PYROCYCLING^{TM} PROCESS FOR THE VACUUM PYROLYSIS OF SOFTWOOD BARK RESIDUES AND TREATED WOOD

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Summary

The Pyrocycling^{TM} process for the vacuum pyrolysis of softwood bark residues has been scaled up from the laboratory bench and process development unit scales to the industrial demonstration scale (3 t/h). The wood charcoal and pyrolytic oil produced in the demonstration plant in Jonquière, Québec, have been analyzed and characterized. The bio-oil has been successfully tested as a phenol substitute in the manufacture of phenol-formaldehyde resins for bonding OSB panels. The organic fractions isolated from the pyrolytic aqueous phase have demonstrated anti-fungal properties when doped with $CuSO_4$ additive. The vacuum pyrolysis of used railway sleepers, contaminated with polycyclic aromatic hydrocarbons (PAH) and heavy metals, was carried out on a bench scale. The fate of the PAH and heavy metal contaminants is discussed.

1. Introduction

Bark is an abundant renewable resource. In the province of Quebec, approximately 3 Mt/y of this waste material are produced as a by-product of forestry-related industries (Gouvernement du Québec, 1993). Bark residues are currently burned for energy recovery or sent to landfills where they lead to potential air, water and soil pollution problems. The wood industry is currently searching for a better utilization of this renewable resource. In addition to this, there is a growing concern in Canada over the use of certain chemical wood preservatives. The industry is now looking for ways to safely dispose of treated wood residues. For example, used railway sleepers cannot be easily disposed of since they contain significant amounts of hazardous polycyclic aromatic hydrocarbons (PAH) and some metallic elements which are difficult to eliminate by direct incineration.

Over the last ten years, a vacuum pyrolysis process has been developed at the bench and pilot scales at the Université Laval and Pyrovac Institute Inc. in Québec, Canada. This thermal decomposition process, known under the trademark of Pyrocycling^{TM}, enables a large variety of solid and semi-liquid wastes to be transformed into useful products. Vacuum pyrolysis of bark residues using the Pyrocycling^{TM} process is typically carried out at a temperature of 400-500°C and a total pressure of 2-20 kPa (Roy, Labrecque and de Caumia, 1990). These vacuum conditions allow the pyrolysis products to be rapidly withdrawn from the hot reaction chamber, thus preserving the primary fragments originating from the thermal decomposition reactions. The pyrolytic products are wood charcoal, pyrolytic oils and a small quantity of non condensable gas. It has recently been shown that pyrolysis of bark converts the biomass into a phenolic-rich oil that has the potential of replacing petroleum-based phenol in the synthesis of wood adhesives (Chum *et al.*, 1993; Himmelblau, 1998; Chan *et al.*, 2000).

After studying the vacuum pyrolysis process at the bench scale (Roy, Labrecque and de Caumia, 1990), the process was then scaled up using a 10 - 20 kg/h multiple hearth furnace (Roy *et al.*, 1988). In the early 90's, a new reactor concept was developed (Roy *et al.*, 1994/95; Roy, Blanchette and de Caumia, 1997 and 1998) and applications of the process have been studied for the recycling of used tires (Roy, Chaala and Darmstadt, 1999), the remediation of contaminated soils (Roy *et al.*, 1994/95) and various biomass materials (Roy *et al.*, 1997) at throughput capacities of 40 – 75 kg/h. The process has now been scaled up to demonstrate the technology on an industrial scale (3000 kg/h) for the conversion of biomass to biofuels and chemicals (Roy *et al.*, 2000).

Herein the Pyrocycling^{TM} of softwood bark is described for the production of a phenolic-rich oil used either as a liquid biofuel or as a petroleum phenol substitute in resol resins. Softwood bark also contains a large quantity of naturally anti-fungal compounds whose wood preserving potential could be exploited. Some preliminary results obtained regarding the anti-fungal properties of pyrolysis oils extracted from the aqueous phase derived from the vacuum pyrolysis of softwood bark residues are also presented. The application of the process for the treatment of used railway sleepers is finally examined in order to convert the organic portion of these waste materials into a liquid fuel while leaving most of the heavy metals behind in the residual wood charcoal.

