



## Hot Filtration of Fast Pyrolysis Vapours

By Jürgen Sitzmann, Aston University, UK



Bio-oil obtained by fast pyrolysis typically contains up to 0.5 wt% char fines which are not removable by conventional cyclone separators. These char fines cause problems in applications like engines and turbines as well as during storage. Furthermore they contain the alkali metal of the oil, as during fast pyrolysis the metals accumulate in the char. In order to reduce char fines to lower levels, a hot vapour filtration test unit was designed and installed downstream of a 1kg/h fluidising bed reactor to filter the product stream prior to condensation (*see Figure 1*).

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Figure 1. Aston's 1 kg/h fast pyrolysis reactor with hot filtration test unit.

## Experiments

The hot filtration test unit consists of one exchangeable filter candle with a maximum length of 600 mm. The system operates at a temperature of 450°C and is equipped with a reverse pulse cleaning system using nitrogen at 400°C and 6 bar.

The experimental set-up includes a sintered metal and a ceramic filter candle. Furthermore the system operates at two different face velocities, with inclusion or exclusion of a primary cyclone and with a pre-coat on the filter candle before filtration.

Beech wood was used as a feedstock and was pyrolysed in the fluidising bed reactor at 500°C.

The experiments were evaluated by determining the mass balance of the process. The pressure difference over the filter candle was also recorded to assess the filtration performance and the effect of the reverse pulse cleaning. The remaining filter cake on the candle was examined by visual inspection, optical microscopy and Scanning Electron Microscopy (SEM). The oils produced were analysed for solids content, water content, viscosity and mean molecular weight (by gel permeation chromatography). Viscosity and mean molecular weight were analysed before and after accelerated aging at 80°C for 24 h to determine the storage stability of the oil.

## Results

### Oil analysis

It was possible to reduce the solid content of the hot vapour filtered oils below 0.01 wt% compared with 0.3 – 0.5 wt% solid content in oil produced with cyclone separation. The filtered oils showed superior quality properties regarding viscosity and storage stability than standard pyrolysis oils. The dynamic viscosity was reduced by half from 42 Pa s to 21 Pa s for the fresh oils and 64 Pa s compared with 100 Pa s for the aged filtered oil which is still significantly less compared to the non-filtered oil (See Figure 2). This is confirmed by the stored oils where the filtered oils are still homogenous, free flowing and without sedimentation after storage at room temperature for 1 year.

