New Bio-refinery Concept to Convert Softwood Bark to Transportation Fuels

Final Report to the Washington State Department of Ecology

Developed by

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Authors:

Manuel Garcia-Perez, Shulin Chen, Shuai Zhou, Zhouhong Wang, Jieni Lian, Robert Lee Johnson, Shi-Shen Liaw, Oisik Das

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Beyond Waste Objectives

Turning organic wastes into resources such as compost, bioenergy and biofuels, recovery of stable carbon and nutrients and other products promotes economic vitality in growing industries, and protects the environment. This creates robust markets and sustainable jobs in all sectors of the economy, and facilitates closed-loop materials management where by-products from one process become feedstocks for another with no waste generated.

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1.-Summary

Key Findings:

This project has identified a new pretreatment concept to enhance the production of sugars from the fast pyrolysis of wood and straw. It also proves, for the first time, that sugars recovered from pyrolysis can be easily converted into ethanol. These two results are important because they show that fast pyrolysis of wood or straw followed by bio-oil hydrotreatment can create green gasoline and green diesel (from the lignin fraction), as well as ethanol (from the cellulose fraction). These three common transportation fuels are of greater value than bunker fuel, which is the only fuel that can be currently replaced with pyrolytic oils. More investigations at the bench scale are needed to generate enough data for scale up of this technology and to evaluate its economic viability.

The concept studied consisted of two steps. The first step was the pyrolysis of bark to produce bio-oils, charcoal and gases. The bio-oil was then refined to produce transportation fuels (ethanol) from cellulose. The US Department of Energy is working with the petroleum industry and National Labs to develop new refineries to convert at least 40 mass % of these bio-oils into green gasoline and green diesel. Although possible, hydrotreating fast pyrolysis oils is a complex technology. The de-oxygenation of the cellulose and hemicellulose sugars consumes large quantities of hydrogen. Furthermore, the sugars tend to deactivate the catalysts and produce more coke, a coal like material that is not useful as liquid fuel.

Our report ends with a chapter devoted to understanding the potential environmental impact of using bio-chars as soil amendments. The last chapter is written in conjunction with the project “Use of bio-char from the pyrolysis of waste organic material as a soil amendment” (Interagency agreement: No: C0800248). Our study concludes that using bio-char is a safe practice and that the levels of dioxins and polyaromatic hydrocarbons measured are well below current environmental specifications of Washington State. More extensive studies are needed to confirm these results.

Process Overview:

Wood and straw contain three main compounds valuable for liquid fuel production: cellulose, hemicellulose, and lignin. This project was carried out using softwood bark from the state of Washington as a feedstock. In spite of the large volumes of bark generated in the state of Washington not a single technology is available to convert these wastes into transportation fuels and chemicals. Most of the bark is now combusted to produce heat or is used as a soil amendment. This project proposes an alternative process to convert this bark into transportation fuels.

The separation of pyrolytic sugars and their conversion to ethanol prior to hydrotreatment could improve the economic and technical viability of bio-oil refineries. In this project the bio-oil was separated with several organic solvents to obtain an organic phase rich in phenols and a water soluble phase rich in sugars. The organic phase, rich in phenols, was neutralized and distilled to produce a fraction rich in mono-phenols, which can be used as fuel additives, as a source of chemicals or can be hydrotreated to produce green gasoline and green diesel. The sugars (levoglucosan and cellubiosan) that are soluble in the aqueous phase were converted into glucose using acid hydrolysis, the remaining phenols were removed (detoxification), and the resulting glucose was fermented to produce ethanol.

Current technologies tend to maximize the conversion of just one of the biomass fractions (cellulose, hemicelluloses and lignin) into a suitable transportation fuel. As a consequence, most of the technologies on the market result in the production of heat from the other two fractions. Developing processes capable of converting all wood biomass fractions into suitable transportation fuels will considerably enhance the economic viability and fuel recovery of these bio-refineries.