2. Methodology

2.1 Industrial Scale Pyrocycling^{TM} of Softwood Bark Residues

The process flow chart of the new vacuum pyrolysis industrial scale reactor with a capacity of 3000 kg/h is presented in Figure 1. A photograph of the Pyrocycling^{TM} plant is presented in Figure 2. From the feedstock storage facility, separated from the plant building, the feedstock is loaded in a hopper and carried along by extracting screws into a pneumatic conveying system up to a cyclone, located on the roof of the plant building. The feedstock flows down by gravity from the cyclone into a vibrating screen separator, providing a particle size ranging between US Sieves 0.5 and 40 mesh. The feedstock with the specified particle size then sluices out through the vacuum feeding system, consisting of two rotary valves set in line and between which the auxiliary liquid-ring vacuum pump suction line is connected. A positive pressure drop is maintained over the second rotary valve (between the vacuum pump suction and the reactor) in order to avoid the escape of pyrolysis gas from the reactor. The feedstock is then fed into the 14.6 m long and 2.2 m diameter reactor by screw conveyors.

Inside the reactor, the biomass is pyrolyzed on two heating plates, while being carried along and mixed by a raking system. The 10.4 m long by 1.2 m wide heating plates are composed of tubes in which molten salts circulate as a heat carrier medium. The reactor is also heated by electric tracers installed on the exterior shell. The total pressure in the reactor is maintained at 20 kPa.

At the outlet of the reactor, the solid product is moved out of the reactor by a three-stage water-cooled screw conveyor system. The pyrolytic vapours and gaseous products are withdrawn from the reactor via a 600 mm header to a two-stage condensation system, where the heavy bio-oils are condensed in the first packed tower while a mixture of light bio-oil and pyrolytic water is condensed in the second packed tower. The bio-oil/water mixture is afterwards separated by centrifugation. The bio-oil fractions from both packed towers are mixed together and stored (either directly in 1 m^3 polyethylene containers or into a 50 000 L tank). The aqueous phase is neutralized with liquid caustic prior to being disposed of into the municipal sewer system. The non condensable gas drawn up from the second packed tower by the main vacuum pump is further cooled past the pump, compressed to 170 kPa pressure and fired in combination with natural gas into a molten salt heater to provide the energy required for the pyrolysis reaction.

From the molten salt 9 m^3 storage tank, which is equipped with heating elements as well as the piping loop circuit, the molten salt is pumped to the furnace to be heated, circulates then into the reactor heating plates and flows back into the tank. The total surface area occupied by the process equipment, excluding the biomass and product storage rooms, is equivalent to 850 m^2 split into two floors.

The feedstock was air-dry softwood bark purchased from a wood shredding plant. It was composed of approximately 31% v/v balsam fir, 55% v/v white spruce and 14% v/v black spruce. The moisture content of the feedstock at the inlet of the reactor averaged 10.0% by wt. The proximate analysis gave: 74.8% volatile matter, 22.3% fixed carbon and 2.9% ash.

2.2 Anti-fungal Properties of Pyrolytic Oil Doped with $CuSO_4$

The bark mixture was obtained from the Daishowa pulp and paper plant in Québec City and was composed of 70% v/v balsam fir, 28% v/v white spruce and 2% v/v larch. The as-received wet sample was air-dried at room temperature to reduce its moisture content below 12%. It was then ground and sieved to pass across a 0.5" U.S. standard sieve. The pyrolysis run was performed at 450°C and at a total pressure of 20 kPa in a vacuum pyrolysis process development unit (PDU) at an average throughput capacity of 50 kg/h. The PDU has been described elsewhere (Roy *et al.*, 1994/95). A quantity of 206 kg of feedstock was converted to wood charcoal, pyrolysis oils, an aqueous phase and a small quantity of gas. The resulting aqueous phase weighed 56 kg with a moisture content of 80.9%, and thus an organic content of 19.1%. The pyrolysis oil yield was 31.4% on an anhydrous feedstock basis. The highly acidic aqueous phase was adjusted to a pH of 4 to approximate the pH of wood. The aqueous phase was then subjected to a fractionation procedure described elsewhere (Mourant *et al.*, 2000) to obtain four organic fractions, F1 to F4:

- F1: ethyl ether extractibles
- F2: ethyl acetate extractibles
- F3: neutral compounds
- F4: phenolic compounds.

Petri dish inhibition tests were conducted on all four fractions against two brown-rot fungi (*Postia placenta* and *Gloeophyllum trabeum*) and two white-rot fungi (*Irpex lacteus* and *Trametes versicolor*). One set of samples involved the use of the four organic fractions alone, and the other sets used the same fractions doped with 5% $CuSO_4$, a known fungicide. A 5% $CuSO_4$ aqueous solution served as the control. Three holes (5 mm in diameter) were punched with a cork borer in the periphery of each Petri dish containing 20ml of 1.5% malt extract agar, and one hole was punched in the center of the dish. Eighty microlitres of each testing solution were applied in each of the peripheral holes, and 0.1 ml of each ground fungus was added in the central hole. The dishes were incubated at 25°C for two weeks. The inhibition zone was measured from each dish after 7 and 14 days.