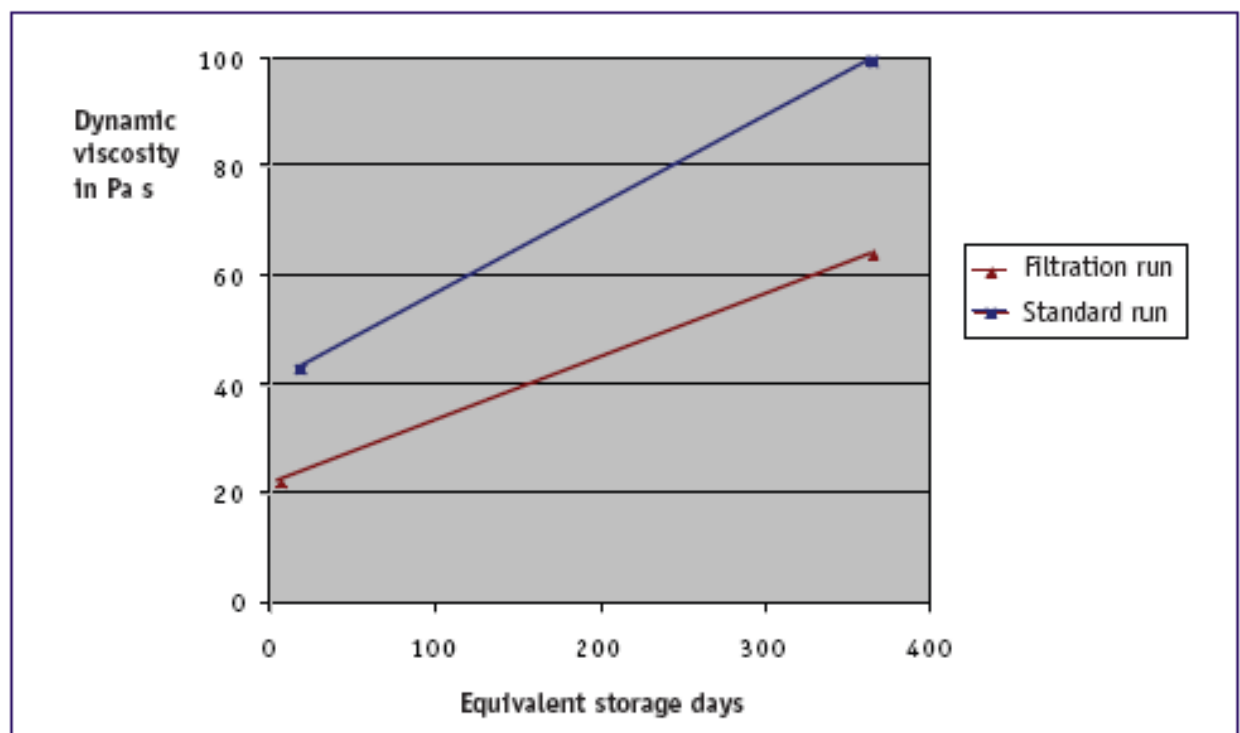


Figure 2. Dynamic viscosity of filtered bio-oil compared with non-filtered bio-oil before and after accelerated aging. The water content of both oils is ca. 16 wt%.

### Mass Balance

The mass balances (based on dry feedstock) of the experiments showed a decrease of organic liquid yield from ca. 55 wt% for the experiments with cyclone separation to 47 – 50 wt% for the filtration experiments. The losses of organic liquid yield were caused by an increase in non-condensable gases and reaction water due to catalytic secondary cracking of the vapours on the filter cake.

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### Differential Pressure

Figure 3 shows the change of differential pressure over the filter candle during the course of a filtration experiment using a Tenmat firefly candle. It can be seen that it is possible to regenerate the pressure difference during the first couple of cleaning cycles. Thereafter only minor pressure drop recovery was achieved leading to a steady increase in pressure. Visual inspection of the filter candles showed patchy cleaning of the filter cake (See Figure 4).

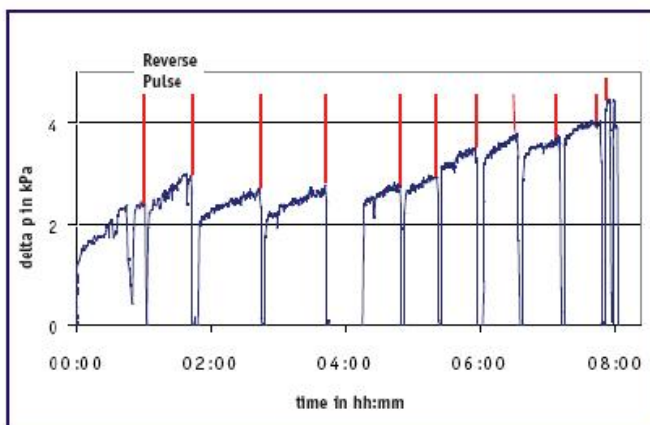


Figure 3. Change of differential pressure over filter candle (filtration experiment with Tenmat firefly candle).



Figure 4. Used filter candle with char filter cake showing patchy cleaning.

