

COMMERCIAL ASPECTS OF THE ENSYN RTP™ PROCESS AND THE DEVELOPMENT OF PRODUCTS FROM TREATED WOOD

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ABSTRACT

Ensyn has developed and commercialized a technology which converts clean wood, wood residues and other biomass to a low viscous "bio-oil" liquid with yields of about 75% of the input biomass material. The process has been termed Rapid Thermal Processing or RTP™ since it is based on the very fast application of heat at moderate temperatures (approximately 930°F or 500°C), essentially without the presence of any air or oxygen. During RTP™, biomass is vaporized by hot sand at atmospheric pressure, and the product vapors are quickly condensed and recovered as a liquid which is pourable and pumpable at room temperature. Since 1989, four commercial RTP™ plants have been commissioned and remain in operation producing boiler fuel and chemicals. Construction will commence on four new commercial RTP™ plants in 1998; two in Europe and two in North America.

In addition to the present fuel and chemical commercial uses for bio-oil, applied R&D is being carried out at Ensyn to apply bio-oil to preservative applications. This R&D has three broad objectives:

1. to use bio-oil derived from clean wood and wood residues as a preservative
2. to use bio-oil as a preservative carrier
3. to recycle treated wood via RTP™ to produce bio-oil with the intention of using the resultant bio-oil as a preservative

This paper briefly reviews the RTP™ technology and its commercial implementation to date and the results of the bio-oil preservative program obtained up to the time of writing. The results are very positive and clearly demonstrate the potential for bio-oil, derived from creosote-treated wood, as a preservative. In addition to achieving toxicity levels equivalent or better than creosote, there is evidence supporting an increase in compressive strength for soil blocks treated with bio-oil.

BACKGROUND

RTP™ Technology

Rapid Thermal Processing (RTP™) is a proprietary technology which converts various carbonaceous feedstocks to value-added fuels and chemicals. Carbonaceous materials which have been processed include biomass and petroleum feedstocks. Biomass is simply a generic term which in its broadest sense includes all natural organic material. However, in terms of commercial interest and for the purposes of this paper, biomass refers primarily to wood, wood residues, bark and agricultural residues (bagasse, straws, husks, etc.).

RTP™ is an extremely fast thermal (or in some special cases, thermo-catalytic) process which occurs at atmospheric pressure and at moderate temperatures, typically 930°F or 500°C. Processing times are in the order of 0.5 seconds. At the heart of the technology is a recirculating, transported bed conversion unit where biomass feedstock is intimately contacted with a hot particulate heat carrier, typically sand. The basic premise of RTP™ is that short contact times and rapid heat transfer result in high yields of non-equilibrium products which inherently have desirable fuel and chemical properties, and therefore have an increased economic value. This premise has certainly been proven in commercial wood conversion where yields of "bio-oil" are typically 75% of the input wood feedstock (note that conventional wood conversion processes such as slow pyrolysis produce 20-30% yields of a thick polymerized "tar").

RTP™ has been in commercial use, producing bio-oil from wood, since 1989. At present, Ensyn's commercial production is as follows (1997 figures):

Wet wood processed (through the dryer):	29,100 T/y (26,500 t/y)
Dry wood processed (in the RTP unit):	16,200 T/y (14,700 t/y)
Bio-oil produced:	12,100 T/y (11,000 t/y)

In addition to the above production, which should increase significantly in 1998, construction will commence on four new projects in 1998. Two of these will be in Europe and two in North America, with new production capacity summarized as follows:

Wet wood processed (through the dryer):	880,000 T/y (800,000 t/y)
Dry wood processed (in the RTP unit):	440,000 T/y (400,000 t/y)
Bio-oil produced:	330,000 T/y (300,000 t/y)

RTP™ Bio-Oil Properties

Ensyn's bio-oil, as produced via RTP™ from wood and other biomass, is an oxygenated organic liquid having the appearance of espresso coffee. It is not a thick "tar", as is the product of wood pyrolysis, but is a low viscous liquid which is pourable and pumpable at

room temperature. The heating value of bio-oil is greater than that of other oxygenated fuels such as ethanol but is less than that of diesel or light fuel oil. Average heating values are listed below for comparison:

FUEL	HIGHER HEATING VALUE	
	MJ/l	BTU/US gal.
Bio-oil	21.0	75,000
Diesel/Light Oil	38.9	138,000
Ethanol	17.5	62,500

When produced from wood, bio-oil consists of depolymerized wood components which are made up primarily of carbon, hydrogen and oxygen. Sulphur levels are extremely low, typically negligible. The major organic constituents in bio-oil are a liquid lignin derivative (depolymerized "liquid" lignin), alcohols, natural organic acids, and carbonyls. The organic acid content give bio-oil an acidity which is less than lemon juice and comparable to vinegar. Water is also a major component but is not a contaminant, as is the case with petroleum fuels, since the water is fully miscible in the bio-oil. Clearly, bio-oil is an aqueous polar liquid which is not directly miscible with petroleum fuels. Nevertheless, it has been used "as-is" as a substitute for fuel oil in boiler and engine applications, and has the potential for blending with petroleum if appropriate blending/emulsifier technologies are employed.