2.3 Pyrocycling^{TM} of Used Railway Sleepers at the Laboratory Scale

The feedstock was composed of shredded used wooden railway sleepers from the Netherlands and was in the form of small, thin sticks, approximately 20 mm in length and 5 mm in diameter. The shredded railway sleepers had a moisture content of 13.4%. Proximate analysis indicated that the feedstock was composed of 57.8% volatile matter, 27.9% ash and 14.3% fixed carbon.

The polycyclic aromatic hydrocarbon (PAH) content of the shredded railway sleepers and the wood charcoal and condensates obtained after vacuum pyrolysis was determined using the following procedure. The results, which will be discussed below, are provided in Tables 12 and 15. A 10 g pro rata sample of the condensates was extracted twice with 50 ml of toluene and twice with 50 ml of benzene. The soluble fractions were mixed, concentrated to 10 ml and analyzed by GC/MS (gas chromatograph coupled to a mass spectrometer) for the presence of priority PAH compounds listed in the EPA-610 method. A HP 5890 gas chromatograph with a fused silica capillary column coated with 0.25 μm thickness of HP-5m liquid phase was used. The column dimensions were 30 m x 0.25 mm inner diameter. The end of the column was directly introduced into the ion source of a HP 5970 series mass selective detector. A standard sample of EPA 610 polynuclear aromatic hydrocarbons mixture from Supelco was used to calibrate the GC column. Naphthalene-d_8 was used as an internal standard for quantification of the targeted compounds.

For the wood charcoal, a 33 g sample was extracted with toluene in a soxhlet extraction apparatus for 12 hours. The extracted organics were concentrated to 1 ml and analyzed using a method similar to that used for the analysis of the PAH content of the condensates.

The heavy metal content of the wood charcoal was determined by inductively coupled plasma, except for mercury which was determined by SAA/Hg. The values shown in Table 12 were calculated on a weight basis (in ppm) using the as-received wood charcoal described in Table 10.

The stainless steel batch reactor used for the vacuum pyrolysis run had a usable volume of 15 litres and was 30 cm high and 25 cm in diameter. It was externally heated by electrical elements. The feedstock was poured into a metallic container which was placed inside the reactor. A quantity of 1020.5 g shredded used railway sleeper sticks was treated at a temperature of 500°C and a total pressure of 1.7 kPa for 150 minutes, producing wood charcoal, liquid condensates and gases. Other details concerning the equipment can be found elsewhere (Pakdel, Couture and Roy, 1994).

3. Results and Discussion

3.1 Industrial Scale Demonstration of the Pyrocycling™ Process with Softwood Bark Residues

Yields and Energy Balance

The Pyrocycling™ of softwood bark residues produced pyrolysis oils, wood charcoal, an aqueous phase and pyrolysis gas with the typical yields shown in Table 1. The values were obtained at a reactor throughput capacity of 2185 kg/h (at 10% feedstock moisture content) and are supported by a satisfactory mass balance closure (lack of closure of 4.4%). The typical pyrolysis gas composition is given in Table 2. All the gas is consumed in the gas burner at the outlet of the vacuum pump and is entirely used as a make-up heat source for the pyrolysis reactor. A good combustion regime was observed with very low values of 2-16 ppm CO (@ 7.6 - 8.4% O_2) and 16 ppm TGOC (Total Gaseous Organic Concentration). The P. of Quebec Environmental Regulations preclude the requirement for full VOC characterization when TGOC > 20 ppm. The NOx concentrations of 59 - 69 ppm recorded were also within the 83 ppm criterion set for 15 – 70 MW gas combustion units.

An energy balance around the whole process was also determined, at a throughput capacity of 2185 kg/h. The energy balance closed to 15% (loss). The lack of closure was corrected at pro rata among the charcoal, oil and heat losses. The total energy in and out, 45.9 GJ/h, is hence distributed as follows:

Energy in		**Energy out**	
Biomass	93.5%	Wood Charcoal	43.5%
Total Electric Power	4.4%	Bio-Oil	38.3%
Natural Gas	2.1%	Cooling/Heat Loss	18.2%
	100%		100%

Basically the internal energy of the biomass is conserved and converted into wood charcoal and oil products.

Wood Charcoal and Pyrolytic Oil Quality

The wood charcoal obtained during the test performed at a throughput capacity of 2185 kg/h was characterized. Proximate analysis indicated that the wood charcoal was composed of 30.5 wt.% volatile matter, 61.2 wt.% fixed carbon and 8.3 wt.% ash. The charcoal gross calorific value was 28.4 MJ/kg. As expected the sulfur content is low at < 0.1 wt.%.

