were very similar for all compounds and the mixture. Because pyrolysis oil vapors are produced at approximately 450 - 600 °C, a practical temperature for the reforming reaction is 500 °C. Figure 1 shows the approach of many of the model compounds and the mixture of compounds to maximum stoichiometric yields of hydrogen as a function of (S/C_1). The necessary steam is dependent only on the carbon content of the compound. Therefore, regardless of the compounds in the oil, the appropriate amount of steam for high hydrogen yields can be estimated solely from the empirical formula.

CATALYTIC REFORMING OF OXYGENATES

Steam reforming of hydrocarbons (C_1 - C_5 , naphtha and gas oils) is well understood and proceeds readily at steam to carbon ratios (S/C_1) between 3.5 and 5.0, and temperatures up to 775°C. When the objective is to maximize the production of H_2 , the stoichiometry describing the overall process is:



However, in a hydrocarbon reformer, the following reactions take place concurrently:



Reforming of higher hydrocarbons (Equation 2) is irreversible (Tottrup and Nielsen, 1982), whereas the methane reforming reaction (Equation 3) and the shift conversion reaction (Equation 4) approach equilibrium. A large molar ratio of steam to hydrocarbon will ensure that the equilibrium for reactions (3) and (4) is shifted towards H_2 production.

The most commonly used catalyst is Ni on alumina. Ca, K and Mg are often used with the alumina to enhance water adsorption, lower the acidity and favor mobility of the OH species on the surface (Rostrup-Nielsen, 1984). Alternate Ni-based catalyst formulations with mixtures of rare earth oxides and a refractory support, have been developed (Patil, 1987) to increase the resistance of the catalyst to poisoning, particularly by sulfur.

Methanol is readily steam reformed at low temperatures (< 300°C). Cu-based catalysts and recently developed Pd/ZnO preparations are extremely selective towards the formation of CO_2 and H_2 via the formate ester mechanism (Takahashi, 1982). Ethanol requires higher reforming temperatures than methanol. The mechanism proceeds through acetaldehyde and ethylacetate

intermediates on the same Cu-based catalysts (Iwasa-Takezawa, 1991). The existing data on oxygenated aromatic compounds, i.e. cresols, suggest that they can be steam reformed using Pd, Rh or Ni on alumina, silica or chromia-alumina. Little is known, however, about optimum experimental conditions that will result in long-term catalyst activity. The challenge lies in finding a catalyst that can reform both the complex fraction (pyrolytic lignin) as well as the carbohydrate-derived fractions (monomeric sugars, anhydrosugars, and oligomers) while limiting undesirable side reactions which will lower the yields of H₂.

If the oxygen in the aldehydes, alcohols and acids could be removed as CO₂, via ester intermediates as in methanol reforming, the production of H₂ would be maximized. This could be done by separating a low molecular weight fraction of the biocrude from a high molecular weight fraction during the condensation of the pyrolytic vapors. An alternate approach is to conduct the steam reforming of the entire biocrude near equilibrium conditions. This may be possible by choosing a stable Ni-based catalyst operating in the 700°-800°C range. A favored formulation could be: NiO (20-30 wt%), MgO (10-15 wt%), Al₂O₃ (50-65 wt%), rare earth oxides (5-15 wt%), and a promoter like Cr₂O₃, V₂O₅, or WO₃ (5-10 wt%).

PROCESS DESIGN

Unlike other reforming processes, steam reforming pyrolysis oil to produce hydrogen involves very few unit operations, which should increase its economic feasibility. Because of the low sulfur content of biomass, a sulfur removal system is not likely to be required, while one is always used in petroleum and methane reforming. Also, according to current experimental results, only one medium temperature catalytic reformer is required; conventional methane reforming uses a furnace-like converter followed by a high temperature reformer and a low temperature reformer. Since the overall reaction of pyrolysis oil to H₂ is endothermic, the char produced in the pyrolysis of the biomass will be burned to produce heat and steam. Preliminary energy balances indicate that a fraction of the oil may also be used as a source of heat, especially in the centralized reformer supplied by satellite pyrolysis units. In the base-case design, a pressure swing adsorption unit will be used to purify the H₂ produced.

ECONOMICS

Preliminary calculations were performed in order to determine the boundaries of economic feasibility of the process. To examine these boundaries before plant costs can be figured, the ratio of the current market selling price of H₂ to the pyrolysis oil production cost was calculated. If the ratio is greater than one, the process has the potential to be economically feasible. This method assumes that the process to produce H₂ is completely free of capital and operating costs, and therefore sets the minimum limits on the recovery of theoretical hydrogen and product selling price.

The maximum stoichiometric amount of H₂ was calculated as that obtained by reforming all of the carbon in the oil with steam plus the hydrogen in the oil; the oil was defined to have the formula CH_{1.33}O_{0.33}, as described earlier. The current selling price of H₂ in industry is between \$5.00/MM Btu and \$15.00/MM Btu, depending on the size of the production facility.

For these calculations, the feedstock was considered pyrolysis oil rather than biomass, in order to take into account the cost of the pyrolysis process. The cost of the oil is \$0.141/kg, as calculated in an NREL report by C. Gregoire, on producing pyrolysis oil from biomass for power generation. This study used a biomass cost of \$2.50/MMBtu, which is equivalent to \$42/dry ton. If 70% hydrogen recovery can be achieved, the selling price must be at least \$7.50/MM Btu. If the selling price is \$8.80/MM Btu, 60% of the H₂ that is available from reforming pyrolysis oil must be recovered to reclaim the cost of the feedstock. Again, these results do not include capital and operating expenses.

Figure 2 shows the combinations of H₂ selling price and feedstock cost that will result in a ratio greater than one. Hydrogen from pyrolysis oil has the potential to be economically feasible if costs fall within the shaded region. This graph assumes that 70% of the maximum stoichiometric H₂ will be recovered. The pyrolysis oil cost will depend heavily on the cost of the biomass; a regionalized system to produce oil for a central hydrogen facility could utilize waste biomass which would bring down the cost of the oil considerably.

Figure 1: Approach to Maximum Stoichiometric Yield of Hydrogen at 500 °C

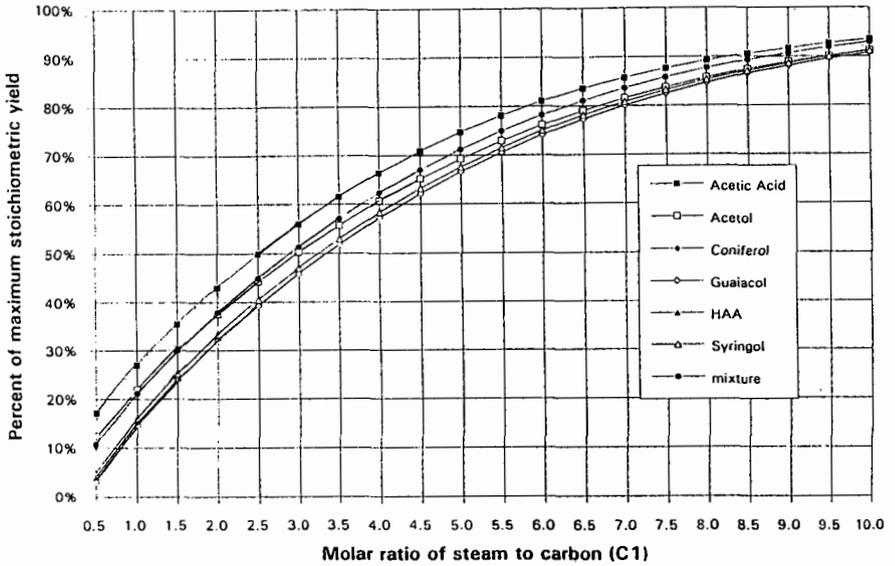
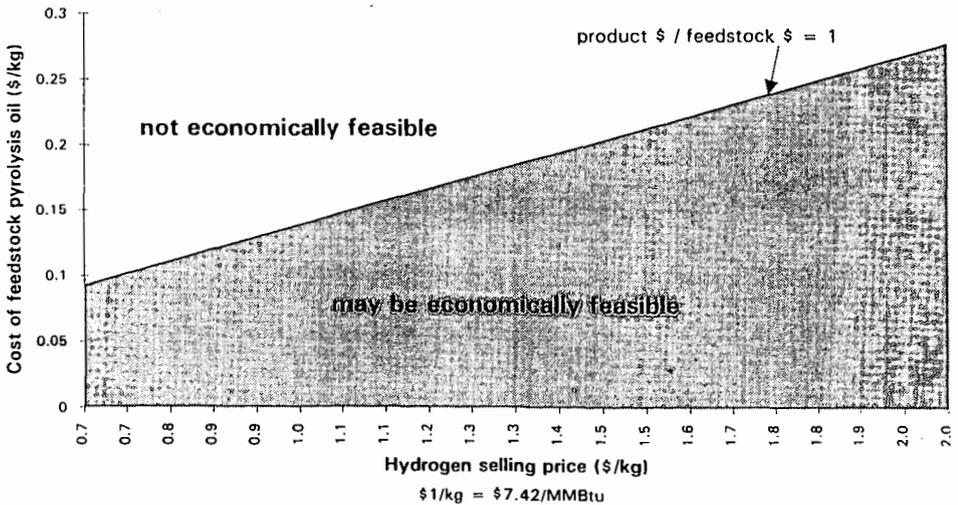


Figure 2: Limit on Potential Economic Feasibility of Hydrogen from Pyrolysis Oil at 70% Stoichiometric Maximum



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CONVERSION OF FATTY ACIDS AND ESTERS TO LOW-AROMATIC GASOLINE

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ABSTRACT

Agricultural oils and by-products have been used as fuels, but they can also serve as precursors for producing transportation fuels that require a highly isoparaffinic composition for high performance. Hydrocracking and reforming of biomass materials to the isoparaffinic composition desired for gasoline are reported in this paper. Several catalysts, including natural and synthetic clays, have been effective for conversion of fatty acids and triglycerides to high-quality gasoline products. Reactions with nickel-substituted synthetic mica montmorillonite gave high yields of distillate in the gasoline range. A high percentage of the product was isoparaffinic or branched alkanes (55%–61%) and a low percentage was aromatic. Rapeseed oil was converted to a highly isoparaffinic product with minimal formation of benzene or toluene. These product compositions are appropriate for transportation fuels with low environmental risks.

INTRODUCTION

Fuels derived from renewable resources currently comprise only a small proportion of the total fuel utilized in the U.S. Renewable biomass-derived fuels recycle carbon so that fuel combustion does not contribute to the accumulation of carbon dioxide in the atmosphere. Other advantages are the consistency of the energy supply in U.S. and even regional markets. Further development of liquid fuels for use in high-performance engines from renewable energy resources is needed. In order to be environmentally acceptable, the transportation fuels must contain very low amounts of benzene and other aromatic components. Catalytic methods are needed for converting crop oils to a low-aromatic fuel. The use of waste oils from vegetable oil processing or cooking and tall acids from paper pulping has the potential for producing a low-cost fuel.

The conversion of tall and vegetable oils to alternative fuels with zeolite catalysts resulted in products containing very high concentrations of aromatic components (1–6). The objective of our investigations is to evaluate the catalytic conversion of oils and fatty acids to highly aliphatic gasoline-range products. Therefore, we have investigated catalysts and conditions that minimize the formation of aromatics and conserve the high hydrogen content of the fatty raw materials.

Synthetic clays, such as nickel-substituted synthetic mica montmorillonite (NiSMM), were effective for cleaving carbon-carbon bonds and isomerizing the alkyl chains to give branched alkanes, without extensive formation of aromatic hydrocarbons (7–9). Reactions of fatty acids and oils with NiSMM catalyst is reported in this paper.

EXPERIMENTAL

Catalytic Hydrotreating Reactions. Preparation and characterization of NiSMM was reported elsewhere (7–9). In a typical run, 0.5 g of the rapeseed oil or oleic acid and 0.25 g of the catalyst were placed in a 12-mL microreactor. The microreactor was evacuated, pressurized with 1000 psi (6.9 MPa) of hydrogen (corresponding to 28 mmoles), and placed in a rocking autoclave heated to the desired temperature. The gas pressure increased from heating the gas (2400 psi at 400°C) and then increased further, owing to decarboxylation and other gas formation reactions. The heating was continued for 1–3 hours. At the end of the reaction period, the microreactor was cooled to room temperature, degassed, and opened. The desired amount of the internal standard was added to the product slurry, and the product slurry was transferred into a centrifugation tube by washing with methylene chloride and the solid catalyst removed by centrifugation.