RTP™ Bio-Oil Applications and Uses

Not only does bio-oil burn cleanly and efficiently once ignited, it also has valuable constituents which can be used in various chemical industries. It is therefore not surprising that the first commercial production and use of bio-oil, in 1989, was for a dual fuel/chemical application. In this case, approximately 50% of the whole bio-oil is extracted and used as a chemical feedstock. The remaining fraction, which has roughly the same fuel properties (i.e., energy content and viscosity) as the original whole bio-oil, is used as a boiler fuel to produce process heat. In this application, there is no co-firing of petroleum nor any need for "pilot" petroleum fuel oil to assist or sustain combustion in the boiler. Since 1989, two additional bio-oil boilers have been built and brought on-line for the production of industrial process heat. Bio-oil has also been used commercially to co-fire a coal utility boiler for power generation at Manitowoc Public Utilities (MPU) (Wisconsin), and has been approved for use in utility boilers in Sweden for district heating applications (note: after an extensive boiler test program in Sweden in 1996 and 1997, this commercial project will commence in 1998).

It is important to note that no significant modifications are required to retrofit the boiler itself for bio-oil use. However, relatively minor modifications to the burner are required, and because of the bio-oil acidity, attention must be given to the design of the fuel storage, handling, delivery and injection systems.

Bio-oil has also been used to fuel certain robust stationary turbines and diesel engines whose basic design is pre-disposed for successful retrofit. The driving force for the development and commercial application of these engines is environmental, particularly in Europe where a premium is paid for power generation if the fuel is a "green" (i.e., renewable, CO₂-neutral, and has a negligible sulphur content).

In addition to specialty chemicals, green fuel and power generation applications, Ensyn has recently developed additional value-added chemical products which have greatly expanded the markets for RTP™ technology. Several projects are now proceeding on the basis of bio-fuel, power and chemicals production from wood and other biomass.

Past R&D work has clearly led to the commercial development of an array of fuel, energy and chemical products via RTP™. Nevertheless, Ensyn's R&D program is dedicated to further expansion of bio-oil markets. One current area of keen interest is an investigation of the application of RTP™ to produce wood preservatives. This research work is focused not only on the use of "clean" bio-oil or a bio-oil fraction (i.e., bio-oil produced from virgin biomass) as a wood preservative, but also the use of bio-oil as a carrier for conventional preservatives and the use of RTP™ to process creosote-contaminated wood as a means of recycling and creosote recovery.

PRESERVATIVES RESEARCH PROGRAMS

Ensyn's work on the production of preservatives from bio-oil and the use of RTP™ to recycle contaminated wood and to recover creosote is being jointly funded by The Tennessee Valley Authority (T.V.A.), the Canadian Department of Natural Resources (NRCAN/CANMET) and Ensyn. Actual testing is being carried out at Ensyn, where wood is processed and bio-oil products are produced, and at Mississippi State University (MSU), where preservative evaluations are being conducted.

The stated objectives of the wood preservatives project are given as follows:

1. To determine whether RTP™ bio-oil made from clean wood feedstock can be used to replace current commercial wood preservatives.
2. To determine whether bio-oil made from clean wood feedstock can be used as a replacement for oilborne or waterborne preservative carriers (i.e., to displace light fuel oil or aqueous solutions as preservative carriers).
3. To determine whether creosote-treated wood can be processed by RTP™ to recycle contaminated wood, recover creosote and produce a recycled wood preservative product.

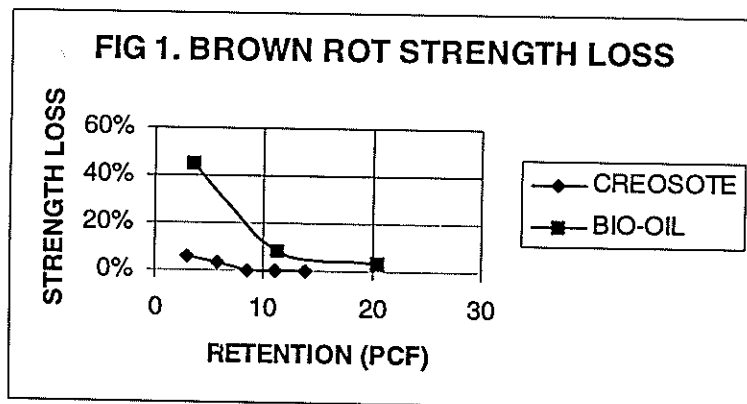
Clean Bio-oil as a Preservative

Chemical analysis of a typical bio-oil reveals several chemicals that can be expected to inhibit the growth of fungi. These include lignin-derived phenolic compounds and their derivatives.