### Filter Cake Analysis

The filter cakes had different particle size distribution at different face velocities. A high face velocity (3.5 cm/s) causes larger char particles to stick on the cake and therefore create a more porous filter cake with a lower specific resistance to flow. On the other hand at a low face velocity (2.0 cm/s) more particles are separated by gravity leading to a smaller average particle size and to a higher resistance to flow of the filter cake. SEM pictures of filter cakes produced at different face velocities can be seen in Figure 5 and Figure 6.

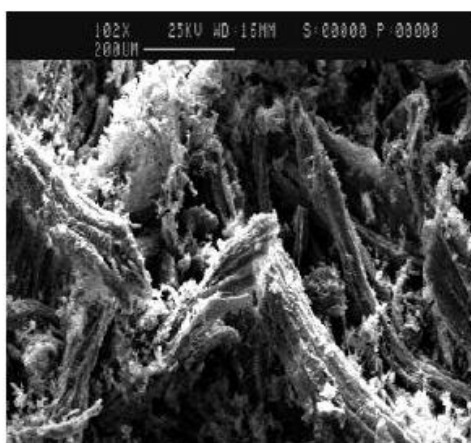


Figure 5. SEM picture of char filter cake produced at 2.0 cm/s face velocity.

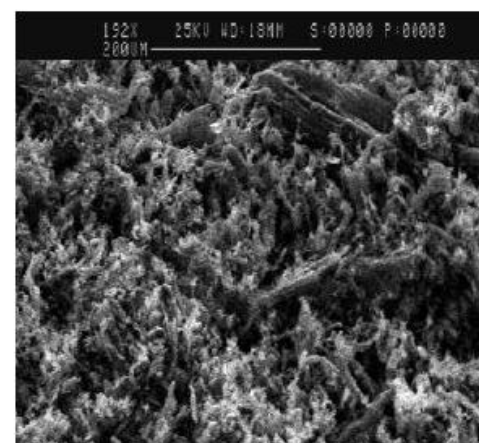


Figure 6. SEM picture of filter cake produced at 3.5 cm/s face velocity.

### Conclusions

With hot filtration of fast pyrolysis vapours a solid content below 0.01 wt% is achievable which improves the quality of the oils significantly. Additionally the absence of char fines protects downstream equipment like the condensation unit from blockage. However the additional residence time and catalytic vapour cracking reduces the organic liquid yield of the process.

The filter cake which accumulates on the candle is difficult to remove and leads to an increase in differential pressure over the filter candle. The resistance to flow of the filter cake is dependent on the face velocity and the particle size distribution of

the particulates to be removed. Further investigations into the filter cake characteristics are required in order to improve the detachability of the filter cake.

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# Opportunities for Biorenewables in Petroleum Refineries

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The US Department of Energy funded collaboration between UOP, the National Renewable Energy Laboratory, and the Pacific Northwest National Laboratory to complete an evaluation of the economics of biofuels integration in petroleum refineries. The purpose of this project was to identify economically attractive opportunities for biofuels production and blending using petroleum refinery processes.

## Background

The production of biofuels is expanding worldwide at a rapid pace. The future widespread use of biofuels depends on solving several issues such as:

- Identifying a large, consistent quantity of renewable feedstock
- Producing biofuels at costs competitive with other fuels
- Transporting the bio-based feedstock or fuel to distribution centres
- Developing new technology to produce fuels from the unique composition of these highly oxygenated feedstocks
- Producing biofuel compatible with the existing transportation and fuel infrastructure

The goal of the study was to identify profitable processing options for integrating bio-renewable feeds and fuels into existing refineries by addressing these issues. A schematic showing several options for biofuel production from different biomass sources is shown in Figure 1. Some of the routes are already in commercial practice, such as ethanol from the fermentation of corn or sugar cane. Several routes have a considerably longer timeframe for commercialisation due to technical challenges or feedstock availability.