Analytical procedures: instrumentation. Identification of the product components in the gasoline range was by retention time measurement on a Petrocol 100-m capillary gas chromatograph (GC) column and by gas chromatography/mass spectrometry (GC/MS) analysis using a Finnigan 800 ITD ion trap detector with a HP 5890A gas chromatograph and a J&W 30-m x 0.32-mm (ID), 1.0-micron DB-5 film.

Quantitative GC/FID analyses were performed with a Hewlett Packard 5880A gas chromatograph equipped with a Petrocol 100-m capillary column. Since it was not found in significant amounts in the reaction products, octadecane was added as the internal standard. Amounts of aromatic components were determined by multipoint calibration of the system with standard mixtures. Alkane components were determined from the area percent ratio with respect to octadecane, assuming the same response factor. To calculate the product molecular size distribution, the quantities of components in two size groups, C₄–C₉ and C₁₀–C₁₇, were added, and are reported as a percentage of the total volatile liquid

product. Quantities of components in the compound type groups, such as n-alkanes, branched and cyclic alkanes, and aromatics, were also added and reported as percentages of the light volatile fraction that includes C₄-C₁₇ components.

GC analyses for higher molecular weight volatiles were obtained using a Quadrex 15-m by 0.25-mm diameter aluminum-clad capillary column with a 0.10- μ m methyl 5% silicone phase with 1.0-ml/min H₂ carrier measured at 400°C and on-column injection. Octadecane was added as the internal standard. Amounts of compounds in the range C₁₀-C₇₀ were determined from the area percent with respect to octadecane and are reported as a percentage of the total volatile product. Total volatile yields were determined by adding the quantities in the three ranges or fractions described above. These are reported as weight percent yield of oleic acid starting material.

RESULTS

Catalytic hydrocracking/hydroisomerization reactions were conducted with a crop oil and a by-product oil to evaluate the potential for synthetic clay catalyst upgrading to environmentally acceptable transportation fuels that contain large amounts of branched alkanes (isoparaffins) and low amounts of aromatics. The crop oil was inexpensive rapeseed oil, a triglyceride that contains large amounts of inedible erucic acid. The paper pulping by-product, tall oil, is composed of several fatty acids (mainly oleic and linoleic acids), resin acids, and sterols. Oleic (9-octadecenoic) acid was used as a model substrate in preliminary studies to determine appropriate conditions for the tests. Two synthetic clay catalysts were used in the reactions. In all the tests, the conversion of the oleic acid to liquid and gas products was 100%, and no coke or insoluble materials were detected on the recovered catalyst.

Noncatalytic Reaction. The noncatalytic reaction of oleic acid was performed to determine the nature of the products and yields for the thermal reactions of fatty materials at 400°C under hydrogen atmosphere. Only a minor portion (26 wt%) of the products consisted of volatile liquids. Analyses showed the presence of large amounts of alkanes higher than C₁₈ (63% of the volatile liquid material). Very small amounts of gasoline-range components (9% of volatile liquid) were produced. The high molecular weight compounds are dimers and other oligomers that are normally found in fatty acid pyrolysis products. Other alkane products resulted from secondary cracking reactions of the oligomeric materials, but very few branched alkanes were formed. The majority of product from the uncatalyzed reaction was nonvolatile polymeric material, since it did not appear in the GC analyses. Thus, the noncatalytic thermal hydrolysis of oleic acid at moderate temperature does not effectively produce a usable fuel for a high-performance engine.

Reactions with NiSMM Catalyst. The NiSMM-catalyzed hydrocracking reaction of oleic acid was carried out under several conditions to determine the effects of temperature, hydrogen pressure, and reaction time for production of low-aromaticity gasoline. The reaction products were a complex mixture of hundreds of components formed as a result of the extensive rearrangements or isomerizations of the primary cracked or oligomeric products. The major products from the synthetic-clay-catalyzed reactions were the desired isoparaffins: mono-, di- and trimethylalkanes.

The reaction of oleic acid with NiSMM at 400°C for 1 hour with 2400-psi-hydrogen pressure gave a high yield (80 wt%) of volatile liquid products. A large percentage of the product (69%) was in the gasoline range. High-resolution GC analysis indicated that the gasoline-range materials were composed mainly of branched alkanes and cycloalkanes (78%), with lower amounts (8%) of n-alkanes. Small amounts of aromatics were present, with only 8% BTEX in the liquid product.

The reaction period for oleic acid with NiSMM catalyst was extended to 3 hours to determine if the longer time would give higher yields of liquids in the gasoline range. The reaction for the 3-hour period also gave a high yield of liquid product (76%), but the distribution with respect to molecular size was similar to the reaction carried out for 1 hour (72% in the gasoline range). More importantly, the composition of the gasoline-range product was more aromatic than that from the 1-hour reaction, with 20% BTEX present. Thus, the longer reaction time period resulted in a less desirable product because of the higher aromatic content.

The reaction of oleic acid with the NiSMM catalyst at a lower temperature might be expected to give a less aromatic product. At 350°C for 3 hours with 2200-psi-hydrogen pressure the reaction gave 76% conversion to volatile product. Low aromatic content was obtained (9% BTEX), but a lower percentage of the volatile liquid product (56%) was in the gasoline range. Despite the lower yields at this lower temperature, the NiSMM catalyst exhibits good selectivity for the hydrocracking and hydroisomerization reaction of the aliphatic chains.

Rapeseed Oil Reaction. Rapeseed oil was reacted with the NiSMM catalyst at 400°C for 1 hour with 2240-psi-hydrogen pressure. The conversion to volatile liquid was a little lower than that obtained with oleic acid (58%). High molecular weight ($> C_{18}$) material was absent, indicating that fewer dimerization or condensation reactions occurred with the triglyceride oil than with the free oleic acid. A higher yield of gas product was obtained with the rapeseed oil, compared to the oleic acid. A possible explanation for these yield results is that the catalyst remained more active in the rapeseed oil reaction.

The composition of the product from rapeseed oil was much more isoparaffinic than that obtained from the oleic acid. Only 4% n-alkanes were present, and branched alkanes comprised most of the product (90%). The aromatic content was very small, BTEX accounted for only 6% of the liquid product, and the benzene concentration was only 0.7%.

CONCLUSION

Conversion of biomass fuels containing fatty acids to a highly calorific and environmentally acceptable fuel can be effected by catalytic processing. In the NiSMM-catalyzed reactions described in this paper, the aliphatic nature and inherent large hydrogen content of vegetable oils is mostly preserved, and the structures were mostly isomerized to isoparaffinic molecules. Thus, not only was a high-performance fuel produced, but also one with low benzene content and consequently low toxicity. Previous investigations of vegetable oil conversions to fuels with shape-selective zeolite (HZSM-5) catalyst gave liquids that were highly aromatic (60%–70% aromatic content). Yields were similar to those reported here.

Coaddition of steam and tetralin could improve the conversion substantially at moderate temperatures (3–5). Steam addition also improved catalyst life and produced less coking.

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CATALYTIC UPGRADING OF BIOCRUDE OIL VAPORS TO PRODUCE HYDROCARBONS FOR OIL REFINERY APPLICATIONS

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keywords: biomass pyrolysis to vapors; catalysis of biocrude vapors to hydrocarbons; zeolite catalysis.

BACKGROUND

Historically, liquid transportation fuels have been processed from petroleum crude oil through a series of chemical processes in a refinery. Initially, the refinery was little more than a distillation tower that made gasoline, kerosene, fuel oils, and asphalt. Over the last 90 years, this industry has become increasingly complex as the public demanded higher octane gasolines; removing tetraethyl lead; reducing aromatics and olefins; reducing vapor pressure; adding ethers and alcohols to promote cleaner burning; and in the future, completely reformulating gasoline to burn even cleaner. As a result of these changes, refiners have already begun to look at using commodity chemicals as a significant fraction of the gasoline pool, e.g., methanol, ethanol, methyl tertiary butyl ether (MTBE), and ethyl tertiary butyl ether (ETBE). This means that refiners are already incorporating non-traditional feedstocks into the gasoline pool.

Because methanol is made through a syngas route, any form of carbon can be used to produce the syngas and therefore the methanol. Although ethanol can be made from ethylene, it is now made commercially by fermentation. These alcohols are currently purchased from the chemical industry to produce MTBE or ETBE in many oil refineries. The interest in producing MTBE within the oil refinery goes back to the reduction of gasoline vapor pressure that resulted in a surplus of butanes at the refinery. These butanes can be converted to the isobutene needed to make MTBE within the refinery in a new process step that is now being widely practiced.

It has been widely predicted that the demand for MTBE or ETBE will exceed the availability of isobutene within the refinery. Ethers made from other feedstocks are now being investigated, e.g., diisopropyl ether (DIPE) made from propene and water, as well as tertiary amyl methyl ether (TAME) made from reactive isopentenes and methanol. However, there will be competition within the refinery for the propene and the isopentenes to react with isobutane to make the isoparaffinic alkylates (Unzelman 1994). It appears that the time may be right for refiners to begin to consider alternative sources of olefins.

The threat of global warming, the current discussion about the capacity of the American farming industry, and the increased dependence upon oil imported from politically unstable parts of the world all combine to create an interest in alternative fuel sources. An alternative fuel source that is commonly overlooked by the petroleum industry is renewable biomass. Currently research is underway to develop agricultural crops for their energy content. Although these crops are not yet widely available for industrial use, there is a large amount of municipal solid waste (MSW) that is generated on a daily basis that would be suitable for feedstocks.

The organic fraction of the MSW is called refuse derived fuel (RDF). After drying, RDF is composed primarily of paper derived from biomass, yard wastes, polyolefinic plastics, and miscellaneous plastics. Current projections are that the paper fraction will slowly decrease while the plastic fraction will increase with time. By the year 2000, it is projected that RDF will consist of 76 wt% lignocellulosic-derived material and 24% plastics. About two-thirds of these plastics are projected to be polyolefinic. (Franklin 1994) During thermal pyrolysis, these plastics tend to depolymerize to oligomers and monomers. With catalytic cracking, the yield of monomers can be increased, similar to cracking waxes. MSW is available now in commercial quantities and the olefin yields will be higher from RDF than from a typical biomass. Because of the increasing cost of landfilling, the projected costs of the RDF are very low.

As an example, the tipping fee paid by a city to the landfill may be \$25 per ton, from which perhaps half a ton of RDF could be derived. If it were to cost \$30 to recover and prepare this RDF for use as a feedstock, it would have a net cost of \$5 for the half ton or \$10 per ton. This RDF has a heating value of about 10,000 BTU/lb that results in a cost of \$0.55/GJ, \$0.50/MMBTU, or \$2.90 per barrel of oil equivalent. This is clearly a bargain, even in today's depressed oil market. The problems with using RDF are many, but tend to be associated with the unknown minute-to-minute variability of its composition, including heavy metals, sulfur, and chlorine content.

For a variety of reasons, many oil refineries are located near large metropolitan areas along the West, East, and Gulf Coasts. Thus, these refineries are also located near potential sources of large amounts of RDF areas set aside for heavy industry, which should facilitate permitting an additional process. Also, the oil refineries typically already know how to deal with a variety of heavy metals, sulfur, and chlorine found in different crude oils. Using RDF as a feedstock in an oil refinery should pose problems of a chemical nature that are similar to those dealt with now on a day-to-day basis. However, feeding biomass and/or RDF into a refinery involves a different set of problems, which we are now addressing in our DOE sponsored Biofuels Program.