Methods:

To accomplish the objectives stated in our original contract it was necessary to build new reactors and to purchase new analytical equipment. The new laboratories created at WSU, together with the kind support of Professors KC Das from the University of Georgia and Chun-Zhu Li from Monash University (Australia) were critical to the completion of this project. The new Auger Pyrolysis reactor and the analytical laboratory built at WSU are briefly described in this report.

Pyrolysis tests with softwood bark from the State of Washington were carried out at 500 ^{o}C in three different pyrolysis reactors (fixed bed batch, Auger, and fluidized bed). The yields of products (bio-char, liquid and gases) were reported. The liquid yields obtained from softwood bark were lower (32-51 mass %) than those reported for other, bark free, lignocellulosic materials (50-64 mass %). This is due to the higher contents of lignin, extractives and ash in bark. As expected the highest yield of liquid was obtained with the fluidized bed pyrolysis reactor (fast pyrolysis reactor). An increase in bio-oil yield was obtained when the alkalines were removed with hot water pretreatment.

The contents of several chemical species in selected bio-oils were quantified by GC/MS. Important compositional differences were observed between the oils derived from softwood bark and those obtained by Dynamotive from hardwood. The content of pyrolytic sugars in the oil was in general, low (4-10 mass %) for softwood bark. Thus, additional studies in a Pyrolyser coupled with a mass spectrometer were carried out to identify the best pretreatment and pyrolysis conditions to maximize the yields of pyrolytic sugars. Our experimental results suggest that removing the alkalines with hot water at 150 ^{o}C followed by heating of the biomass to temperatures around 250 ^{o}C and the pyrolysis at temperatures close to 400 ^{o}C will result in a sizable increase in the yields of pyrolytic sugars from softwood bark.

Oil from Dynamotive and two oils obtained from softwood bark (batch reactor and fluidized bed reactor) were extracted with blends of ethyl acetate and bio-diesel. An organic phase rich in

phenols and an aqueous phase rich in sugars resulted from this process. The contents of selected chemical species in the organic phase and in the aqueous phase were quantified and used to calculate the distribution coefficients (K) for each of these species. This coefficient is commonly used as an index of the capacity of the organic solvent studied (in this case blends of ethyl acetate and bio-diesel) to extract the desired compounds (in this case the phenols). Solvents with higher distribution coefficients are desirable because they will result in more compact extraction units and more economic processes. For the Dynamotive oil, the distribution coefficients for most of the phenols studied increased as the content of ethyl acetate in the solvent increased. Thus, using pure ethyl acetate to extract the phenols from the Dynamotive oil should result in a more economic process than blends of ethyl acetate and bio-diesel. Conversely, for the softwood bark derived oil, the distribution coefficient for the phenols, in general, decreased as the content of ethyl acetate increases. The result of solubility studies indicates that the best extraction conditions (solvent type, temperature, ratio of phases), which will maximize the separation of phenols from the sugars, will be a function of the phenol/sugar/water composition of a given bio-oil.

The acetic acid extracted by the organic phase reduces the pH of the resulting blend making the product more corrosive. Two methods were successfully tested to remove acetate from the organic phase. The first method consists of extraction with an aqueous solution of $NaHCO_3$. This step resulted in the removal of carboxylic acids and the formation of salts in the aqueous phase. The second method was the esterification of acetic acid with Isoamyl alcohol to produce Isoamyl acetate. The Isoamyl acetate can be commercialized as a flavoring agent, as a solvent for varnishes and as a fuel additive. The organic phase was distilled and the resulting mono-phenols characterized. These mono-phenols can be used to produce resins or can be further converted to transportation fuels.