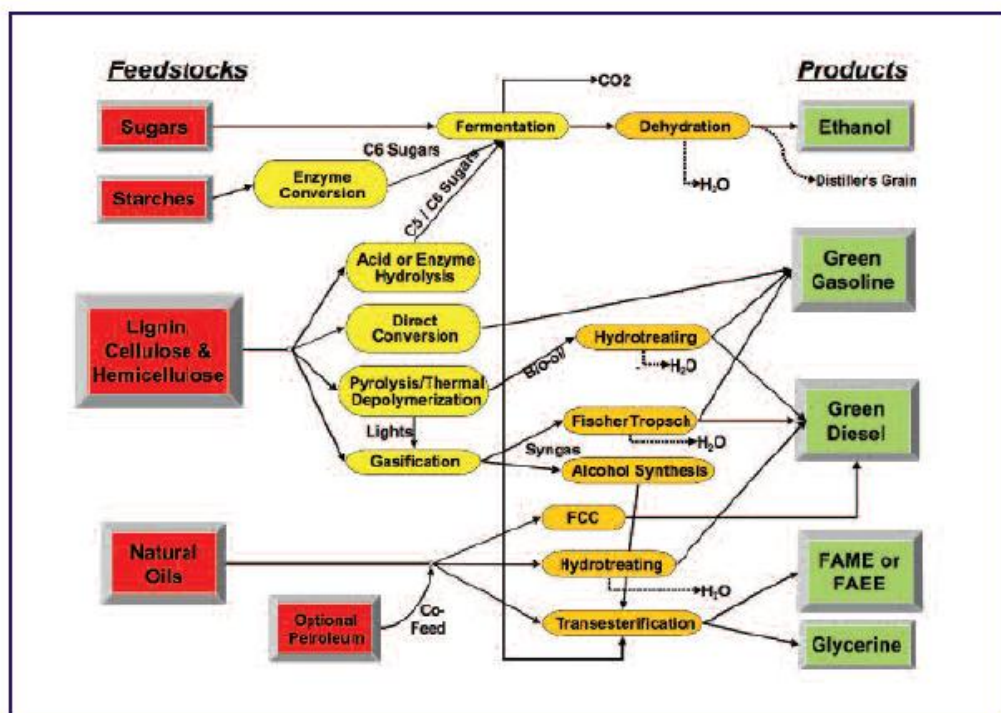


Figure 1: Overview of Biofuel Production.

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### Feedstock Availability

The first question addressed was the availability of bio-renewable feedstocks at 2005 levels. Table 1 shows the U.S. availability of several bio-feedstocks while Figure 2 compares the global volume of petroleum-based liquid transport fuels with available vegetable oil and greases in 2005. For example, vegetable oils and greases could only replace a very small fraction of transport fuel. However, the potential large supply of ligno-cellulosic biomass could supply a high percentage of future liquid transport fuels if commercial processes were available to convert these feeds. One such process evaluated in this study was fast pyrolysis but the quantity of pyrolysis oil is currently very low since commercial production is still at an early stage.

Table 1. Availability of bio-renewable feedstocks in the U.S.<sup>1,2,4,8</sup>

Biorenewable Feedstock	Definition	Amount produced in the U.S. (bpd)	Amount available for fuel production in U.S. (bpd)
Vegetable Oils	Produced from soybeans, corn, canola, palm	194,000	33,500
Recycled Products	Yellow grease, brown (trap) grease	51,700	33,800
Animal Fats	Tallow, lard, fish oil	71,000	32,500
Pyrolysis Oil	Made from pyrolysis of waste biomass (cellulosic)	1,500	750