INTRODUCTION

We have developed a thermal cracking or pyrolysis process in which the solid feed is metered into a vortex reactor. An extremely rapid heat transfer to the solid particles through the reactor wall results primarily in the vaporization of the lignocellulosic and thermoplastic feedstock mixtures. Byproduct char is removed from the hot vapor stream. The vapors can then be condensed to form a biocrude oil or they can be passed immediately to a catalytic cracking and deoxygenation reactor. This pyrolysis technology has been demonstrated at the 20 kg/h scale at NREL (Diebold and Scahill 1988) and is being scaled up to the 35 TPD scale by Interchem (Johnson, et al. 1993).

The biocrude oil made from lignocellulosic biomass is a fairly fluid, highly oxygenated, and polar liquid. More than 200 compounds have been identified in the biocrude, but typically at less than 5% each. However, the RDF-derived crude is a multiphase material because of the presence of polar liquids derived from the lignocellulosics and non-polar liquids and solid waxes that represent partially cracked plastics (Diebold, et al. 1989). If the pyrolysis step is integrated into an oil refinery, it is more efficient thermally to close-couple the pyrolysis step to a vapor-phase catalytic cracking step, than to condense the oil and then reheat it for further refining. Because of the highly oxygenated nature of the biocrude, it is a reactive material at elevated temperatures and does not distill well.

The challenge for the agricultural industry of the future will be to develop low cost biomass crops that have high hydrocarbon or lipid contents, which in turn would have high olefin yields in the process discussed here. In the mean time, a process that can convert RDF containing mixed plastics, paper, and yard wastes to an olefin rich stream has a niche market application that may have good economic potential. Initially using low cost RDF in this process will pave the way for the eventual use of more expensive, dedicated feedstocks produced by the agricultural industry.

This paper discusses the process of catalytically deoxygenating and cracking biocrude vapors to form hydrocarbons. The reaction of several oxygenated organic compounds over zeolite catalysts, especially ZSM-5, has been studied and reported in the literature, e.g., methanol, ethanol, acetic acid, acetone, methyl acetate, fatty acids, triglycerides, phenols, and carbohydrates. In general, the reactions that take place over ZSM-5 are those that result in forming hydrocarbons by the rejection of oxygen from the oxygenated feedstock as carbon oxides or as water. The oxygen-rejection mode is strongly dependent upon the feedstock. For example, water is rejected from methanol, carbon monoxide and water are rejected equally from propionaldehyde on a molar basis, and carbon dioxide and water are equally rejected from acetic acid on a molar basis (Chang and Silvestri, 1977) (Chen, et al., 1989).

Using the ZSM-5 catalyst (donated by Mobil) to crack the pyrolysis vapors made from biomass (Evans and Milne 1988) and from RDF (Rejai, et al 1991) has been extensively studied at NREL, using a molecular beam mass spectrometer (MBMS). With this analytical technique, the vapor effluent from a reactor containing 1 gram of catalyst can be followed in real time, with several scans per second. This allows the study of transient and steady-state products from the catalytic reactor over a range of molecular weights from near zero to several hundred.

EXPERIMENTAL

A larger reactor containing 100 g of Mobil's extruded ZSM-5 catalyst was used to study the conversion of a 1 to 3% slipstream of pyrolysis vapors made with the vortex reactor. This reactor was fitted with an axial thermocouple well and originally with a thermocouple that could be moved axially. This single thermocouple was replaced with a bundle of 12 miniature thermocouples with a 2.54 cm axial spacing. The reactions of the biomass vapors over the ZSM-5 were mildly exothermic with temperature rises of about 20°C commonly seen. These temperature rises correspond to about 75 J/g of biomass fed or the equivalent heat release of the combustion of 0.2 g of coke per 100 g of biomass fed. The gradual decline in the catalyst activity was monitored by the movement of the exothermic temperature profile down the bed, as it "band-aged." A series of experiments at different temperatures showed quite dramatically that when steam was used as the carrier gas, the rate of band-aging was reduced at higher operating temperatures to become relatively low at 525°C. This rate of catalyst deactivation is relatively high for fixed-bed operation, but is very low for riser cracker operation. The catalyst was repeatedly regenerated by controlled air oxidation. Gas analysis was by gas chromatography (GC). The mass balance of Run 119 for the slipstream reactor system is shown in Table 1.

The fixed-bed reactor was then scaled up to be large enough to be fed the entire output of the vortex pyrolysis reactor. It has a diameter of 25 cm, a bed height 30 cm, and 7500 to 8500 g of ZSM-5 extrudate donated by Mobil. This reactor was originally fitted with an axial thermocouple well into which a bundle of 12 miniature thermocouples was placed, with an axial spacing of the thermocouples of 2.54 cm.

RDF was obtained from the MSW facility at Thief River Falls, MN, to be used as feed for the vortex pyrolysis reactor coupled to the large catalytic reactor. This RDF results after removing recyclables and non-organic materials. In Run 142, the oven dried, plastics-containing RDF was fed initially at a rate of 10 kg/h with a carrier-steam-to-RDF weight ratio of 2. The exothermic reactions appeared to take place near the entrance of the bed, with an exotherm of 15 to 20°C measured 2.5 cm into the bed. This exotherm corresponded to a heat of reaction of about 100 J/g of RDF. The feeding rate was then increased to 15 kg/h with a steam-to-RDF weight ratio of 1.3. Because of this decrease in the relative amount of steam present to absorb the heat of reaction, the temperature was seen to increase an additional 15°C. The heat of reaction was calculated to be a slightly higher value of 130 J/g of RDF for this higher feeding rate. However, the exotherm was still appearing in the first 2.5 cm of the 30 cm bed. The rest of the bed exhibited a slight cooling and then a slight exotherm near the outlet of the bed. We speculate that three sequential global reactions could be taking place that would have a net exothermic, endothermic, and finally exothermic effect. However, the temperature measuring arrangement was subject to apparent conductive errors that were progressively more severe in the last 7.5 cm of the reactor. These errors were because of a combination of poor convective heat transfer from the axially flowing gases and heat conduction and radiation to the cooler exit flange of the reactor (which was massive and difficult to heat). Gas analysis was by GC. The yields from this run are shown in Table 1. We think that the plastics content of the RDF contributes to the relatively higher yields of olefins.

This reactor was later modified by adding 12 gas sampling tubes at 2.54 cm intervals along the reactor length. Each sampling tube penetrated two-thirds across the reactor diameter. Projecting a millimeter past the entrance of the sampling tube was a thermocouple to measure the local temperature, with the thermocouple serving to reduce the volume of the sampling port. The sample ports were angularly spaced in a helical fashion to minimize their interaction. With the thermocouples heated directly by cross-flowing gases at 15 cm from the reactor wall, the conduction errors were greatly reduced. In addition, three thermowells were installed on diameters to allow the diametrical temperature gradient to be followed with a bundle of eight miniature thermocouples spaced 2.54 cm apart. With just carrier gas passing through this large fixed-bed reactor and with thermocouples from one manufacturer's lot, the helically spaced thermocouples showed that an isothermal bed could be maintained to within $\pm 1^\circ\text{C}$. With this reactor, the progress of the conversion of the pyrolysis vapors as a function of the amount of catalyst encountered could be monitored by temperature measurements and gas samples. Thus, 12 different space velocities could be evaluated in a single experiment. Each sample port was fitted with an evacuated sample bottle so that the samples could be taken manually at essentially the same time in the run.

An example of using the modified large fixed-bed reactor was Run 144. This run used oven-dried Southern Pine sawdust at a feeding rate of 15 kg/h. The steam-to-biomass weight ratio was 1.33. The weight hourly space velocity varied from 19 at the first sampling port to 1.6 at the twelfth sampling port. The initial bed temperature prior to the start of feeding the sawdust was 520°C. The temperature profile through the bed was different than had been measured for the smaller 100-g reactor using an axial thermowell. The temperature profile in this run with wood showed a steady

increase in temperature over the length of the bed. This is indicative of exothermic reactions occurring throughout the bed. The initial temperature rise was 91°C and gradually decreased to 46°C after two hours of operation. These increases in temperature corresponded to exothermic reactions on the fresh catalyst of about 350 J/g of wood fed and on the partially deactivated catalyst of about 175 J/g after two hours on stream. It has been reported that with methanol as feed, ZSM-5 has an initially high rate of coke formation, followed by a long period of a lower rate of coke formation, while slowly losing activity (Bibby, et al. 1986). GC analysis of gas samples taken 43 minutes into the run showed that most of the methane, carbon monoxide, and carbon dioxide were formed in the first 3 cm of the 30 cm long bed. At 113 minutes into the run, the catalyst showed some deactivation and these permanent gases were produced in the first 10 cm of the bed. The olefin yields were shown to steadily increase throughout the bed, but the overall olefin yield appeared to decrease as the experiment progressed. The overall olefin yields were about 5 to 6 wt% of the wood fed. We speculated that the initially observed high heat of reaction corresponds to an initially high rate of coke deposition on the catalyst, as well as to a lowered activity with time toward the more refractory compounds in the vapor stream.

DISCUSSION AND CONCLUSIONS

The limited operation of the 100 and the 8500 g fixed-bed reactors demonstrated general agreement with operating the 1 g reactor used in the MBMS experiments. Operating the larger reactors is not considered to have been sufficient to optimize the yields. However, we demonstrated that the overall reactions of the RDF and the wood vapors over ZSM-5 catalyst are slightly exothermic in nature, which was not observable with the 1 g reactor. The largest reactor appeared to be more adiabatic to result in higher temperatures from the reactions. The heat of reaction appears to be about 175 to 350 J/g of wood and 100 to 135 J/g of RDF. Much of the variation in the calculated heat of reaction is thought to be because of different products being made by the catalyst at different activity levels.

These heats of reaction are relatively small and correspond to the heat that would be released by the combustion of less than about 1 g of coke per 100 g of feed. However, the exothermic reactions have a very large impact on the design of a riser cracker. In the cracking of petroleum in an FCC refinery unit, the overall reactions are quite endothermic. This heat requirement is met by burning off some coke from the catalyst after each time the catalyst passes through the catalytic riser cracker in the FCC unit. This balance of heat around the FCC unit poses operational requirements, which dictates the rate of catalyst circulation and reduces the amount of heat that can be recovered from the catalyst regenerator. With an exothermic reaction taking place in the case of cracking pyrolysis vapors, the rate of catalyst circulation is dictated only by the chemistry involved, not a tradeoff of the chemistry against the energy balance.

With a fixed-bed reactor, there must be extra catalyst present to allow for some catalyst deactivation to occur prior to taking the bed out of service for regeneration. If the purpose of the reactor is to take the products toward thermodynamic equilibrium, there is no loss in the intended products by exposure to the added catalyst. However, at the high temperatures we must operate to minimize coke formation, any olefins initially formed are being rapidly converted irreversibly to aromatics (Chen, et al. 1989). Thus, if the preferred products are olefins for manufacturing reformulated gasolines, rather than aromatics, it is desirable to have just enough catalyst present to prevent breakthrough of the unwanted pyrolysis materials. In a riser cracker, this can be easily accomplished by simply adjusting the relative rate of catalyst circulated to the feeding rate. The non-steady state operation of a fixed-bed reactor undergoing rapid catalyst deactivation would tend to upset any downstream processing. For these and other reasons, the petroleum refining industry moved from fixed-bed to fluidized-bed catalytic cracking (FCC) about 50 years ago, which in turn evolved into the riser cracker about 40 years ago. The results of the larger fixed-bed reactors presented here were relatively preliminary, but they were used to confirm the conclusion that the preferred cracking reactor for pyrolysis vapors would be a more complex riser cracker.

We have constructed a catalytic riser cracker matched to the output of the vortex pyrolysis reactor. We currently are in the final stages of shakedown and expect to be generating experimental data very shortly. We will be evaluating the use of different feedstocks, e.g., wood, a uniform plastic-coated paper, real RDF, and a biomass naturally containing large amounts of oils or waxes for producing hydrocarbons of interest to petroleum refineries.