The systematic evaluation of bio-oil as a preservative has commenced. Bio-oil samples were produced and sent to M.S.U. for impregnation and testing. At M.S.U., a modified AWWA soil-block test (AWWA E10-91) is used to establish the toxic threshold value for the bio-oil against a brown-rot fungus, *Gloeophyllum trabeum* (*G. trabeum*) and a white-rot fungus, *Trametes versicolor* (*T. versicolor*). Southern yellow pine sapwood is being used for *G. trabeum* and aspen sapwood for *T. versicolor*. Methanol is the carrier and diluent, and creosote is the preservative with which bio-oil will be compared.

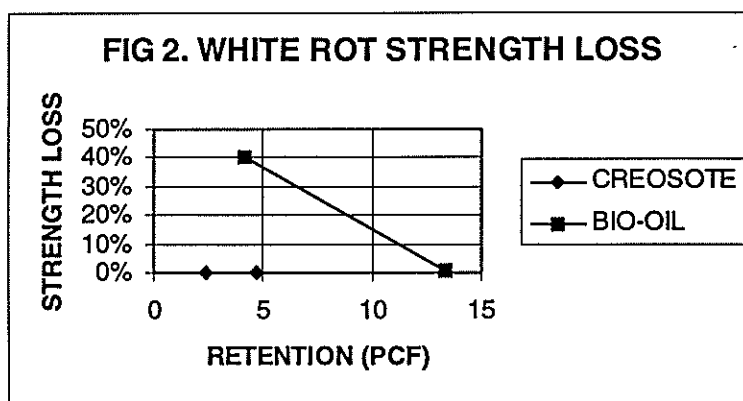
The test series for both fungi employ a methanol "control" (100% methanol), and creosote concentrations in methanol of 5, 10, 15, 20 and 25 percent. Test bio-oil concentrations are 10, 30 and 50 percent in methanol.

Figure 1 is a plot of strength loss versus preservative retention for creosote and bio-oil when exposed to brown-rot fungus. The toxicity threshold for creosote is 9 pounds per cubic foot (PCF) and approximately 15 PCF for bio-oil. The curves represent the mean strength loss over eight (8) samples for each retention. At 9 PCF creosote completely protects the wood against brown-rot decay. Even at 20 PCF the bio-oil can not be considered effective protection against brown-rot.



Bio-oil is more effective against white-rot decay. Bio-oil affords nearly total protection against decay at retentions in excess of 13 PCF (see Figure 2). Creosote provides the same level of protection at a retention of 2.4 PCF.

While clean bio-oil does provide a measure of protection against brown and white rot fungi, it must be used in significantly higher concentrations than creosote.



Clean Bio-oil as a Preservative Carrier

Bio-oil may be attractive as a carrier for certain commercial preservatives because of its chemical composition, its renewable nature, and its inherent preservative properties. If it can be established that either oilborne or waterborne preservatives are miscible with bio-oil, then it should be possible to use bio-oil as a carrier to replace the fuel oil or aqueous solvents now used in the industry. In the case of oilborne carriers, a large volume of high value petroleum could be economically displaced by renewable liquids produced from wood residues, which are often a disposal problem in their own right. The inherent preservative properties of this renewable carrier suggest that the concentration of the principle preservative could be reduced.

A study to evaluate bio-oil as a preservative carrier has therefore been included in the joint program with M.S.U. Pentachlorophenol (penta), the predominant oilborne preservative, has been selected for this task and testing is now in progress. Bio-oil samples have been prepared at Ensyn and delivered to M.S.U. for carrier testing. The results of these tests were not available at the time of writing and therefore, one can not speculate on the potential use of bio-oil as a preservative carrier.

The RTP™ Processing of Creosote-Contaminated Wood

Since it remains as such an enormous solid waste disposal problem, one of the most important tasks in Ensyn's preservative research program is the development of a value-added preservative from creosote-treated wood. The task is designed to determine whether the creosote compounds are retained in the bio-oil after RTP™ processing of creosote-treated wood, and if this bio-oil can be used directly as a creosote solution to treat fresh wood. If so, then the industry would have a solution to the solid waste disposal issue and would at the same time have an effective method for recycling creosote.