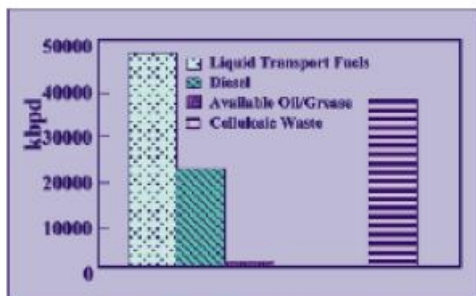


Figure 2: Availability of bio-renewable feedstocks in the U.S.<sup>4,7</sup>

The study took into account both feedstock costs and the projected prices of potential products. Prices of raw vegetable oils, greases, and pyrolysis oils were determined and used in the economic assessment. The costs ranged from \$16/bbl for pyrolysis oil to \$75/bbl for raw vegetable oils. Each economic analysis was primarily based on a West Texas Intermediate (WTI) crude feedstock price of \$40 per barrel, a level considerably lower than the recent \$60/bbl price. The cost of each potential biofuel was compared to this crude feedstock price after incorporating a number of factors including capital costs; transportation costs; CO<sub>2</sub> credits; subsidies; and cetane and octane numbers. Most of the feedstocks looked promising when current subsidies were applied and several were economically attractive without subsidies such as pyrolysis oil and brown grease. Raw vegetable oils were not attractive without subsidies until crude prices are > \$70/bbl.

The properties of bio-renewable feedstocks were compared to petroleum as shown in Table 2. The biggest difference between bio-renewable and petroleum feedstocks is oxygen content. Bio-renewables have oxygen levels from 10-40% while petroleum has essentially none making the chemical properties of bio-renewables very different from petroleum. For example, these feedstocks are often more polar and some easily entrain water and can therefore be acidic. All have very low sulfur levels and many have low nitrogen levels depending on their amino acid content during processing. Several properties are incompatible with typical refinery operations such as the acidity and alkali content so that processes were identified to pretreat many of these feeds before entering refinery operations.

Table 2. Typical Properties of Petroleum and Bio-renewable Feedstocks.

	Crude Typical	Resid	Pyrolysis Oil
% C	83-86	84.9	56.2
%H	11-14	10.6	6.6
%S	0-4 (1.8avg)	4.2	-
%N	0-1 (.1avg)	.3	.3
%O	-	-	36.9
H/C	1.8-1.9	1.5	1.4
Density	.86(avg)	1.05	1.23
TAN	<1	<1	78
ppm alkali metals	60	6	100
Heating value kJ/kg	41,800	40,700	15,200

### Refining Opportunities for Pyrolysis Oil

Fast pyrolysis is a thermo-chemical process with the potential to convert the large volumes of cellulosic biomass available in the U.S. and globally into liquid fuels and feeds. A solid biomass feedstock is injected into a fluidised bed with high heat transfer capability for short contact times followed by quenching to condense a liquid bio-oil in 50-75% yields with gas and char forming the balance. The bio-oil contains the thermally cracked products of the original cellulose, hemi-cellulose, and lignin fractions present in the biomass. It also contains a high percentage of water, often as high as 30%. The total oil is often homogeneous after quenching but can easily be separated into two fractions, a water soluble fraction and a heavier pyrolytic lignin fraction. The addition of more water allows the pyrolytic lignin fraction to be isolated and the majority of it consists of the same phenolic polymer as lignin but with smaller molecular weight fragments. Pyrolytic lignin is a better feedstock for liquid fuel production than the water-soluble fraction because of its lower oxygen content and therefore the study focused on evaluating it as a potential feedstock for the production of highly aromatic gasoline. Commercial outlets for the water-soluble oil were identified and evaluated, such as the production of hydrogen and as a fuel for power generation. These latter applications will not be discussed here.

Table 3 shows an estimated performance for hydro-processing pyrolytic lignin to produce biofuels based on experimental results. These estimates were used as a basis for economic calculations. The naphtha and diesel are produced along with a large amount of water and CO<sub>2</sub> due to water removal and deoxygenation. As with the vegetable oil the consumption of hydrogen and yield of CO/CO<sub>2</sub> will vary depending on the mechanism of deoxygenation.

The economics for producing fuels from pyrolytic lignin are shown in Table 4, assuming \$18/bbl pyrolysis oil (\$16/bbl + \$2/bbl transportation charges) and two crude oil prices: \$40 & \$50/bbl.