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Table 1. Yields from Upgrading Pyrolysis vapors with Mobil's ZSM-5 catalyst

	<u>Run 119</u>	<u>Run 142</u>
Feed	So. Pine	RDF
Catalyst bed size, g	100	7500
H ₂ , wt % of dry feed	0.1	0.3
CO	15.4	20.8
CO ₂	8.1	16.7
CH ₄	1.1	1.9
C ₂ -C ₄	3.6*	10.7*
C ₅ + gasoline	8.8	4.9
Fuel Oil	13.2	4.3
Pyrolysis Char	15.1	19.8
Coke on catalyst	9.4	6.8
H ₂ O (by difference)	25.2	13.8
	-----	-----
	100.0	100.0

* 94 wt% olefins

CHARACTERIZATION AND CATALYTIC CONDITIONING OF SYNTHESIS GAS PRODUCED BY BIOMASS GASIFICATION

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Keywords Biomass gasification; hot gas clean up; synthesis gas conditioning; steam reforming

1. INTRODUCTION

Synthesis gas (syngas) is a mixture of carbon monoxide and hydrogen used as a feedstock for methanol, higher alcohols, and Fischer Tropsch hydrocarbon synthesis. Syngas generated by thermal biomass gasification (referred to as biosyngas in this paper) represents a renewable feedstock because alcohol/hydrocarbon combustion returns the carbon and hydrogen to the atmosphere as CO_2 and H_2O . These are converted back into plant material during photosynthesis when new biomass is cultivated. Biomass gasification in this respect is a form of solar energy conversion.

Syngas from biomass gasification cannot be used directly for fuel synthesis because it contains particulate matter, methane, C_2 hydrocarbons, and tar.¹ These impurities cannot be tolerated by downstream catalytic fuel synthesis processes. Unprocessed biosyngas is also unacceptably rich in CO for most syngas chemistry; for example a H_2/CO ratio equal to 0.7 is typical in biosyngas but methanol synthesis stoichiometry requires that H_2/CO be equal to 2 (in industrial methanol synthesis some CO_2 is also added).

The most cost effective way to prepare biosyngas for fuel synthesis is by syngas conditioning.²⁻⁴ This is a direct on-stream process that destroys tars, reduces the level of methane and other low molecular weight hydrocarbons and simultaneously adjusts the H_2/CO ratio. Excess steam from gasification is used to catalytically reform tar and methane and simultaneously adjust the H_2/CO ratio *in-situ*.

A fluidized bed syngas conditioning process using a proprietary catalyst, designated DN-34, is currently being developed in a joint effort between the National Renewable Energy Laboratory (NREL) and Battelle Columbus Laboratory (BCL).^{4,5} DN-34 is active for tar destruction, exhibits water-gas shift activity and contains no nickel. DN-34 has also been tested for more than 50 hours on stream in a gasifier slip-stream reactor at BCL without detectable deactivation.⁵

The effectiveness of DN-34 in syngas conditioning was recently confirmed using the NREL transportable molecular beam mass spectrometer (TMBMS). DN-34 was tested in a slip-stream fluidized bed catalytic reactor attached to the BCL 9 tonne/day indirectly heated biomass gasifier. Real time mass spectra were obtained for unprocessed syngas and syngas processed over DN-34. In addition to methane and other permanent gases, the unprocessed syngas contained aromatic hydrocarbons including benzene, naphthalene, methylnaphthalenes, phenanthrene/anthracene and pyrene, as well as oxygenated aromatic compounds such as phenol and cresol. The oxygenated compounds were essentially eliminated by syngas conditioning, however, some benzene, naphthalene and smaller amounts of higher molecular weight aromatic hydrocarbons remained. This is qualitatively consistent with the results from two separate 50-hour microscale lifetime tests with DN-34 and other, previous, microscale experiments.⁴

This paper discusses the performance of DN-34 measured with the TMBMS and compares these results with the results of microscale tests performed in the laboratory.

2. EXPERIMENTAL METHODS

2.1 Syngas Analysis by Mass Spectrometry

A transportable molecular beam mass spectrometer (TMBMS) has been designed by NREL that can be moved by common carrier to a pilot plant or other engineering scale biomass conversion facility. The instrument weighs about 500 kg and there are about 200 kg of supporting electronics and ancillary instrumentation. The footprint of the TMBMS is approximately 1 m deep by 2 m wide by 1.5 m tall. The TMBMS uses a 1-750 Da quadrupole mass spectrometer with a differentially pumped molecular beam sampling interface and is computer controlled. The TMBMS is based on molecular beam mass spectrometry (MBMS) which uses extractive sampling and mass spectrometric analysis to identify chemical compounds in complex, highly reactive, high temperature process streams and systems.⁶ In addition to reactive systems, particle laden streams can also be sampled.

A sample transfer system was constructed from stainless steel tubing and fittings to interface the TMBMS to the BCL gasifier. Figure 1 shows the transfer line design concept. The combined length of transfer line tubing was about 11 m (36 ft) when installed on the gasifier. Separate laboratory experiments were performed prior to the BCL work to test for possible artifacts in sampling. Based on the results of that work both the raw and conditioned syngas from the BCL gasifier were diluted with nitrogen preheated to 300°C at a ratio of 5:1, and the residence time in the transfer line system was kept to less than one second.

2.2 Microscale DN-34 Lifetime Testing

Microscale tests were performed with a model biosyngas and tar to examine DN-34 deactivation during syngas conditioning. The composition of the model biosyngas is shown in Table 1. For comparison, the table also shows a typical analysis of real biosyngas from the BCL gasifier. Two 50-hour lifetime tests with DN-34 were performed at the Colorado School of Mines (CSM) using a two stage up-flow tubular reactor. The model syngas flow rate was controlled with a rotameter. Separate syringe pumps were used to meter water and model tar. The model tar was a solution of 10 wt % naphthalene dissolved in toluene. Both liquids were vaporized and mixed with the model syngas in a separate vaporizer located just before the catalytic microreactor inlet. The catalytic microreactor was a 1/2 inch O.D. quartz tube with a fritted quartz disk used to support a 2.0 gram DN-34 catalyst bed. The reactor exit lines were heated to approximately 300°C to prevent any condensation. Two gas chromatographs were used; the first to analyze unreacted model tar and the second to determine the concentration of the permanent gases and water. The conditions for the lifetime catalyst tests were: temperature = 815°C; steam in the feed = 40 vol %; and gas hourly space velocity (GHSV) = $2000 \text{ cm}^3_{\text{gas at } 815^\circ\text{C}}/\text{cm}^3_{\text{catalyst}}/\text{hour}$.

3. RESULTS AND DISCUSSION

3.1 Raw Syngas Analysis by TMBMS

Figure 2 is a time trace for the benzene peak (m/z 78) for the second of two raw biosyngas samples taken in real time from the BCL gasifier using the TMBMS. The figure shows how the flow rate (as measured by this trace component) fluctuated over 25 minutes. These data were taken during a shakedown run of the BCL gasifier using hog fuel as the feedstock. Considerable difficulty was encountered in feeding the hog fuel to the gasifier because a continuous dryer had not yet been installed. As a result, the wet hog fuel would bind and jam periodically in the screw feeding equipment, and we think that this is the origin of the large pulse-like fluctuations in Figure 2.

The two arrows in Figure 2 indicate the time interval used to obtain the averaged mass spectrum shown in Figure 3 (the m/z 50-350 tar region for unprocessed biosyngas). The peak intensities are roughly proportional to the relative concentrations of these compounds because they are chemically similar and because the instrument was tuned so that the mass spectral response was approximately constant as a function of m/z .⁷ Therefore, Figure 3 indicates that benzene (m/z 78), toluene (m/z 92), phenol (m/z 94), styrene (m/z 104), cresol (m/z 108), indene (m/z 116), naphthalene (m/z 128), methyl-naphthalene (m/z 142 isomer unknown) and phenanthrene/anthracene (m/z 178) are among the more abundant tar compounds. The tar in Figure 3 also appears to have a greater proportion of benzene and naphthalene, and somewhat lower amounts of aromatic hydrocarbons with 3 rings or greater, or oxygenates such as phenol and cresol. This is expected because the BCL gasifier is operated at approximately 800°C.^{5,8,9} Oxygenates and unsaturated substituted aromatic hydrocarbons (e.g. styrene, m/z 104) are more abundant under conditions of less severe thermal cracking of the pyrolysis vapors formed during the initial stages of biomass gasification.⁸⁻¹⁰ The exact composition of gasifier tar depends on both gasification temperature and residence time.⁹

3.2 Conditioned Syngas Analysis by TMBMS

DN-34 was tested in a slip-stream fluidized bed reactor attached to the BCL gasifier during the hog fuel shakedown run. The total slip-stream flow was about 2.8 m³/h (100 SCFH) and the catalyst was operated at a GHSV of about $2000 \text{ cm}^3_{\text{gas at } 800^\circ\text{C}}/\text{cm}^3_{\text{catalyst}}/\text{hour}$ at a temperature of approximately 800°C. Details of the reactor configuration are reported elsewhere.⁵

Figure 4 shows the mass spectral peak intensities between m/z 50 and m/z 350 for the conditioned syngas stream exiting the fluidized bed slip-stream reactor. Direct comparison of intensities between Figures 3 and 4 should not be made because the exact syngas flow rates in each case were unknown. Comparison of relative peak intensities within each spectrum, however, indicates the composition of tar in that sample. Figure 4 shows that the peak intensities for the aromatic hydrocarbons were reduced, and the substituted aromatic and other hydrocarbon peaks were essentially eliminated, by catalytic conditioning with DN-34. This shows that DN-34 is active for destroying many of the compounds present in biomass gasifier tar, however, benzene, naphthalene and smaller amounts of higher molecular weight aromatic hydrocarbons were detected in the outlet gas. This is consistent with previous microscale activity tests using a synthetic syngas and tar different than that listed in Table 1.⁴ In that work, DN-34 exhibited high activity for cresol, indene, 1-methylnaphthalene and 2-methylnaphthalene destruction at 815°C, with 50 vol % steam at a GHSV = 1500 h⁻¹, but benzene and naphthalene destruction levels were typically 30 and 50 mole % respectively.⁴ We were not able to perform quantitative analysis of the BCL syngas with the TMBMS due to the limited time on-line so exact tar conversion levels are not reported. Future work will address quantitative analysis. Kinetic data are not yet available for DN-34, however lower space velocity operation may improve benzene and naphthalene destruction with DN-34. The small peaks at m/z 55, 73, 91 and 109 in Figure 4 are from water clusters formed from the steam in the syngas sample. They form during adiabatic cooling of the sample gas in the first differentially pumped stage of the TMBMS inlet. Using hot N₂ to dilute the sample gas minimized their formation.

3.3 DN-34 Lifetime Performance and Selectivity

Two 50 hour microscale tests of DN-34 were made using a model syngas and model tar (Table 1). The results from a duplicate lifetime test were essentially identical to the first test. Toluene was not observed in these experiments but benzene (not originally in the feed) was. This is thought to be steam dealkylation of toluene to form benzene and syngas as this reaction has been observed with different catalytic systems.¹¹

Gradual loss in benzene destruction activity was observed during the test. Benzene destruction was initially 95 mole % and decreased to 75 mole % by the end of the 50 hours. Further data were not taken, thus, it could not be determined if catalyst selectivity would continue to change. Naphthalene destruction was essentially complete during the entire 50 hours. The loss of benzene destruction activity in the microscale tests is in contrast with the lack of measurable deactivation seen in earlier slip-stream gasifier tests.⁵ The reason for the difference is not clear at this time. While quantitative comparisons are not possible at this time, the observation that DN-34 exhibits somewhat superior performance for destroying the higher molecular weight aromatic hydrocarbons is consistent with the other microscale experiments⁴ and with the TMBMS work discussed here. This may simply reflect the difficulty in steam reforming more stable hydrocarbons using DN-34. Current efforts in catalyst development are aimed at determining the origin of activity in DN-34 and using this information to guide the formulation improved catalysts.

4. SUMMARY

The NREL transportable molecular beam mass spectrometer (TMBMS) was successfully used to monitor unprocessed and catalytically conditioned biosyngas. Variations in the biosyngas flow rate were attributed to variations in the biomass feed rate. A large number of tar compounds were observed in the unprocessed syngas in addition to the known low molecular weight permanent gases (not shown) including, oxygenated and substituted aromatic hydrocarbons, and polynuclear aromatic hydrocarbons. Catalytic conditioning with DN-34 effectively destroyed the more reactive compounds, but some benzene, naphthalene, phenanthrene/anthracene and pyrene remained.