Our results confirm that the hydrolysis of pyrolytic sugars (chiefly levoglucosan and cellobiosan) soluble in the aqueous phase leads to the formation of glucose, and that the compounds toxic to the yeasts which remain in the pyrolysate, mainly phenols and carboxylic acids, can be easily removed by adsorption on activated carbon followed by a neutralization step. In future studies

we will develop techniques to recover and utilize the phenols adsorbed in the activated carbon. The detoxified aqueous glucose solution was easily fermented to produce high yields of ethanol. No significant differences in fermentation were observed between the detoxified solutions derived from bio-oil and the control solutions prepared with glucose. Although several elements of the concept proposed to convert pyrolytic sugars into ethanol have been proposed before[1], this is the first time that the pyrolytic sugars from crude bio-oils have been fermented to produce ethanol.

The funds provided by Ecology were critical to start building a thermochemical program at WSU. A new pyrolysis reactor was built and a new laboratory to characterize bio-oils is now fully operational. This project has made important scientific and social contributions as can be evaluated by the following actions:

Publications directly resulting from this project:

Johnson R L, Liaw S-S, Xiaochen Y, Ha S, Lin S-S, Chen S, Garcia-Perez M, Thermal Pretreatment of Wheat Straw to increase the yields of pyrolytic Sugars. *Submitted to Energy & Fuels* **2008** *(Currently in revision)*

Garcia-Perez M and Metcalf J: Formation of polyaromatic hydrocarbons and dioxins during pyrolysis. Review of biomass thermochemical Reactions. (57 pages) *Available at:* (http://www.pacificbiomass.org).

[1] Brown R.C. : Hybrid Thermochemical/Biological Processing. Putting the car before the horse? Applied Biochemistry and Biotechnology. Vol. 136-140, 2007

Joint Publications resulting from collaborations with our partners at UGA and Monash:

With the University of Georgia

Garcia-Perez M, Adams TT, Goodrum JW, Das KC, Geller D: DSC Studies to Evaluate the Impact of Bio-oil on Some Cold Flow Properties and Oxidation Stability of Bio-diesel *Submitted to Bioresources Technology* **2009**

Smith J, Das K.C., *Garcia-Perez M*: Producing Fuel and Speciality Chemicals from the Slow Pyrolysis of Poultry DAF Skimmings. Submitted to the *Journal of Analytical and Applied Pyrolysis,* **2008**.

With Monash University (Australia)

Garcia-Perez M, Shen J, Wang X-S, Li C-Z: Production and Fuel Properties of Fast Pyrolysis Oil/Bio-diesel Blends. *Submitted to Fuel Processing Technology **2009***

Shen J, Wang X-S, *Garcia-Perez M*, Mourant D, Rhodes M, Li C-Z: Effect of Particle Size on the Fast Pyrolysis of Oil Mallee Woody Biomass. *Fuel 88*, **2009,** *1810-1817*.
Garcia-Perez M, Wang S, Shen J, Rhodes MJ, Lee W-J, Li C-Z: Effects of Temperature on the Formation of Lignin Derived Oligomers during the Fast Pyrolysis of Mallee Woody Biomass. *Energy and Fuels* **2008,** 22, 2022-2032.

Garcia-Perez M, Wang S X, Shen J, Rhodes M J, Tian F-J, Lee W-J, Wu H, Li C-Z: Fast Pyrolysis of Oil Mallee Biomass: Effect of Temperature on the Yield and Quality of Products. *Industrial and Engineering Chemistry Research,* **2008,** 47, 1846-1854

Book chapter:

Garcia-Perez M: Biomass Pyrolysis and bio-oil refineries. (Editor, A. Nag Indian Institute of Technology. Introductory book to Bio-Systems Engineering) (McGraw Hill Publisher, USA)

Federal and International Grants obtained:

1.- **High quality transportation bio-fuels from Australian and American biomasses via pyrolysis and bio-oil refinery.**
PI: Dr. Chun-Zhu Li
Co-PI: Dr. Manuel Garcia-Perez
Funding Agency: International Science Linkages. Australian Government
Period: January 2009-January 2011