Preliminary laboratory trials clearly indicated that creosote-treated wood could be processed in RTP™ equipment giving bio-oil/creosote liquid yields of about 75%. Gas Chromatograph/Mass Spectra (GCMS) characterization of creosote showed that the

creosote passes through the pyrolysis process apparently undegraded. The effectiveness of bio-oil derived from the pyrolysis of railway ties was similar to that of commercial grade creosote. Table 2 lists the toxicity thresholds for brown-rot and white-rot fungi when the wood is treated with bio-oil and creosote. The test results show that bio-oil and creosote have essentially the same toxicity threshold when tested with the two fungi. Bio-oil appears to be more effective against white-rot fungus.

Figures 3 and 4 show the decrease in strength loss for brown and white rot fungi respectively. In both cases the bio-oil showed slightly better preservative performance than creosote. Given the variability in the test, it is not possible to conclude that one preservative is better than the other, only that they are equally effective.

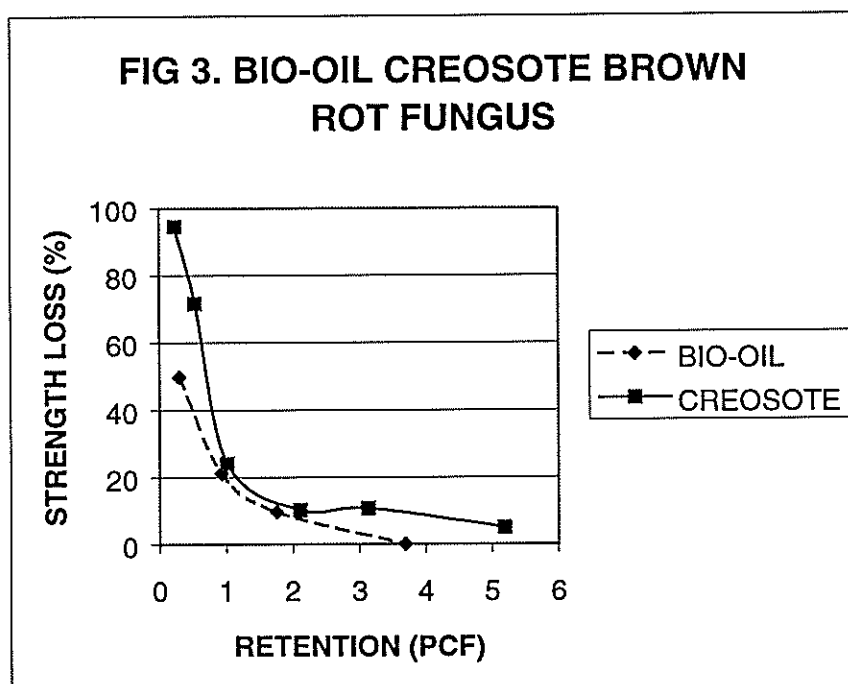
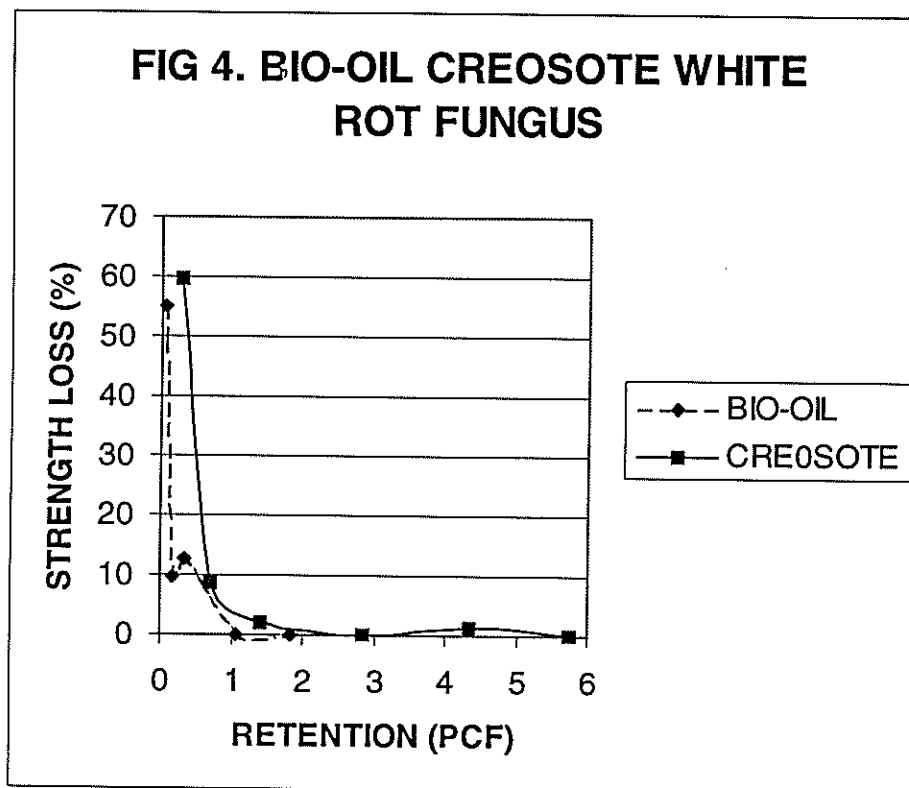