The results from the gasifier slip-stream experiment are qualitatively consistent with the results of similar experiments performed at the microscale with DN-34, that is stable hydrocarbons (e.g. benzene) are less reactive than oxygenated or substituted aromatic hydrocarbons. The 50-hour lifetime tests indicated that the conversion of benzene gradually decreased during the test period.

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Component	Gasifier Biosyngas (mole %)	Model Biosyngas (mole %)
H ₂	15.8	15.3
CO	23.0	22.6
CO ₂	9.2	8.8
CH ₄	9.1	8.8
C ₂ H ₂	0.4	0.3
C ₂ H ₄	3.0	2.9
C ₂ H ₆	0.3	0.3
TAR	0.2*	1.0**
H ₂ O	39	40

Table 1. Gasifier product gas and model syngas compositions
 * for average molecular weight of 100
 ** 10 wt % naphthalene dissolved in toluene

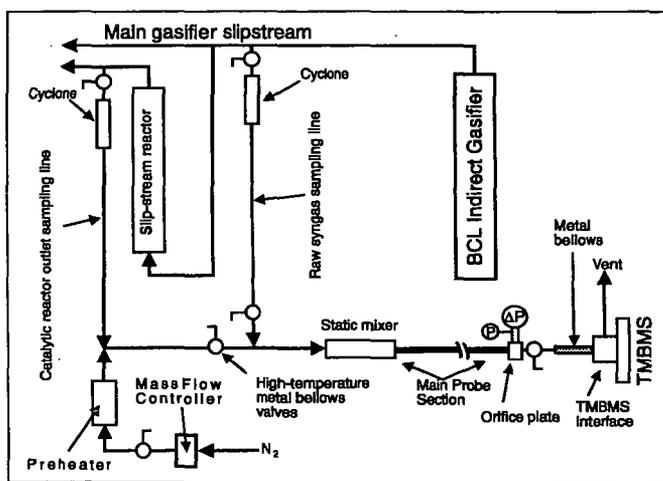


Figure 1. Schematic of TMBMS interface to Battelle gasifier

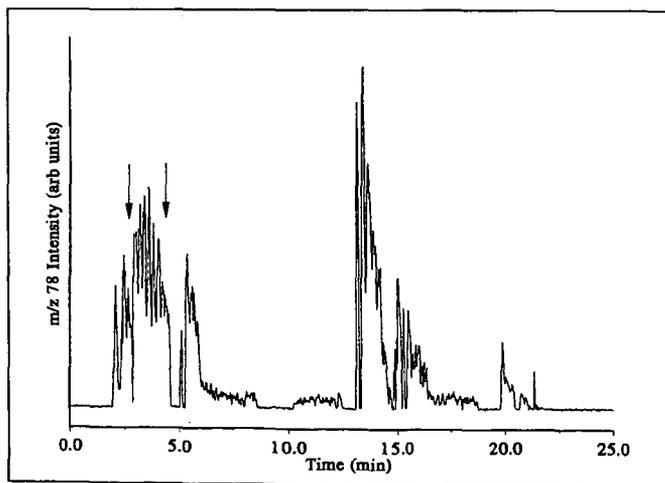


Figure 2. Benzene (m/z 78) intensity vs. time for unprocessed biosyngas

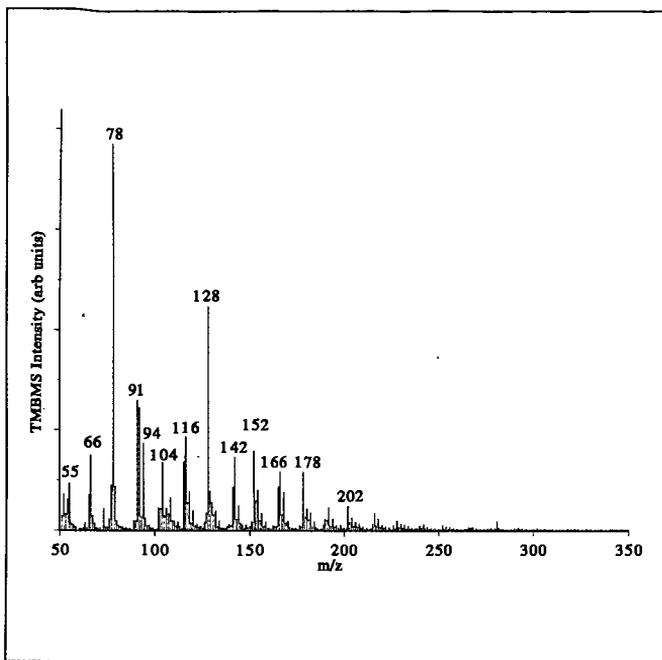


Figure 3. Mass spectrum for raw hog fuel gasifier tar

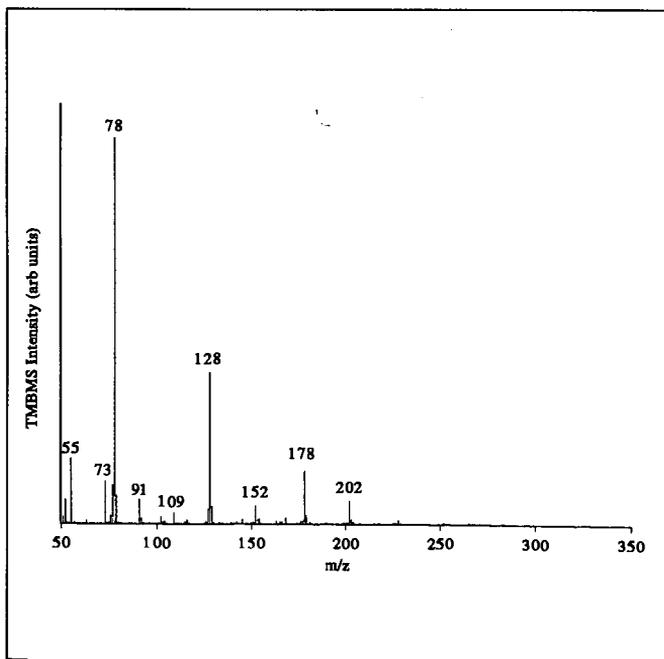


Figure 4. Biosyngas conditioned with DN-34 catalyst

**THE APPLICATION OF GASIFICATION TECHNOLOGY TO PRODUCE
TRANSPORTATION FUELS**

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The genesis of the alternative fuels industry at the end of the 1970's was based on the expectation of ever-increasing crude oil prices throughout the rest of the century. Fortunately, or unfortunately, depending on one's perspective, this has not come to pass. Recent worldwide crude oil prices have dipped to record lows in recent months and the OPEC countries have not demonstrated the ability to cope with the challenges of controlling crude oil production to counter the increases of supply from geographically diverse regions of the world. Further shadowing the energy market is the potential for Iraq to reenter the world market with their crude production and the potential for the former states of the Soviet Union to upgrade and increase the export of crude oil into the world markets to raise much needed foreign currency.

These factors, combined with the significant reduction in federal support for the development of synthetic fuels in the early 1980's, have forced many companies to rethink their original strategy to enter the alternative energy business.

At Texaco, the development of alternative energy sources has been largely focused on gasification technologies that would convert a carbon source like coal and organic waste streams to produce syngas, a combination of primarily carbon monoxide (CO) and hydrogen. These products can be converted to steam and electricity through combined cycle turbines, or converted to methanol or synthetic gasoline as a potential transportation fuel or feedstock for chemical manufacturing. In addition, the application of gasification technologies can be used to provide hydrogen that will be necessary for refiners to produce reformulated gasolines in the future.

While this technology has been repeatedly demonstrated to be technically successful, the economics of the energy market have forced a refocusing of the marketing strategy. The proliferation of environmental requirements on stationary sources of air pollution under the Clean Air Act Amendments of 1990, together with restrictions placed on waste disposal by the federal Resource Conservation and Recovery Act Amendments passed in 1984, has created new opportunities for gasification technology. This technology is ideally suited to produce energy from coal or waste materials that significantly reduce the environmental impacts of coal or waste combustion for power generation.

To quantify the environmental and economic benefits of gasification technology over alternatives, it is necessary to identify the environmental media that are of concern. Air

pollution emissions of particulate matter, oxides of nitrogen (NOx), and sulfur dioxide (SO₂) are the principal air pollution concerns from coal combustion. Carbon dioxide (CO₂) emissions, a greenhouse gas, are not considered an air pollutant; however, they are a concern, given the current commitments by the federal government to reduce the U.S. CO₂ emissions over the next decade. Finally, the generation and disposal of solid waste materials including ash, scrubber sludge, petroleum coke, plastics, municipal wastewater sludge, and industrial waste is an important environmental concern throughout much of the industrialized world.

As will be presented in more detail later in this paper, gasification technologies can present a number of environmental advantages over other methods of coal combustion for power generation or the manufacture of synthetic fuels. Not only are the generation of solid wastes reduced using gasification technology, but the application of gasification technologies can also convert waste materials, including hazardous wastes, to syngas and other desirable forms of energy. Quantifying the value of these advantages is critical to determining the economic attractiveness of any particular gasification technology and its ability to compete.

In comparing a gasification technology with alternatives, it is necessary to establish a set of standard operating assumptions as a common basis. These assumptions are shown in Table 1. Note that these assumptions are based on the configuration of a 250 megawatt power plant and indicate the appropriate coal capacities for the three types of competing technologies -- Texaco advanced gasification with combined cycle electricity generation (TAGCC); pulverized coal with scrubbers (PCWS); and pressurized fluidized bed combustion (PFBC).

Based on the above operating conditions, an estimate of the annual emissions of air pollutants and production of solid waste is shown in Table 2. The information provided is based on emission factors shown in parentheses on the table for each technology. The factors for the PCWS and PFBC technologies are derived from an Electric Power Research Institute Technical Assessment Guideline published in 1991. Emissions factors for the TAGCC technology are derived from work done by Texaco. Using TAGCC technology in lieu of the alternatives provides significant reductions in SO_x, NO_x, particulate matter, CO₂, and solid waste production.

The valuation of these emission reductions is a function of the environmental standards adopted for air pollution limits and waste disposal transportation costs and treatment requirements. These costs can be expected to vary significantly from one location to another.

To provide further insight into this issue of valuation, an Externality Valuation comparison of TAGCC with PFBC and PCWS technologies is shown on Tables 3 and Table 4, respectively. The emissions reduced represent the total emissions stream differential over the twenty-year life of a project. The values per ton are based on an estimate from a study of externality costs conducted by Pace University in 1992 that estimated the cost per ton of emissions reduced for various air pollutants, including CO₂. Solid waste disposal costs assume a twenty-dollar-per-ton transportation charge for disposal. In these tables, the cost numbers are unadjusted for inflation and calculated on a straight-line basis. The emissions and waste reductions achieved from these technologies is substantial. As illustrated in the lower right-hand corner of Tables 3 and 4, the net reduction in cost for TAGCC technology over either of the competing technologies is also substantial. The ability of these savings to offset the additional capital cost requirement for building an AGCC facility is discussed in more detail below.

The capital cost of conventional PFBC and PCWS technologies is approximately \$1000 per kilowatt of electrical generating capacity. TAGCC technology has a capital cost of approximately \$1200 to \$1400 per kilowatt of capacity. This differential amounts to between 50 and 100 million dollars of increased capital cost for constructing a new facility with 250 megawatts of capacity.

To offset these capital cost differentials, it is critical that state and federal regulatory agencies recognize the value of the environmental benefits of gasification technologies over alternative combustion technologies. These costs include the responsibility from cradle to grave for the safe disposal of hazardous components in solid waste, the elimination of air pollution emissions of heavy metal compounds, and a reduction in emissions of oxides of nitrogen and particulate material. This recognition, when translated into government policies that provide incentives for utilities and others to recognize and reduce the real operating costs for waste disposal and air pollution emissions, will continue to make TAGCC technology even more competitive with conventional technologies.

The general public and government agencies will continue to demand actions by industry to produce a cleaner environment. A prudent operator should anticipate these requirements and select a technology that not only reduces the amount of waste generated, but can actually consume hazardous wastes as well.