2.- **A Forest Residue-Based Pyrolysis Bio-refinery**
PI: Dr. Karl Englund
Co-PI: Dr. Manuel Garcia-Perez, Dr. Marie-Pierre Laborie
Funding Agency: Sun Grant (US Department of Transportation)
Period: September 2009-August 2011

3.- **New Concept to Obtain High Yields of Pyrolytic Sugars for Ethanol Production**
PI: Dr. Manuel Garcia-Perez
Co-PI: Dr. Shulin Chen
Funding Agency: Sun Grant (US Department of Transportation)
Period: September 2009-August 2011

Presentations:

Garcia-Perez M, Overview of Biomass Pyrolysis Technologies "Thermochemical Reactions leading to charcoal formation" Pacific Northwest Bio-Char Group Meeting, Tri-Cities, WA, May 21-22, 2009.

Johnson R.L., Garcia-Perez M, Liaw S-S, Ha S, Lin S-S, Chen S: Py-GC/MS studies to Evaluate the effect of Thermal pretreatment on the yield of sugars Resulting from Fast Pyrolysis. Accepted at the 8th World Congress of Chemical Engineering. Montreal, Qc, Canada, August 23-27, 2009.

2.- Project Background

2.1.- Energy Situation and Availability of Softwood Bark in the State of Washington

The Washington State biomass inventory (http://www.ecy.wa.gov/biblio/0507047.html) shows that there is over 16.4 million tons of underutilized dry biomass available annually which represents an underutilized resource with a potential to generate about 15.5 billion kWh of electricity every year. Woody materials account for 84.2 % of the biomass considered in this assessment. One of the most significant sources of waste woody biomass are mill residues, which represent over 5.2 million tons/year. These residues are composed of residue/bark left over from the operation of the state's sawmill, pulp and paper industry, whole log chipping, veneer plywood, post/pole/piling and log export businesses. A very large fraction of this bio-resource is currently used in hog fuel boilers to produce heat and power for consumers. The logging residues of almost 1.9 million tons/year also represent another large bio-resource for the state which is mostly under-utilized. An important fraction of these wastes is softwood bark. On average, bark comprises between 13 and 21 mass percent (dry basis) of a typical log. Thus, the disposal of large volumes of bark is a serious logistical problem facing the forest industry in the state.

In the United States, well over 20 million tons of bark is produced every year[1]. As a result of current debarking operations huge amounts of bark are accumulated in central locations and are a very attractive potential feedstock because most of the collection fees have been paid by existing industries. Despite obvious potential to develop broad markets for bark products, current markets remain limited. The goal of this project is to move "beyond waste" by creating a sustainable biomass economy throughout Washington State. Underutilized softwood bark generated by the forest and paper industries is abundant and presents opportunities to spur rural economic activity in the region. It is important to point out that although this proposal focuses on the reclamation of softwood bark to produce transportation fuels, the proposed concept can be easily applied to other lignocellulosic materials underutilized in the state.

2.2. Bark Composition

Bark is composed of the outer part of woody stems and branches. Table 2.1 shows the differences in composition between bark and bark free woody biomass[2].

Table 2.1. Proximate Composition of Wood and Bark[1]

	Softwood		Hardwood	
	Wood	Bark	Wood	Bark
Lignin	25-30	40-45	18-25	40-50
Polysaccharides	66-72	30-48	74-80	32-45
Extractives	2-9	2-25	2-5	5-10
Ash	0.2-0.6	Up to 20	0.2-0.6	Up to 20

Although the contents of cellulose and hemicelluloses in the bark are much lower than in free woody biomass, the actual chemical structures of these bio-polymers are similar. The Lignin content shown in Table 2.1 for the bark could be misleading since in the case of bark the content of "lignin" obtained by standard analyses consists of a mixture of true lignin and suberized phlobaphene (cork) having lower contents of methoxyl groups (8-10 mass %). Softwood and hardwood lignins have contents of methoxyl groups of 15-17 % and 20-22 % respectively[1]. During pyrolysis the methoxyl groups are converted to methanol. Because of the lower content of methoxyl groups, the pyrolysis of bark will result in bio-oils with lower contents of methanol. Barks are generally much richer in extractives than wood. The extractives are substances other than cellulose, hemicelluloses, and lignin which do not contribute to the cell wall structure and that can be easily removed with the aid of solvents. Some of the most common extractives are: tannins, waxes, balsams, essential oils, gums, mucilages, resins, lattices, and dyestuffs. This high content of extractives is responsible for the formation of unique type of bio-oil formed by two