Table 3. Performance Estimates for the Production of Naphtha and Diesel from Pyrolysis Oil.

Feed	Wt%	bpd
Pyrolytic Lignin	100	2,250
H <sub>2</sub>	4-5	-
Products	-	-
Lt ends	15	-
Naphtha	30	1,010
Diesel	8	250
Water, CO <sub>2</sub>	51-52	-

Table 4. Performance Estimates for the Production of Gasoline and Diesel from Pyrolysis Oil.

		bpd	\$40/bbl Crude	\$50/bbl Crude
			\$/D	\$/D
Feed	Pyrolytic Lignin	2,250	40,500	40,500
	H <sub>2</sub>	21.4 T	25,680	25,680
Products	Lt Hydrocarbons	64T/D	19,303	23,164
	Naphtha	1,010	52,520	62,510
	Diesel	250	12,000	15,000
Other	Utilities		-4,800	-5,760
	Net		12,843	28,734
	Annual Value		\$4.2MM	\$9.5MM

### Summary

Many economically attractive opportunities were identified in this study for the integration of bio-renewable feedstocks and biofuels in petroleum refineries, including pyrolysis oil to produce green gasoline. Pyrolysis oil processing requires more commercial development and is also limited by the availability of pyrolysis oil since commercial production is still in its infancy. In the long term, however, the potential volume of pyrolysis oil could replace shortages in petroleum fuel since it can process the large amount of cellulosic biomass available.

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# Current Status of Biomass Pyrolysis in Brazil

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Biomass to energy is becoming more widespread and generating a significant amount of the primary energy in Brazil due to the optimal conditions in all regions of Brazil, such as availability of indigenous raw materials, low biomass cost, great experience in bioenergy use, technology development, local equipment suppliers, high level of human resources, and legal and legislation base. 47.5% of the overall primary energy consumption is non-fossil, 13.5% is firewood and charcoal, and 16.6% sugar cane products (fuel ethanol and bagasse for bio-electricity). There are many possibilities to introduce biomass pyrolysis and also bio-oil gasification to syngas in the Brazilian market. The commercialisation of the technology has the potential of starting in the range of up to 1 t/h dry biomass.

As well as the successful Brazilian Fuel Ethanol Program which has been running for 30 years, the recently created Biodiesel Program (PNPB) and many other biomass technologies are under development or are running as commercial plants nationwide. The ECI conference, "BIOENERGY II: Fuels and Chemicals from Renewable Resources" in Rio de Janeiro in March 2009 will be a great opportunity to see the rapid development of the biofuel field in Brazil.



Figure 1. Plant Located at Unicamp.

## Research at Unicamp

### Unicamp Pyrolysis plant

Biomass fast pyrolysis R&D is progressing well in Brazil. The research group at the University of Campinas (Unicamp) in the city of Campinas and the spin-off company BIOWARE have fully developed a pyrolysis technology based on a fluidised bed reactor. The new demo plant has a capacity of 200 kg/h and is under Brazilian patent submission. See Figure 1 for an updated picture of the plant located at Unicamp. The main characteristics are the innovative two-stage bio-oil recovering system, heat recycling process, and two phase separation equipment. Feedstocks such as tobacco waste, orange bagasse, sugar cane straw, and sawdust have been tested successfully.

### Bio-oil as an emulsion agent

A partnership with Prof. José Falcón from the University of Oriente in Cuba has enabled the application of bio-oil as an emulsion agent to heavy oil, asphalt, fuel oil, diesel, and gas-oil. Interest in using bio-oil based emulsifiers to dilute heavy oil is very high, as almost half of Brazilian petroleum production has a high viscosity. Asphalt dilution will also avoid the use of naphtha or diesel as a solvent in road paving. These solvents are expensive and highly pollutant for air and soils and are also potentially underground water contaminants. A large scale test involving bio-oil emulsion with fuel oil and diesel co-firing in thermoelectric plants located in Southern Brazil is under contract. This type of test is necessary to measure the yield and emissions of the new fuel as a mixture of fossil and renewable fractions. Gas-oil/bio-oil mixtures are being tested in a catalytic cracking unit at Petrobras Research Centre (CENPES) in Rio de Janeiro. Results will be published soon to assess the possibilities of this use in conventional refineries. The equipment built to prove the emulsions is shown in Figure 2.