If a power generating facility is located in an air pollution non-attainment area that requires emissions reductions, a market-based emissions trading system is one mechanism that will provide additional incentive to pursue TAGCC technology over other alternatives.

Tables 5 and 6 compare the potential value of emissions reduction credits over the life of a project for an TAGCC facility versus PFBC and PCWS facilities, respectively. The current cost of solid waste disposal is relatively easy to quantify compared to air pollution emissions reductions credits. For the purpose of this illustration, it was assumed that the slag generated from gasification would incur no disposal cost since this material has value as a saleable commodity. For these cases no disposal costs were included for the PFBC and PCWS combustion technologies beyond a \$20 per ton transportation charge. In addition, no credit was given to TAGCC technology for the recovery of saleable elemental sulfur.

The value of environmental credits, as developed by Pace University, represents reasonable approximations of per-ton control cost for the various pollutants in the United States. It should also be noted that while the United States Government has a stated policy of reducing greenhouse gas emissions, including CO₂ to 1990 levels, the substantial reductions achieved by the TAGCC technology due to its higher overall efficiency were not credited in these cases.

Given the uncertainties in valuing emissions reduction credits, it is difficult to forecast the expected value of these credits at some future date. However, it is not hard to speculate that many regions of the United States will have difficulty demonstrating attainment of the ozone and particulate air quality standards, while continuing to pursue economic growth. These two competing concerns will increase the demand, and, therefore, the value of technologies that can produce emissions reduction credits in the future since the supply of potential credits is limited by the current sources in a region. The requirements for emissions offsets for new and rebuilt sources in most of the U.S. metropolitan areas will also stimulate demand for emissions reduction credits. The same case can be made for expected increases in waste disposal costs as landfill capacity declines over the next decade and increasingly stringent environmental regulations govern disposal of all types of wastes.

Tables 5 and 6 also show the value of this twenty-year stream of credits on a before-tax, discounted cash flow basis, assuming a 10% cost of capital and a 4% inflation rate. Using conservative estimates of emissions credit values, the net present value of these credits would range from 136.8 million dollars to 140.3 million dollars for TAGCC versus PFBC and PCWS technologies, respectively.

Recently, the EPA adopted regulations for reducing emissions of NO_x, a component of ozone formation in the major urban areas, with estimated cost per ton of emissions reduced in excess of \$7,000. These controls are for both motor vehicle emissions and reformulated gasolines that will be required by

early in the next century. These cost-benefit ratios have been determined to be necessary by federal and state regulatory authorities in many regions of the United States. If the Value/Ton Environmental Credits column in Tables 5 and 6 is adjusted to use \$7,000 for NOx reduction and the net present values are recalculated, then the advantage of Texaco's Advanced Gasification Technology increases substantially to range from 209 to 318 million dollars on a before-tax basis as is shown in Table 7.

Texaco's Advanced Gasification Combined Cycle technology can also be used by petroleum refiners in producing federally mandated reformulated gasolines. Because of the limits on gasoline, sulfur levels, and distillation ranges, production of these gasolines will require the expansion of hydrogen-consuming processes like catalytic hydrotreating and hydrocracking. Concurrently, limits on gasoline benzene content will move refiners towards lowering catalytic reformer severities, which will reduce hydrogen production. TAGCC technology can be used to convert low-value petroleum coke, gaseous fuels, and refinery organic wastes to produce electricity, steam, and hydrogen for refinery utilization. This will reduce refiner utility costs, allow for optimization of coker operations through crude oil selection and coker liquids yield, and provide a means of cost effectively disposing of organic wastes produced at the refinery. These multiple benefits are expected to make TAGCC an important technology in the evolution of the refining industry over the next decade.

Conclusion:

Inherently low emissions technologies like Texaco's advanced gasification process that produce significantly lower levels of pollution will have an increasing competitive advantage in the future. An important factor in expanding the commercialization of innovative technologies like Texaco's AGCC is their ability to capture the true value of environmental credits. This ability is, in large part, dependent on the level of support given by state and federal regulatory agencies and policymakers in promoting markets for environmental credits. In many cases, these are the same government agencies that are promoting alternative fuels as clean fuels for transportation purposes.

Texaco's AGCC has the potential to be more cost competitive than current technologies used for electricity generation when environmental benefits are considered. The value of these credits should increase in the future as more areas struggle to balance the demands for environmental compliance with the need for economic growth. It is critical that the private sector work with state and federal regulators to recognize the value of environmental credits by establishing market-based mechanisms that will provide incentives for innovative technologies to emerge.

Table 1
OPERATING ASSUMPTIONS

	Advanced Qualification Comb. Cycle	Pulverized Coal with Scrubbers	Pressurized Fluidized Bed
Capacity - Tons Coal / Day	2,378	2,881	2,766
% Sulfur Removal	99%	95%	95%
Coal HHV - Btu / Lb	10,100	10,100	10,100
Heat Rate - Btu / kWh	8,000	9,700	9,378
Operational Life - Years	20	20	20
Availability %	60.0%	60.0%	60.0%
Annual Availability Hours	7,008	7,008	7,008
Output Megawatts - Mw	250.0	250.0	250.0
Maintenance Hours - Yr	1,752,000	1,752,000	1,752,000
MMS11Us Consumed / Yr	14,016,000	18,994,400	18,430,256

Table 2
ANNUAL EMISSIONS - Tons Per Year

1. BASIS EPRI 1091 TECHASSESSMENT GUIDE DATA
2. BASIS TEXACO TEST DATA

	Advanced (2) Qualification Comb. Cycle	Pulverized (1) Coal with Scrubbers	Pressurized (1) Fluidized Bed
Sulfur Dioxide (SO ₂)	(.08)* 651	(0.40)* 3,378	(.40)* 3,249
Nitrogen Oxides (NO _x)	(.08)* 448	(0.40)* 3,402	(.20)* 1,950
Carbon Dioxide (CO ₂)	(205)* 1,440,002	(210)* 1,787,500	(224)* 1,842,250
Particulates	(NA) 1	(0.10) 75	(0.08) 77
Solid Waste	135,500	324,000	454,002

* Rate in Parenthesis Based on Lbs of Emissions
Per Million BTUs of Heat Input.

Table 3
**ENVIRONMENTAL CREDIT VALUATION
AGCC vs. PFBC**

	Reduced Emissions	Value Per Ton	Basely Source	Total (000)
Sulfur Dioxide (SO ₂)	63,947	\$350.00	Price '92	\$18,881
Nitrogen Oxides (NO _x)	24,017	\$1,640.00	Price '92	\$39,386
Carbon Dioxide (CO ₂)	6,044,985	\$14.00	Price '92	\$112,630
Particulates	1,518	\$2,380.00	Price '92	\$3,614
Solid Waste	9,090,000	\$20.00	Transport	\$181,800
Total				\$358,113

Table 4
**ENVIRONMENTAL CREDIT VALUATION
IGCC vs. PC W/SCRUBBERS**

	Reduced Emissions	Value Per Ton	Basely Source	Total (000)
Sulfur Dioxide (SO ₂)	56,502	\$350.00	Price '92	\$19,776
Nitrogen Oxides (NO _x)	59,057	\$1,640.00	Price '92	\$96,853
Carbon Dioxide (CO ₂)	6,949,985	\$14.00	Price '92	\$97,300
Particulates	1,482	\$2,380.00	Price '92	\$3,527
Solid Waste	6,480,000	\$20.00	Transport	\$129,600
Total				\$347,056

Table 5
AGCC vs. PRESSURIZED FLUID BED - PFBC

CAPITAL COST ASSUMPTIONS		Dollars Per Kilowatt	
PFBC Capital Cost		\$1,000	
AGCC Capital Cost		\$1,200 - \$1,400	
Incremental Investment (250 MW Plant)		\$50 - \$100 Million	
AGCC POLLUTION CREDIT VALUE			
	SO ₂	NO _x	CO ₂
SULFUR	53,947	\$1,640	\$0.0
NITROGEN	24,017	\$0.0	\$3.6
CARBON DIOXIDE	6,045,966	\$2,380	\$3.6
PARTICULATES	1,518	\$20	\$181.6
SOLID WASTES	6,000,000	\$20	\$181.6
TOTAL NPV (Before Tax) 10% Cost of Capital 4% Escalation			\$136.8

Table 6
AGCC vs. PRESSURIZED COAL W/SCRUBBERS

CAPITAL COST ASSUMPTIONS		Dollars Per Kilowatt	
PFBC Capital Cost		\$1,000	
AGCC Capital Cost		\$1,200 - \$1,400	
Incremental Investment (250 MW Plant)		\$50 - \$100 Million	
AGCC POLLUTION CREDIT VALUE			
	SO ₂	NO _x	CO ₂
SULFUR	56,800	\$1,440	\$0.0
NITROGEN	56,100	\$0.0	\$66.9
CARBON DIOXIDE	6,960,000	\$2,360	\$3.6
PARTICULATES	1,482	\$20	\$129.8
SOLID WASTES	6,400,000	\$20	\$129.8
TOTAL NPV (Before Tax) 10% Cost of Capital 4% Escalation			\$140.3

Table 7
NPV OF POLLUTION CREDIT
HIGH VALUATION FOR NO_x CASE

ASSUME: Value of NO_x reduction increased to \$7000 / ton
all other values held constant
Cost of Capital - 10%
Inflation Rate - 4%
Before Tax Basis

NET PRESENT VALUE - TAGCC vs. PFBC Technology:
208 Million Dollars

NET PRESENT VALUE - TAGCC vs. PCWS Technology:
318 Million Dollars

SYNTHETIC CRUDE OIL FROM PETROLEUM WASTE MATERIALS

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Keywords : VEBA-COMBI-Cracking, Residual oil conversion, plastic to oil conversion

Introduction

As the demand for petroleum and petrochemical products is steadily increasing, there is also an increase of petroleum derived wastes and residues from crude processing. These materials are considered to be an environmental problem of increasing significance, as further utilisation will become more and more difficult due to restrictive emission limitations in most countries.

The VEBA-COMBI-Cracking (VCC) process is capable to convert a.m. materials. It is a hydrogen addition technology, which directly combines liquid phase hydrogenation with an integrated catalytic hydrofinishing step. The process had been developed and commercially applied for coal liquefaction and for conversion of residual oils as well as for upgrading of heavy crudes. Two licences have been granted, one for upgrading Canadian tar sand derived bitumen and the other to a refinery for crude processing without heavy fuel oil production. Its most recent application is given by its plastic to oil operation. The capability to convert mixed waste plastics into chlorine free oil, enables industry to perform a close recycling loop for plastics on a raw material base.

The Basics of the Hydrogenation Process

The main objective of the hydrogenation is to convert organic materials like coal, vacuum residues or difficult to handle organic wastes like chlorine contaminated solvents, used tubes, PCB's or particularly mixed plastic wastes into valuable clean hydrocarbon products.

Liquid phase hydrogenation takes place at temperatures between 450 °C and 490°C and hydrogen partial pressures of 160 to 250 bar. Under those conditions large molecules are cracked and hydrogen is added to the cracked organic bonds. Sulfur, nitrogen and chlorine after being separated are transferred to their corresponding hydrogen containing components which can be recovered.

The cracking process starts at the weak bonds of the molecules. The bond strength is decreasing from carbon/carbon over sulfur/carbon and nitrogen/carbon to chlorine/carbon bonds. The decontamination of used solvents and other chlorinated organic wastes like mixed plastic wastes take advantage of this fact, as shown in Figure 1 for e.g. for trichloroethane, trichlorobenzene and PCB's. Basically the chlorine is converted into HCl and neutralised in situ by the addition of a caustic material forming an inorganic salt.

The VEBA COMBI Cracking Technology

The VCC technology is a thermal hydrocracking/hydrotreating process for conversion of petroleum residues at high conversion rates (>95%, 624°C+). A simplified flow scheme of the VCC process is shown in Figure 2.

The feedstock is stirred with a small amount of coal derived additive, which is added to suppress coke formation at elevated temperature. After being fed into the high pressure section, which is operated at a pressure level between 150 bar and 250 bar, the slurry is mixed with make up hydrogen and recycle gas. This mixture is preheated and routed to the liquid phase hydrogenation (LPH) step for primary conversion. The LPH reactors are operated in a temperature range between 440°C and 460 °C. Temperature is controlled by a cold gas quench system.