The pyrolysis oil was also characterized. Its water content was 15.7 wt.%. Its gross calorific value on an as-received basis was 23 MJ/kg. The non-filtered oil contained a substantial amount of methanol insolubles, mostly wood charcoal particles, ranging between 4 and 6%. There is presently no cyclone between the reactor gas outlet and the first condensing tower, a situation which will be corrected in the near future. However, the solid particles can be filtered out as their size typically ranges between 10 and 100 µm. After filtration through Whatman Paper #4, the methanol insoluble content is reduced to 0.3 wt.%. Other physico-chemical characteristics of the filtered oil are given in Table 3.

The chemical composition of this oil has been thoroughly investigated as the intent is to use this bio-oil as a phenol substitute in the manufacture of phenol-formaldehyde resins for bonding oriented strandboards (OSB), an exterior grade wood composite product (Chan *et al.*, 2000). This product has been registered as Biophen™. Resins having a 50% pyrolytic oil content may be used as surface resins for bonding OSB panels. At 25% oil content, they may serve as core resins. Three-layer panels made with resins having 50% phenol replacement in the surface and 25% phenol replacement in the core met the Canadian Standards (CSA 0437 Series 93) for dry IB (internal bonding) and bending properties MOR (modulus of rupture) and MOE.

3.2 Anti-fungal Properties of the Softwood Bark–Derived Pyrolytic Oil Doped with $CuSO_4$

The pyrolytic aqueous phase derived from waste softwood bark was fractionated into fractions F1 (ethyl ether extractibles), F2 (ethyl acetate extractibles), F3 (neutral compounds) and F4 (phenolic compounds) as described in section 2.2. The composition of the four fractions was analyzed by GC/MS. Fraction F1, containing organic acids, phenols and derivatives (3.0 wt. %), benzenediols (3.9 wt. %) and a variety of other products (quinones, furans, etc.) was the most promising to inhibit the growth of decay fungi (Tables 4 and 5). Fraction F3, composed of neutral compounds, showed no inhibitive effect in the Petri dish agar test. The addition of 5% $CuSO_4$ to the fractions had a synergetic effect on the performance of the fractions and improved their ability to inhibit growth of decay fungi (Tables 6 and 7). It may be possible to reduce the concentration of $CuSO_4$ in the fractions and still maintain an effective protection against the fungi. The brown rot fungus, *P. placenta*, was the most sensitive to these fractions, while the white rot fungus, *I. lacteus*, was the least sensitive, as shown in Tables 4 - 7. These preliminary results tend to indicate that pyrolytic oils as a whole may serve as a carrier for a copper-based wood preservative and increase the effectiveness of the latter against copper-tolerant fungi. Certain compounds in the fractions may form a complex with Cu^{++} and therefore may help the fixation of copper in the wood.

3.3 Pyrocycling™ of Used Railway Sleepers

Yields

Following the recovery of the pyrolysis products, the mass balance was found to close at 98.6%, which is a very satisfactory result. The yields are shown in Table 8. The pyrolysis products consisted of 38.6% wood charcoal, 50.8% pyrolytic condensates and 9.2% non condensable gas. In the batch reactor, the pyrolysis oils and aqueous phase are collected together as pyrolytic condensates. In the process development unit, these condensates can be collected separately as heavy pyrolysis oils in the first condensing tower and an aqueous phase in the second condensing tower.

Pyrolysis Gas

During the batch pyrolysis run, the non condensable gas phase was not burned. The average composition of the gas in % volume, is presented in Table 9. The average molecular mass is 31.3 g/mol and the gross calorific value is 15 MJ/kg.

Wood Charcoal: PAH and Heavy Metal Content

The moisture content, proximate analysis (ash, volatile matter, fixed carbon) and gross calorific value of the wood charcoal are presented in Table 10. The wood charcoal has a high ash content (40.1%) and consequently a low heating value (18.4 MJ/kg).

The polycyclic aromatic hydrocarbon content of the wood charcoal was determined and the identified and quantified PAH compounds are listed in Table 11. All PAH compounds are present in concentrations below the limits set by the Netherlands for solid fuels, with the exception of phenanthrene (0.067 mg/kg) and fluoranthene (0.022 mg/kg) which only slightly exceeded the limits of 0.010 mg/kg and 0.020 mg/kg, respectively.

The original feedstock has an ash content of 27.9%. A portion of this mineral content corresponds to certain heavy metals which found their way into the wood charcoal. Indeed the ash content of the wood charcoal is 40.1% according to Table 10. The wood charcoal loaded with heavy metals can be burned in coal-fired plants as it will represent only 0.5 to 1.0% of the feed. The ash from a coal-fired plant is used as a raw material for the production of cement.