*Figure 2. The Equipment Built to Prove the Emulsions.*

### Bio-Fertilisers

Unicamp have also driven the research to replace traditional fertilisers with bio-fertilisers from biomass fast pyrolysis products. Char can be aggregated in soil as a kind of young Terra Preta de Índio, an archaeological practice of Amazonians. Bio-oil and a mixture of bio-oil and char can also help in fixing nitrogen in soils. Acid extract is an aqueous solution produced in the pyrolysis process and is already an agricultural input in organic production. A chapter of a book concerning this subject will be released in the second quarter of this year.

### Carbonisation of biomass

Bioware is also developing an innovative carbonisation system based on its proprietary technology of a screw and shell reactor. The first plant, with a capacity of 300 kg/h, will process a variety of agriwaste and elephant grass into sustainable charcoal briquettes and tar. The facility is autothermic and will burn the pyrolysis gas as a source of process heat. Financial support is being provided by a bank (Caixa Econômica Federal).

Another commercial development is the extrusion briquette machine with a capacity of 100 to 500 kg/h and a continuous torrefaction oven to process briquettes. Both the briquette machine and the oven are enterprises financed by the São Paulo Research Agency (FAPESP) in its special PIPE program (Innovative Research in Small and Micro Companies). This is being developed under Bioware with the guidance of a collaborator Dr Felix Felitti, an expert in biomass briquette torrefaction.

### Syngas production

The group will also soon look at gasification tests for bio-oil. Syngas production in a high pressure, oxygen gasifier can be a great opportunity to achieve synthetic liquid or gaseous biofuel. There is high interest in this as a thermo-chemical route. The demand for bio-oil as a liquid feedstock to feed this kind of process can increase the production. The central idea is to produce the bio-oil in a small/medium distributed system followed by a shipment from numerous pyrolysis plants to a large gasification plant connected to a gas cleaning system, a pressurisation unit and a catalytic plant.





# Transportable Pyrolysis: a Solution to Poultry Litter Disposal

By F.A. Agblevor, Virginia Polytechnic Institute and State University, USA



The safe and economical disposal of poultry litter is becoming a major problem for the USA poultry industry. Current disposal methods such as land application and cattle feeding are now under pressure because of pollution of water resources due to leaching and runoffs and concern for mad cow disease contamination of the human food chain.

Incineration or combustion is potentially applicable to large scale operations, but for small growers and EPA non-attainment areas, this is not a suitable option because of the high cost of operation. Thus, there is a need to develop suitable technologies to dispose of poultry litter. To this end Virginia Polytechnic Institute and State University are involved in a project to develop suitable solutions to the problem of poultry litter disposal. The ultimate goal of this project is to develop transportable pyrolysis units to process the waste from growers within one locality and thus reducing transportation cost. This technology will not only solve the waste disposal and water pollution problems but it will convert a potential waste to a high-value product such as energy and fertiliser.



Figure 1. Poultry Litter Bio-Oil

Pyrolysis is a high temperature process in the absence of oxygen that converts organic matter into a complex mixture of non-condensable gas (producer gas), vapours, and solid residue. The vapours can be condensed into liquids (bio-oil) see Figure 1. Poultry litter from broiler chicken and turkey houses, as well as bedding material were converted into bio-oil in a laboratory scale fast pyrolysis fluidised bed reactor. The bio-oil yields ranged from 36 wt% to 50 wt% depending on the age and bedding material content of the litter. The bedding material which was mostly hardwood shavings had a bio-oil yield as high as 63 wt%. The biochar (solid residue) yield ranged from 27 wt% to 40 wt% depending on the source, age and composition of the poultry litter.