The LPH products are routed to the hot separator (HS), where gases and vaporised products are separated from the nonconvertibles. Distillates in the HS bottoms are recovered by a vacuum flash. The bottom product leaving the flash tower is the hydrogenation residue, which includes the additive.

The HS overheads, together with the recovered HS distillates are the feedstock for the integrated gas phase hydrogenation (GPH) step which is operated at same pressure level as LPH. To adapt the product slate to seasonal demands straight run distillates can be treated additionally in the GPH step. The temperature of the catalytic fixed bed reactors are adjusted with respect to the required product qualities. Typical temperatures are in the range between 340°C and 390 °C (SOR). Temperature control is performed by an hydrogen quench.

The separation of the synthetic crude oil and the hydrocarbon carbon gases is performed in the cold separator. The Syncrude is depressurised and sent to a stabiliser and fractionation column, where as the gases are routed to a scrubber. Part of the gases after passing a lean oil wash are fed back as recycle gas to the feed of the LPH section.

Processing of Plastic Wastes

Plastic wastes need special attention with regard to its feeding to high pressure processes like the VCC process. One option is to grind the plastics down to particle sizes below 1 mm, slurry it with petroleum residue and pump the slurry into the process. The disadvantages of this procedure are the high costs for grinding and the limitation of the plastic/oil ratio to below 10 % due to viscosity restrictions.

The other option is to depolymerize the plastics to a certain degree by applying elevated temperature and then pump the liquefied material to the hydrogenation process. This enables a significantly higher plastic/oil ratio and decreases the amount of chlorine which has to be neutralised in the hydrogenation process. The plastic wastes are split into four fractions: gas, hydrochloric acid, condensates and depolymerisates containing the inerts. Figure 3 shows the result of plant operation. A simplified process scheme of the depolymerisation unit is shown in Figure 4.

The VCC Demonstration Plant

The demonstration plant has been constructed and operated to demonstrate the improved Bergius-Pier technology for hard coal liquefaction from 1981 to 1987. In parallel the basic test runs for development of the high conversion mode of residual oils in VCC had been run in small pilot plants and a large pilot plant. Figure 5 shows the feedstocks processed and Figure 6 indicates the feedstock quality ranges covered. The data basis generated by these test works made it possible to transfer this technology into commercial scale.

In 1987 the demonstration plant was modified to enable petroleum residue conversion with a capacity of 24 t/h. Yield structure and the achieved product qualities are given in Figure 7 and Figure 8. After successful operation with residues from crude distillation and visbreaker operation an increasing share of the residues were substituted by a. m. chlorine containing wastes.

In October 1983 a depolymerisation unit with a design capacity of 5 t/h was erected at site of the demonstration plant to liquefy the plastics. Together with the vacuum residue the liquid products of the depolymerisation step are fed to the VCC unit. In Figure 9 the qualities of the VCC syncrude derived from the coprocessing of vacuum residue and plastic wastes are compared to those of the straight run products of Arabian Light, indicating the high quality standard of the VCC products.

According to new developments in PDU tests the process of plastics depolymerisation can be triggered in such way, that app. 70 wt % of the plastics are converted into light condensates and only 20 wt % will leave the process as heavy depolymerisates. This enhanced mode of operation offers a new and very economic sound possibility of processing depolymerisation products. As the condensates do not contain any solids, only mild hydrotreating needs to be applied for removal of the organic bound chlorine.

The enhanced mode of operation will be applied to the demonstration plant after having integrated an hydrotreater unit for separate processing of the condensates. Then only the heavy depolymerisates have to be fed to the VCC unit. A simplified flow scheme of this operation is given in Figure 10. According to this mode of operation it is possible to increase the capacity for plastic conversion from app. 40 000 t/y up to 120 000 t/y.

Large scale VCC-plant connected to a refinery including waste processing

As mentioned above, for VCC operation the plastic wastes are hydrogenated commingled with crude oil residue. Part of the syncrude produced needs further treatment, be it in a reformer (gasoline) or a cracker (vacuum gasoil). It is therefore very advantageous to have the upgrader closely connected to a refinery, which can also supply energy and water and can take over the waste streams. Such an arrangement is shown in Figure 11.

For a plant with a total conversion capacity of 1.35 Mio t a year, the relevant input and output streams are listed in Figure 12. The investment costs for such a plant have been estimated based on an estimated basic engineering and on quotes for all larger pieces of equipment. The estimate for the investment is as high as 1,020 Mio DM (1983 basis).

Assuming today's market prices for syncrude, vacuum residue, energy etc. the plastic wastes have to pay a "gate-fee" of roughly 200 DM/t in order to keep the operation profitable according to refinery standards.

Another example is given for the processing of chlorine containing waste materials. A plant capacity of 25 000 t/yr has been chosen, out of which one-third is used for waste materials.

Value of waste materials (free upgrader plant in Germany)

- Used lube oils	\$/t	approx.	0
- Materials \leq 0,2 Chlorine	\$/t	approx.	200-250
- Pure PCBs	\$/t	approx.	1500-1800

For the purpose of this evaluation an average credit of 300 \$/t is assumed. Operating expenses are nearly covered by the value of the syncrude produced from processing these materials.

- Savings	MM\$/year
- 8330 BPD vacuum resid ¹⁾	27
- Credits ²⁾ from waste processing	110
	<u>~ 130 - 140</u>

1) at 10 \$/BBL (HFO)

2) density 1.2 [g/ml]

This example illustrates drastically the high profitability of processing those materials at least under the conditions prevailing in Germany. These high credits can buffer almost any swing in crude/HFO prices.

Summary

Feedstock recycling of post consumer plastics is reality also in commercial terms. The main advantages of the depolymerisation/hydrogenation process are

- no sorting in different kinds of plastic is necessary
- high liquid yields
- high quality chlorine free syncrude which enables its use in existing refineries without restrictions
- no feedstock related pollution

The cost estimation for a large scale unit had shown that feedstock recycling by hydrogenation is very well competitive to alternative processes and may well compete with thermal utilisation if stringent environmental restrictions have to be taken into account.

Crude	API	Gravity
Distillate	wt-%	0-14
Sulfur	wt-%	0-80
Nitrogen	wt-%	0.7-7.0
Methan (V + N)	wt-%	0.3-1.5
Corrosion Carbon	ppm	up to 2,100
Hexane Insolubles	wt-%	12-60
	wt-%	10-80

Figure 6: Feedstock Quality Ranges covered

Crude	API	Gravity	Hexane Insolubles	Corrosion Carbon	Nitrogen	Sulfur
wt-%	wt-%	wt-%	wt-%	ppm	wt-%	wt-%
0-14	0-80	0.7-7.0	0.3-1.5	up to 2,100	12-60	10-80

Figure 8: Qualities of the Synthetic

Product	Quality	Quantity
Gasoline	wt-%	0.750
Jet Fuel	wt-%	1.0
Light Diesel	wt-%	1.0
Heavy Diesel	wt-%	1.0
Gas	wt-%	1.0
Water	wt-%	1.0
Residue	wt-%	1.0

Figure 9: Product Qualities from Plastic Hydrogenation compared to Arabian Light Crude Oil

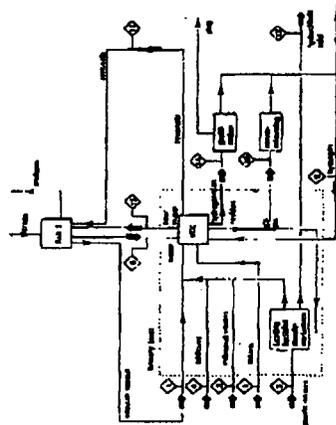


Figure 11: Integration of the VCC-Plant into a Refinery Scheme

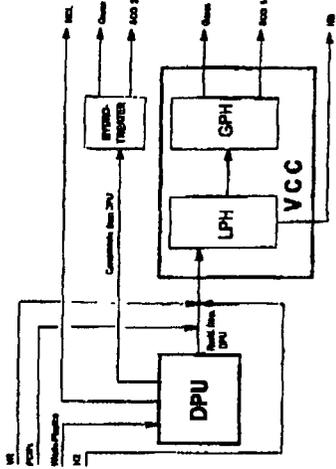


Figure 10: Enhanced Mode of Operation for Plastics/Oil Conversion

Feed	Quantity
Crude Oil	1,000,000
Hydrogen	2,000,000
Electricity	40,000
Water	50,000
Total	3,000,000

Figure 12: Main Input/Output Data

Coliquefaction of Waste Rubber Tires with Coal.

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Keywords: EPMA, coliquefaction of waste materials, coal, rubber tires

Introduction

There is an interest in the conversion of coal to liquid fuels because of the abundant supply of coal and the diminishing reserves of petroleum. Standard coal liquefaction techniques utilize H₂ gas as a source of hydrogen to cap the radical species produced during liquefaction. Waste materials such as plastics, oils, and rubber tires with a high hydrogen content could be an alternative source of hydrogen that, in principle, could be transferred from the waste materials to the coal during liquefaction. An added benefit of such a program of waste material utilization would be a diminution in materials disposed of in landfills or incinerators.

Rubber tires are approximately one third by weight carbon black. Farcasiu and Smith have shown that carbon black increases yields in coal liquefaction.¹ Since carbon black is one of the top fifty chemicals produced in America during 1993 (3.22 billion pounds)² the recovery and reuse of carbon black from tires could become economically attractive. Giavarini has shown in recent work that carbon black could be reclaimed and activated to produce quality carbon blacks after pyrolyzing waste rubber tires.³ Rubber tires also contain zinc oxide which is added as a filler and also aids in the vulcanization of the rubber.⁴ The zinc oxide could play a role as a catalyst in liquefaction reactions. It could also decrease the amount of sulfur that ends up in the coal liquids.

Waste plastics contain many metals used for coloring, waste oils contain metals acquired while used as a lubricant, and waste rubber tires contain zinc. A past investigation suggested that coal undergoing liquefaction may act as a "scavenger" for heavy metals.⁵ The ability of coal to trap metals will be discussed in the present paper.

Electron probe microanalysis (EPMA) is a technique which can map the dispersion of an element within a sample by the detection of characteristic X-rays.^{6,7} Using EPMA, samples of the insoluble fraction produced by the coliquefaction experiments were analyzed to determine whether several heavy elements of interest were trapped in coal particles.

Experimental

Blind Canyon (Utah) coal (DECS-6, -60 mesh) was obtained from the Penn State Coal Sample Bank and ground under nitrogen to -100 mesh. Waste rubber tire samples were obtained (University of Utah waste material bank) that had been ground to -25 mesh. The catalyst, ammonium tetrathiomolybdate (Aldrich) was used to make an aqueous solution of molybdenum. The ground waste rubber tire and coal were mixed dry (40 % tire and 60 % coal, by weight) with different heavy metals (1 % by weight) (nickel acetylacetonate, vanadium oxide, manganese acetylacetonate, chromium acetylacetonate, and zinc oxide obtained from Strem and Aldrich) and then mixed with 1 % by weight molybdenum using the incipient wetness technique. The mixture was vacuum dried for 2 hours at 100° C. The dried mixture was placed in glass tubes and stoppered with glass wool. The glass tubes were placed in 35 cc tubing bombs, purged with nitrogen, and pressurized to 1000 psig H₂ (cold). Tubing bombs were placed in a fluidized sandbath held at 350° C. The tubing bombs were shaken at 160 rpm for one hour and removed. The tubing bombs were allowed to cool overnight while under pressure. Samples were removed and extracted

with cyclohexane using a soxhlet extractor. Products soluble in cyclohexane were isolated using a rotary evaporator and then dried two hours under vacuum at 100 °C. The insoluble sample (char/ash) was vacuum dried under similar conditions and then mixed with Petropoxy 154 (Pullman, Washington) and polished with a Syntron diamond paste polisher for eight hours. Micrographs were obtained using a CAMECA Model SX-50 electron microprobe (Courbevoie, France). Two different micrographs are presented: secondary electron images (SEM) and the characteristic X-ray micrograph for a specific element of interest (all micrographs shown are for a 50 μm x 50 μm field of view).