Condensates: PAH and Heavy Metal Content

The moisture content of the condensates, containing both the pyrolysis oil and the aqueous phase, was determined to be 47.7%. The gross calorific value of the condensates was 28.4 MJ/kg. The characteristics of the pyrolysis condensates are listed in Table 13.

The polycyclic aromatic hydrocarbon content of the pyrolysis condensates was determined and Table 14 provides a list of the PAH compounds identified and quantified in the condensates. It should be noted that PAH compounds, such as chrysene, pyrene and anthracene are also present in crude oil in concentrations of 30 000 mg/kg, 20 000 mg/kg and 10 000 mg/kg, respectively (Drabkin, 1981). The aromatic fraction content of crude oils can vary between 10% and 20% by wt. Blending the pyrolysis condensates with petroleum fuels, for example, would therefore not increase the PAH content of the mixture. During their combustion in boilers, engines and turbines, PAH-containing fuel oils form CO_2 and H_2O. PAH-containing oils require the same attention as any distilled or residue petroleum fractions in terms of safety, storage, handling and processing. Alternatively, spraying the pyrolysis condensates over mineral coal burned in thermal stations would have no impact either on the level of PAH contaminants found in the coal-oil mixture, since coal itself already contains the same PAH molecules at very high concentrations.

The heavy metal content of the condensates was determined by inductively coupled plasma, except for mercury which was determined by SAA/Hg. The values shown in Table 15 were calculated on a weight basis (in ppm) using the as-received pyrolysis condensates described in Table 13. In the pyrolysis condensates, lead (14.4 ppm) and antimony (6.7

ppm) are the only two elements which are slightly more concentrated in the condensates than in the original feedstock. As the pyrolysis oil can be blended with large volumes of heating fuel, the concentration of Pb and Sb in the mixed oil should be acceptable.

4. Conclusions

The vacuum pyrolysis Pyrocycling^{TM} of softwood bark residues in the industrial demonstration Pyrocycling^{TM} plant in Jonquière, Québec, produces 29.2% wood charcoal and 30.7% pyrolytic oil (@ 15.7% water content), as well as 19.6% aqueous phase and 20.5% pyrolysis gas. A high biomass conversion was achieved at a throughput capacity of 3000 kg/h. The gas is entirely used as a make-up heat source for the pyrolysis reactor. The wood charcoal has a gross calorific value of 28.4 MJ/kg and a low sulfur content of < 0.1 wt.%. The bio-oil can be used to replace up to 50% of the phenol used in the manufacture of phenol-formaldehyde resins for bonding oriented strandboards which meet the Canadian Standards, CSA 0437 Series 93. The organic fractions isolated from the pyrolytic aqueous phase might act as a good carrier for Cu^{++} and exhibited a good potential for wood preservation when doped with $CuSO_4$.

The vacuum pyrolysis of used railway sleepers, contaminated with polycyclic aromatic hydrocarbons (PAH) and heavy metals, was carried out on a bench scale. The wood charcoal loaded with heavy metals can be burned in coal-fired plants as it will represent only 0.5 to 1.0% of the feed. The ash from a coal-fired plant is used as a raw material for the production of cement. The bulk of the heavy metals in the feedstock found its way into the wood charcoal product. The wood charcoal had a PAH content which respected the limits set by the Netherlands for solid fuels. The pyrolysis condensates have a low heavy metal content. The condensates can be blended with petroleum fuels or with mineral coal burned in thermal stations since the PAH content of the pyrolysis condensates would have no impact on the PAH level of such mixtures.

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5. Literature

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Tables

Table 1. Softwood Bark Pyrolysis – Yields (wt.%, anhydrous feedstock basis)

Product	Yield
Pyrolysis oils @ 15.7% water content	30.7%
Aqueous phase	19.6%
Wood charcoal	29.2%
Pyrolysis gas	20.5%

Table 2. Softwood Bark Pyrolysis – Typical Pyrolysis Gas Composition (% vol.)

Compound	Vol. %
Hydrogen	2.9
Oxygen	0.6
Nitrogen	19.6
Methane	3.6
Carbon monoxide	24.1
Carbon dioxide	41.2
Ethene	0.9
Ethane	0.6
Propene	1.4
Propane	0.0
Water	1.0
Others	4.1
Total	100.0
Average Molecular Weight (g/mol)	35.4
Net Calorific Value (MJ/kg)	8.1

Table 3. Softwood Bark Pyrolysis – Typical Properties of the Filtered Bio-Oils

Water content (wt.%)	15.7
Gross Calorific Value (MJ/kg, as-received basis)	23
Density @ 25°C and 40°C (g/ml)	1.25 and 1.23
Kinematic Viscosity @ 50°C and 80°C (cSt)	100 and 20
Methanol Insolubles (wt.%)	0.34
Pour Point (°C)	< 5
Flash Point (°C)	> 59
pH	4.2
Na, K, Ca content (ppm)	16; 8.5; 578

Table 4. Growth Inhibition of Brown Rot Fungi, *G. trabeum* and *P. placenta*, by the Four Fractions of Pyrolytic Aqueous Phase at Various Concentrations after 14 Days of Incubation at 25°C.