TABLE 2 RAILWAY DERIVED BIO-OIL

Formulation	Fungus	Toxicity Threshold (PCF)
Creosote	Brown-rot	1.4
Bio-Oil	Brown-rot	1.4
Creosote	White-rot	0.7 - 0.8
Bio-Oil	White-rot	0.2 - 0.3

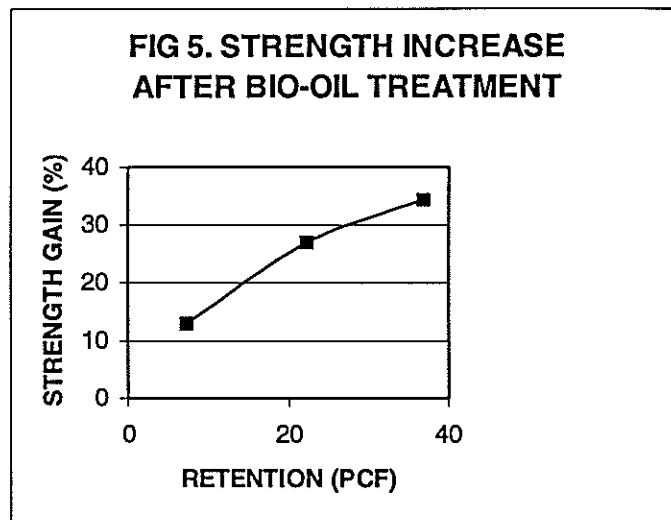
Strength Increase of Bio-Oil Treated Wood

Preliminary wood penetration tests conducted by Ensyn several years ago using a heavier, slow pyrolysis derived tar has indicated that bio-oil can effectively penetrate the



wood. The lighter, low viscosity oils derived from the RTP™ process are expected to penetrate more easily and provide adequate penetration depth for all preserved wood applications. In addition, bio-oil contains components that polymerize upon exposure to air forming a solid skin. It is expected that the bio-oil will thus form a continuous coating that will seal the wood surface, locking in the preservative to prevent leaching, and also inhibit water penetration.

Bio-oil contains natural wood resins that can be used to bond wood fiber. Soil block testing at MSU identified the potential for increased wood strength with increasing bio-oil retention. It was noted that samples with high bio-oil retention exceeded the load capacity of the testing apparatus. A second set of tests was commissioned whereby wood blocks were tested for strength only. The preliminary results show that at a retention of 36 pcf, the strength increased by 34%. Figure 5 shows a plot of strength increase as a function of retention. Should this trend withstand more rigorous testing it would confirm that bio-oil has additional positive properties over creosote.



SUMMARY

The conversion of wood and other biomass residues to high yields of liquid bio-oil has been proven commercially since 1989 in energy, fuel and chemical markets. R&D is focussing on the development of additional value-added products to expand RTP™ markets and enhance the profitability of current commercial projects. One of the major value-added R&D efforts deals with the wood preservative industry with the stated objectives of investigating the use of bio-oil directly as a preservative, the use of bio-oil as a preservative carrier, and the use of RTP™ technology to recycle creosote-treated wood and recover creosote for re-use as a preservative.

When bio-oil is obtained from wood treated with creosote the bio-oil is as effective or more effective as commercial grades of creosote. Bio-oil also appears to form a protective skin on the exterior of the treated wood and act as a physical barrier to decay. The increase in strength with bio-oil treated wood could provide bio-oil preservatives with a fundamental advantage over creosote.

RTP™ technology provides a viable means of recycling creosote treated wood. The process produces high liquid yields of preservative solutions that are as good or better than existing creosote. Work in progress will determine if pentachlorophenol treated wood can be recycled in a similar fashion. It is Ensyn's ultimate goal to develop processes that will allow for recycling of all treated wood and thereby provide industry with an economical means of disposing of treated wood products.