The higher heating value (HHV) of the poultry litter bio-oils ranged from 26 MJ/kg to 29 MJ/kg which is close to the heating value of low quality coal but has very little sulphur content. The oils had relatively high nitrogen content ranging from 4 wt% to 8 wt%, very low sulphur content that was below 1wt%. The biochar could potentially be used as fertiliser or a soil amendment while the non-condensable gases could be recycled and used as fuel for the process.



Figure 2. The Transportable Pyrolysis Unit.

A community advocacy group, Waste Solutions Forum, consisting of farmers and researchers, was formed in the Shenandoah Valley and worked with Virginia Tech researchers to secure funding (of one million dollars) from the National Fish and Wildlife Foundation to build and demonstrate a scaled-up pyrolysis technology in the Valley. A transportable pyrolysis unit with a design capacity of one to five tons per day has been designed and constructed for demonstration on the farm during the Spring of 2008 (see Figure 2 and Figure 3).



Figure 3. The Transportable Pyrolysis Unit.

We are cooperating with farmers in the Shenandoah Valley who plan to use the poultry litter bio-oils to heat the chicken houses during the winter. Mr Oren Heatwole, a poultry farmer in the Valley has volunteered his facilities to be used in demonstrating the technology. He has subsequently constructed a waste heat burner that will be used to demonstrate the technology. To ensure that this technology does not create air emission problems, the Farm Pilot Projects Corporation has provided funding support to evaluate all emissions from both the pyrolysis process and the combustion of the bio-oil.

ADI Sterling Inc, a Minnesota based company also plans to use the bio-oils to generate electricity. We will investigate and demonstrate the suitability of this technology during the summer of 2008.

Apart from providing energy and disposing of the litter, the technology also addresses bio-security concerns such as avian flu. In case of a flu outbreak, the transportable pyrolysis unit could be moved to the poultry houses and the litter pyrolysed in place. Because of the high temperatures (400-500°C) used for the process, all pathogens and prions will be destroyed during the process.

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**JAN ALEXANDER MYGIND  
BARYNIN**

**OCTOBER 3RD, 1937 –  
JANUARY 15TH, 2008**

## In Memoriam to Jan Barynin

It is with profound sorrow that we announce the passing of our friend and colleague, Dr. Jan Barynin. Jan was the Vice President of Engineering at Dynamotive for many years. He was involved in numerous BioOil development activities in Europe, and the applications of combusting BioOil in North America. In Europe, he became acquainted with PyNe members participating in several meetings and visits. He always believed in the success of the commercialisation of fast pyrolysis technology and his optimistic attitude helped significantly in overcoming the challenges. Friends and colleagues will miss his active correspondence. Jan was passionate about his work and committed world-wide to the advancement of the fast pyrolysis technology.

Dr. Barynin graduated from Royal Technology University of Denmark in 1961 as a Chemical Engineer. He arrived in Canada in 1964 and spent 30 years of his professional career in steam, power, and boiler engineering with Combustion Engineering (CE-Canada), Babcock and Wilcox and H.A. Simons. His latest endeavours have been dedicated to renewable energy and use of agricultural and forestry residues. He developed the full scale BioOil 10 tpd demonstration plant for the Vancouver based Dynamotive Energy Systems Corp. and thereafter the gasifier technology for the Nexterra Energy Corporation. Jan returned to Dynamotive as VP of Engineering with the responsibility of bringing the 100 tonnes/day BioOil plant in West Lorne in Ontario on stream. Jan received his doctorate in 1970 in Chemical Engineering and Chemical Technology from Imperial College, UK.

**Jan, you will be missed and remembered with appreciation for  
your contributions to pyrolysis.**