Fungi and fractions	Concentration of the fraction in deionized water (g/ml)			
	0.20	0.15	0.10	0.05
	Growth inhibition %			
G. trabeum				
F1	100.00 (0.00)	64.28 (43.42)	0.00 (0.00)	0.00 (0.00)
F2	63.69 (47.04)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
F3	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
F4	80.74 (39.94)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
P. placenta				
F1	100.00 (0.00)	100.00 (0.00)	36.58 (16.39)	0.00 (0.00)
F2	12.27 (12.45)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
F3	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
F4	100.00 (0.00)	93.76 (10.78)	37.11 (22.67)	0.00 (0.00)

Note: Values are means of 15 replicates; standard deviations are given in parentheses. All controls, composed of only deionized water, showed no inhibition (0%).

Table 5. Growth Inhibition of White Rot Fungi, *I. lacteus* and *T. versicolor*, by the Four Fractions of Pyrolytic Aqueous Phase at Various Concentrations after 14 Days of Incubation at 25°C.

Fungi and fractions	Concentration of the fraction in deionized water (g/ml)			
	0.20	0.15	0.10	0.05
	Growth inhibition %			
I. lacteus				
F1	98.38 (3.52)	37.12 (30.89)	0.00 (0.00)	0.00 (0.00)
F2	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
F3	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
F4	73.47 (38.66)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
T. versicolor				
F1	100.00 (0.00)	100.00 (0.00)	62.80 (22.06)	0.00 (0.00)
F2	6.22 (12.47)	0.95 (3.69)	0.00 (0.00)	0.00 (0.00)
F3	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
F4	100.00 (0.00)	23.62 (28.77)	4.30 (7.40)	0.00 (0.00)

Note: Values are means of 15 replicates; standard deviations are given in parentheses. All controls, composed of only deionized water, showed no inhibition (0%).

Table 6. Growth Inhibition of Brown Rot Fungi, *G. trabeum* and *P. placenta*, by the Four Fractions of Pyrolytic Aqueous Phase at Various Concentrations, Enriched with 5% $CuSO_4$, after 14 Days of Incubation at 25°C.

Fungi and fractions	Concentration of the fraction in deionized water (g/ml)			
	0.20	0.15	0.10	0.05
	Growth inhibition %			
G. trabeum				
F1	100.00 (0.00)	100.00 (0.00)	100.00 (0.00)	100.00 (0.00)
F2	100.00 (0.00)	100.00 (0.00)	100.00 (0.00)	99.44 (1.47)
F3	99.74 (0.99)	98.89 (2.44)	98.63 (2.55)	96.85 (4.09)
F4	100.00 (0.00)	100.00 (0.00)	99.14 (1.78)	98.92 (2.36)
Control	97.74 (3.10)			
P. placenta				
F1	100.00 (0.00)	100.00 (0.00)	94.66 (11.17)	100.00 (0.00)
F2	98.35 (4.56)	97.16 (5.46)	85.41 (21.69)	89.36 (16.76)
F3	78.55 (40.77)	80.00 (41.40)	56.96 (49.25)	98.47 (3.47)
F4	100.00 (0.00)	100.00 (0.00)	100.00 (0.00)	86.61 (27.92)
Control	78.96 (40.23)			

Note: Values are means of 15 replicates; standard deviations are given in parentheses.
The control is composed of a 5% $CuSO_4$ aqueous solution.

Table 7. Growth Inhibition of White Rot Fungi, *I. lacteus* and *T. versicolor*, by the Four Fractions of Pyrolytic Aqueous Phase at Various Concentrations, Enriched with 5% $CuSO_4$, after 14 Days of Incubation at 25°C.