Results

Table 1 shows the percentage (by weight) of gas, cyclohexane solubles (oil), and char produced from coliquefaction of coal and tire samples. Percentages were calculated without including the weight of catalyst, weight of heavy metals added, and the ash weight of the coal (6.6 %). Also not included were the weight of carbon black, sulfur and zinc oxide in the tire sample that together constitute 35 % by weight of a rubber tire.

The oil yields indicate that the addition of zinc oxide and nickel acetylacetonate, in combination with the catalyst ammonium tetrathiomolybdate, have a positive effect on the oil yields. No effect is observed for samples doped with vanadium, manganese, and chromium.

Table 2 contains the elemental analysis of the Blind Canyon (DECS-6) Coal, and the trace analysis of heavy metals naturally found in the coal. EPMA is only sensitive to concentrations of approximately 200 ppm or greater. Therefore, metals in their natural abundance in the coal are undetectable by EPMA.

Table 3 shows an approximate percentage of the components of a tire. The zinc oxide is useful in the EPMA micrographs since it permits the operator to distinguish between tire particles and coal particles.

Figure 1 shows a variety of tire particles and coal particles from a sample that was doped with zinc oxide. The tire particles contain both sulfur and zinc which allows them to be easily distinguished by comparison of the sulfur and zinc micrographs. The particle in the upper right hand corner is a tire particle. Moving from the tire particle towards the lower left hand corner, a roughly circular coal particle can be observed in the sulfur micrograph. The coal particle contains less sulfur than the tire particles. In the zinc micrograph, the coal particle shows that some zinc is found in and around the edges of the coal particle. It appears as if the coal has scavenged some of the artificially added zinc during liquefaction.

Figure 2 shows a tire particle and a coal particle from a sample that has been doped with nickel acetylacetonate. The coal particle is distinguished in the left hand side of the sulfur micrograph and the tire particle in the right hand side of the sulfur micrograph. The nickel micrograph shows an outline of nickel around the left hand side of the coal particle indicating the presence of nickel in the borders of the coal particle. Also interesting to note is the presence of zinc in the coal particle even though zinc was not added to this sample. The only source of zinc present is the tire. This further indicates that the coal could be acting as a scavenger for heavy metals.

Figure 3 shows a tire particle and a coal particle from a sample that has been doped with vanadium pentoxide. The coal particle makes up over half of the micrograph on the right hand side of the micrograph. The tire particle, observed in the left hand side of the micrograph, shows an increased sulfur density and is easily distinguished by the zinc abundance shown in the zinc micrograph. The vanadium micrograph shows that there is no evidence of vanadium in the coal particle.

Figure 4 shows a combination of tire particles and coal particles taken from a sample that was spiked with chromium acetylacetonate. The sulfur micrograph shows a coal particle at the center of the micrograph and three other coal particles surrounding the center particle at the 2, 3, and 6 o'clock positions. There are three tire particles. One tire

particle is found in the upper right hand corner and the other two are found on the left hand side of the sulfur micrograph. The tire particles are easily distinguished from the coal particles by the presence of zinc observed in the zinc micrograph. The chromium micrograph shows an enhanced presence of chromium in all four coal particles.

Conclusion

Our experiments indicate that zinc oxide, nickel acetylacetonate, and chromium acetylacetonate are scavenged by coal particles during liquefaction. This scavenging effect could decrease the amount of heavy metals that end up in the derived liquids. Further work is needed to determine whether there is a decrease in the amount of zinc, nickel, and chromium found in the derived liquids.

The oil yields indicate an interesting effect arising from mixing zinc oxide or nickel acetylacetonate with the molybdenum catalyst. Further work is needed in order to determine the effect of these two metals on the type of liquids produced from liquefaction.

Acknowledgments

We would like to thank Ray Lambert for technical assistance with the EPMA, Professor Henk Meuzelaar for the ground rubber tire samples, Professor Henry White for the use of his computer to aid in printing micrographs and the U.S. Department of Energy (contract no. DE-FC22-93PC93053) through the CFFLS, University of Kentucky, for funding the research.

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Product Distribution of Coliquefaction

Table 1

Composition	Percentage of Gas	Percentage of Oil	Percentage of Char
Tire/Mo/Coal	8.0	35.1	56.9
Tire/Mo/ Zn /Coal	5.9	39.0	55.1
Tire/Mo/ Ni /Coal	5.7	38.3	56.0
Tire/Mo/ V /Coal	5.5	29.5	65.0
Tire/Mo/ Mn /Coal	5.7	27.8	66.5
Tire/Mo/ Cr /Coal	5.4	27.6	67.0

Blind Canyon Coal Analysis

Table 2⁸

Elemental Analysis	Percentage	Trace Elements	ppm
Ash	6.67	Zinc	70
Carbon	76.7	Nickel	25
Hydrogen	5.80	Vanadium	140
Sulfur	0.37	Manganese	155
Oxygen	9.43	Chromium	95

Rubber Tire Tread Composition

Table 3⁹

Component	Percentage by weight
Styrene-Butadiene Rubber	35
Carbon Black	33
Aromatic Oil	20
<i>cis</i> -Polybutadiene	8.5
Sulfur	1
Zinc Oxide	1

Figure 1

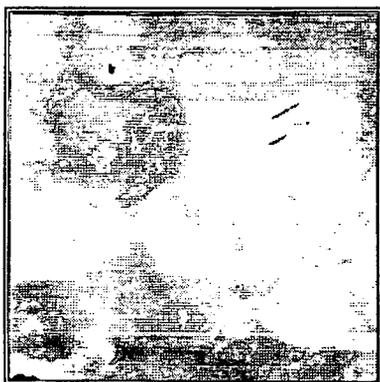
EPMA Micrograph

40 % waste rubber tire mixed with 60 % Blind Canyon DECS-6 by weight

Catalyst: 1 % ammonium tetrathiomolybdate

Doped with: 1 % zinc oxide

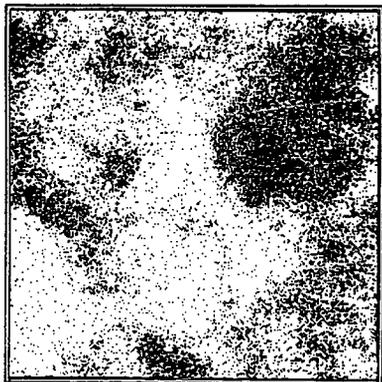
Hydrotreated for 1 hour at 350° C under 1000 psig hydrogen (cold)



Secondary Electron Image



Sulfur K_α



Zinc L_α

Figure 2

EPMA Micrograph

40 % waste rubber tire mixed with 60 % Blind Canyon DECS-6 by weight

Catalyst: 1 % ammonium tetrathiomolybdate

Doped with: 1 % nickel acetylacetonate

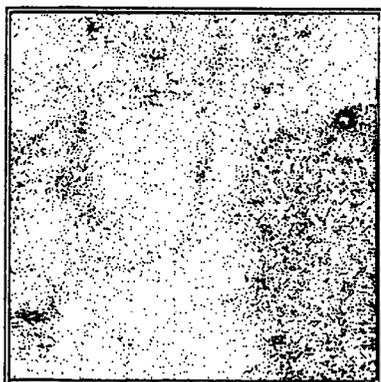
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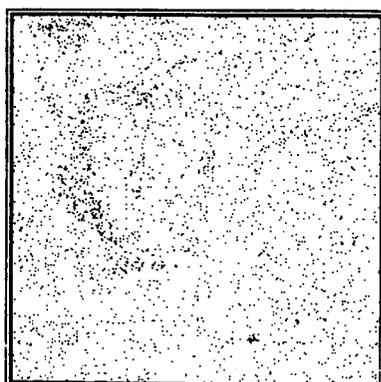
Secondary Electron Image



Sulfur K_α



Zinc L_α



Nickel K_α

Figure 3

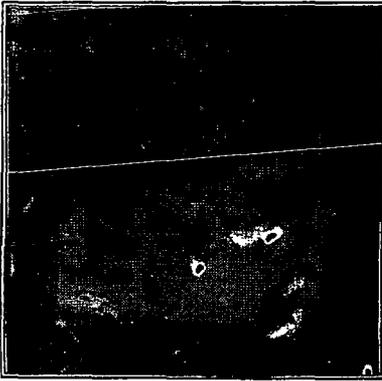
EPMA Micrograph

40 % waste rubber tire mixed with 60 % Blind Canyon DECS-6 by weight

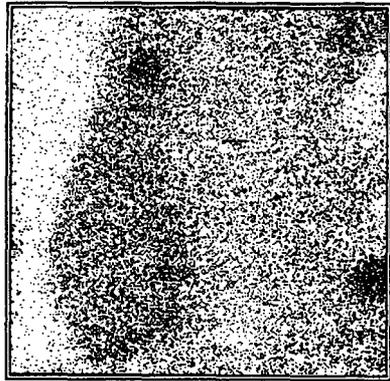
Catalyst: 1 % ammonium tetrathiomolybdate

Doped with: 1 % vanadium pentoxide

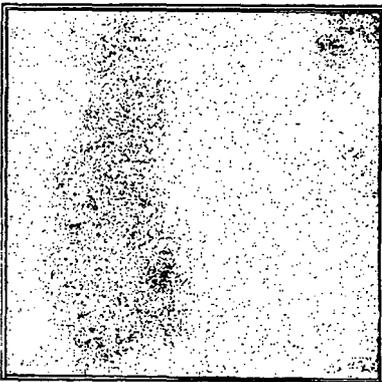
Hydrotreated for 1 hour at 350° C under 1000 psig hydrogen (cold)



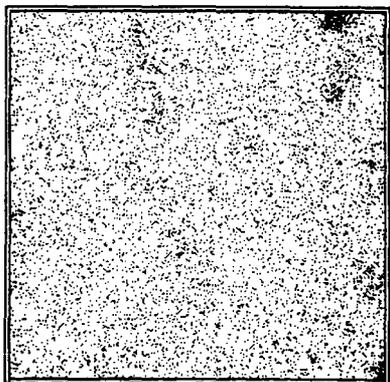
Secondary Electron Image



Sulfur K_α



Zinc L_α



Vanadium K_α

Figure 4

EPMA Micrograph

40 % waste rubber tire mixed with 60 % Blind Canyon DECS-6 by weight

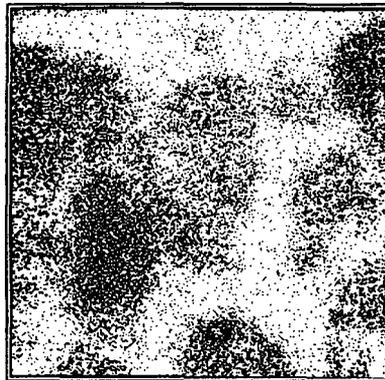
Catalyst: 1 % ammonium tetrathiomolybdate

Doped with: 1 % chromium acetylacetonate

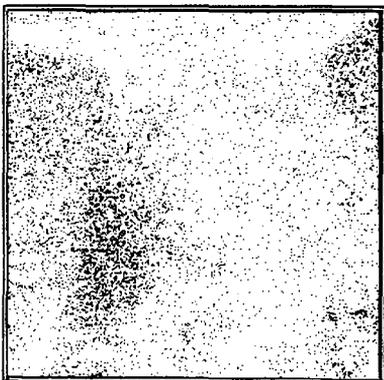
Hydrotreated for 1 hour at 350° C under 1000 psig hydrogen (cold)



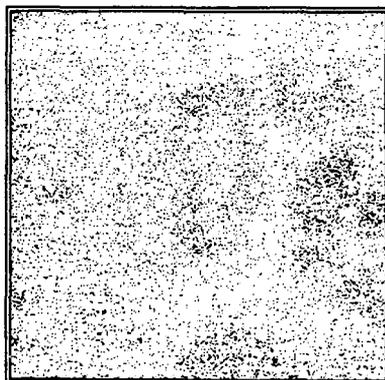
Secondary Electron Image



Sulfur K_α



Zinc L_α



Chromium K_α