Fungi and fractions	Concentration of the fraction in deionized water (g/ml)			
	0.20	0.15	0.10	0.05
	Growth inhibition %			
I. lacteus				
F1	100.00 (0.00)	96.97 (3.34)	94.05 (4.43)	94.48 (4.44)
F2	96.03 (2.19)	97.56 (2.56)	91.55 (3.17)	90.43 (6.06)
F3	86.66 (4.29)	88.58 (5.57)	90.15 (4.34)	87.50 (3.51)
F4	95.47 (3.08)	93.47 (3.98)	93.09 (4.33)	89.72 (5.56)
Control	87.18 (5.65)			
T. versicolor				
F1	100.00 (0.00)	100.00 (0.00)	100.00 (0.00)	100.00 (0.00)
F2	100.00 (0.00)	100.00 (0.00)	98.95 (1.80)	88.95 (7.48)
F3	100.00 (0.00)	87.59 (6.85)	89.53 (6.69)	78.84 (7.82)
F4	100.00 (0.00)	98.50 (3.99)	100.00 (0.00)	97.63 (3.25)
Control	70.71 (7.59)			

Note: Values are means of 15 replicates; standard deviations are given in parentheses. The control is composed of a 5% $CuSO_4$ aqueous solution.

Table 8. Used Railway Sleepers Pyrolysis - Yields and Mass Balance

Product	Yield (%)
Wood charcoal	38.6
Condensates	50.8
Gas	9.2
Loss	1.4
Total	100.0

Table 9. Used Railway Sleepers Pyrolysis - Pyrolysis Gas Composition (vol. %)

Compound	Vol. %
Hydrogen	13.1
Methane	14.0
Carbon monoxide	25.7
Carbon dioxide	32.5
Ethene	1.3
Ethane	1.8
Propene	2.8
Methanol	0.8
Acetaldehyde	1.5
Butene	0.3
Butane	0.2
Pentane	0.3
Others	4.5
Total	100.0
Average Molecular Weight (g/mol)	31.3
Gross Calorific Value (MJ/kg)	15.0

Table 10. Used Railway Sleepers Pyrolysis - Wood Charcoal Characteristics

Moisture Content (wt. %, as-received basis)	2.1
Proximate Analysis	
Volatile matter	17.3%
Ash	40.1%
Fixed carbon	42.6%
Gross Calorific Value (MJ/kg, as-received basis)	18.4

Table 11. Used Railway Sleepers Pyrolysis - Polycyclic Aromatic Hydrocarbons in the Feedstock and the Wood Charcoal (mg/kg)

Compound	Used Railway Sleeper Feedstock	Wood Charcoal	Reported Limit for Solid Fuels (The Netherlands)
Naphthalene	4500	0.073	0.100
Acenaphthylene	33	---	0.200
Acenaphthene	3100	0.014	0.200
Fluorene	3100	0.004	0.020
Phenanthrene	12000	0.067	0.010
Anthracene	1300	0.007	0.010
Fluoranthene	8700	0.022	0.020
Pyrene	5200	0.016	0.100
Benzo(a)anthracene	1700	0.011	0.010
Chrysene	1400	0.012	0.010
Benzo(a)pyrene	470	0.011	0.020
Benzo(k)fluoranthene	330	---	0.010
Benzo(b)fluoranthene	630	0.003	0.010
Indeno(1,2,3-c,d)pyrene	140	---	0.050
Dibenzo(a,h)anthracene	58	---	0.200
Benzo(g,h,i)perylene	84	---	0.100
Total		0.240	

Table 12. **Used Railway Sleepers Pyrolysis - Heavy Metals in the Feedstock and the Wood Charcoal (mg/kg)**

Element	Used Railway Sleeper Feedstock	Wood Charcoal	Reported Limit for Solid Fuels (The Netherlands)
Mercury (Hg)	0.087	< d.l.	0.030
Arsenic (As)	0.95	7.41	0.50
Cadmium (Cd)	0.22	1.32	0.20
Cobalt (Co)	< 2.0	< d.l.	2.0
Copper (Cu)	15	141	2.0
Iron (Fe)	2200	12 268	5.0
Manganese (Mn)	100	280	5.0
Nickel (Ni)	< 3.0	17.8	3.0
Lead (Pb)	8.4	88.5	5.0
Antimony (Sb)	< 3.0	13.2	3.0
Vanadium (V)	< 1.0	13.2	1.0
Tin (Sn)	4.7	n.a.	2.0

Table 13. **Used Railway Sleepers Pyrolysis - Pyrolysis Condensate Characteristics**

Moisture Content (wt. %)	47.7
pH	2.6
Gross Calorific Value (MJ/kg, anhydrous basis)	28.4

Table 14. Used Railway Sleepers Pyrolysis - Polycyclic Aromatic Hydrocarbons in the Feedstock and the Pyrolysis Condensates (mg/kg)

Compound	Used Railway Sleeper Feedstock	Pyrolysis Condensates
Naphthalene	4500	8
Acenaphthylene	33	86
Acenaphthene	3100	372
Fluorene	3100	486
Phenanthrene	12000	3010
Anthracene	1300	1056
Fluoranthene	8700	1425
Pyrene	5200	2815
Benzo(a)anthracene	1700	808
Chrysene	1400	692
Benzo(a)pyrene	470	108
Benzo(k)fluoranthene	330	198
Benzo(b)fluoranthene	630	318
Indeno(1,2,3-c,d)pyrene	140	51
Dibenzo(a,h)anthracene	58	12
Benzo(g,h,i)perylene	84	26
Total		11 500

Table 15. Used Railway Sleepers Pyrolysis - Heavy Metals in the Feedstock and the Pyrolysis Condensates (mg/kg)

Element	Used Railway Sleeper Feedstock	Pyrolysis Condensates
Mercury (Hg)	0.087	< d.l.
Arsenic (As)	0.95	0.14
Cadmium (Cd)	0.22	0.27
Cobalt (Co)	< 2.0	< d.l.
Copper (Cu)	15	0.75
Iron (Fe)	2200	0.75
Manganese (Mn)	100	0.22
Nickel (Ni)	< 3.0	0.40
Lead (Pb)	8.4	14.4
Antimony (Sb)	< 3.0	6.7
Vanadium (V)	< 1.0	< d.l.
Tin (Sn)	4.7	n.a.

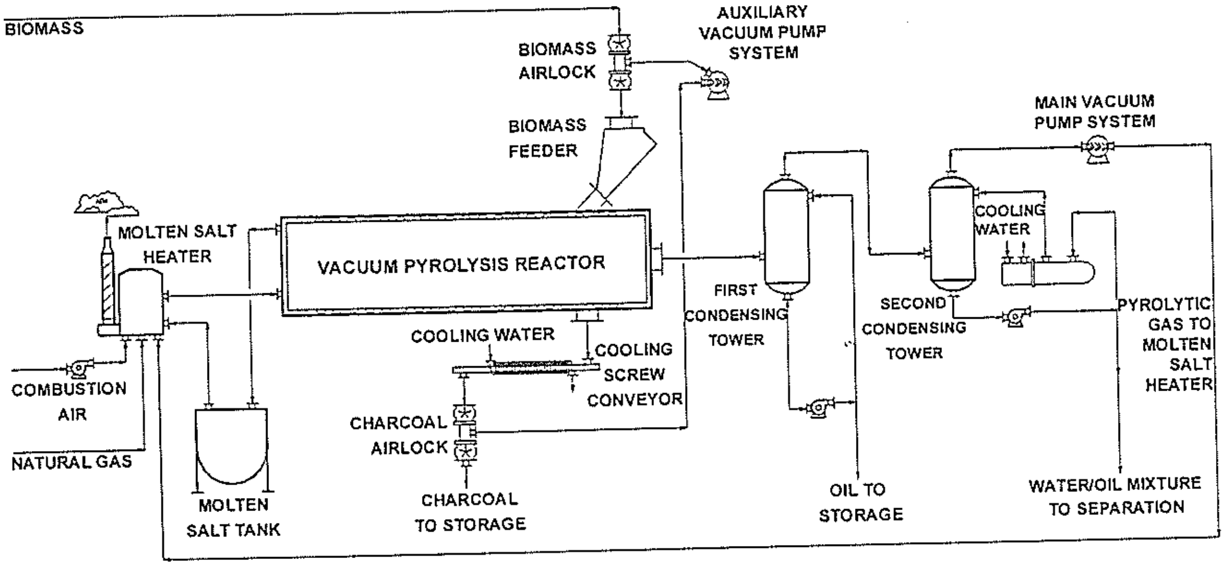

Figure 1. Process flow sheet of the new vacuum pyrolysis industrial scale reactor

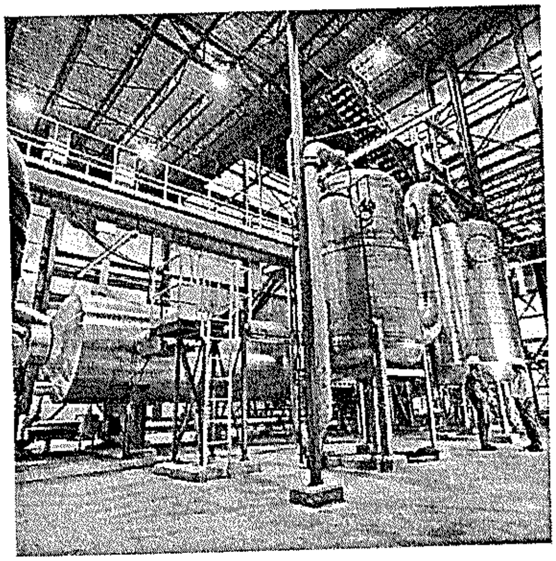

Figure 2. Photograph of the 3.5 t/h Pyrocycling^{TM} plant