[2] Bark and its possible uses. U.S. Department of Agriculture. Forest Service Forest Product Laboratory. Madison, Wisconsin. http://www.fpl.fs.fed.us/documnts/fplrn/fplrn091.pdf

phases (an upper layer rich in extractives derived compounds, and a dissolved oil rich in compounds derived from cellulose, hemicelluloses and lignin[3,4]).

2.3.- Current uses of Softwood Bark

All current uses of bark are low value products with very limited market. Most of it is currently used as hog fuel to generate heat. The calorific value of bark is quite low; ten tons of dried bark is needed to provide the same amount of heat as seven tons of coal. It can be pressed into briquettes for use in a fireplace. Although bark is normally assumed to have a high ash content, and clean bark has ash contents slightly higher than wood, much of the ash in bark results from dirt accumulated when the tree is still standing and from the ground during felling and dragging[1]. Many industries also use bark as a substantial fraction of the feedstock for charcoal production. Bark is also utilized as a construction material in various types of building insulation boards, hardboards, fiberboards, and particleboards. Although, small amounts of bark can also be added to certain papers, this practice is not considered advantageous[1]. A large market for bark is as a soil conditioner. It does not have intrinsic value as fertilizer but lends body to sandy soils, increases water adsorption and penetration[1]. Because bark degrades in soils slower than wood, less nitrogen starvation of crop plants and smaller corrective addition of fertilizers is needed. The difficulties to transport low density bark is one of the main factors limiting a wider use of this waste.

2.4.- Current Energy Situation and Biomass Pyrolysis

While there are other renewable sources to produce electricity such as wind, solar, or tidal, biomass remains our only renewable alternative for carbon based fuels and chemicals. Indeed, the production of transportation fuels from cellulosic biomass is a national priority, with the Department of Energy calling to replace at least 10 % of all transportation fuels with bio-fuels by

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[3] Garcia-Perez M, Chaala A, Pakdel H, Kretschmer D, Roy C: Vacuum Pyrolysis of Softwood and Hardwood Residues. Comparison between Product Yields and Bio-oil Properties. *Journal of Analytical and Applied Pyrolysis.* **2007.** *Volume 78, Issue 1, Pages 104-116***.**

[4] Oasmaa A, Kuoppala E, Gust S, Salantausta Y, Fast pyrolysis of Forest Residue 1. Effect of Extractives on Phase Separation of Pyrolysis Liquids. ***2003***, *Energy and Fuels,* Vol. 17, No 1, pages. 1-12.

2020. One key bottleneck is that low energy density biomass located in remote areas cannot be economically transported long distances for further processing. Pyrolysis is one of the leading technologies considered for densification since it can convert between 60 and 75 mass % of the original biomass into a crude bio-oil with an energy density of around 26,800 MJ/m^3. therefore bio-oil can be economically transported to bio-refineries located up to 500 km (312 miles) from the bio-resources or a 3-5 times greater distance than un-processed biomass (around 100 km (62 miles)). According to Pootakham and Kumar[5] the energy consumed to transport bio-oil by truck trailers is around 1.68 MJ/km.m^3. The concept herein proposed conceives the existence of distributed pyrolysis units (http://www.advbiorefineryinc.ca/products.html) close to biomass resources, to produce crude bio-oils and chars, and refineries close to consumption centers (cities) to further convert these oils into transportation fuels and chemicals[6] (see Figure 2.1).

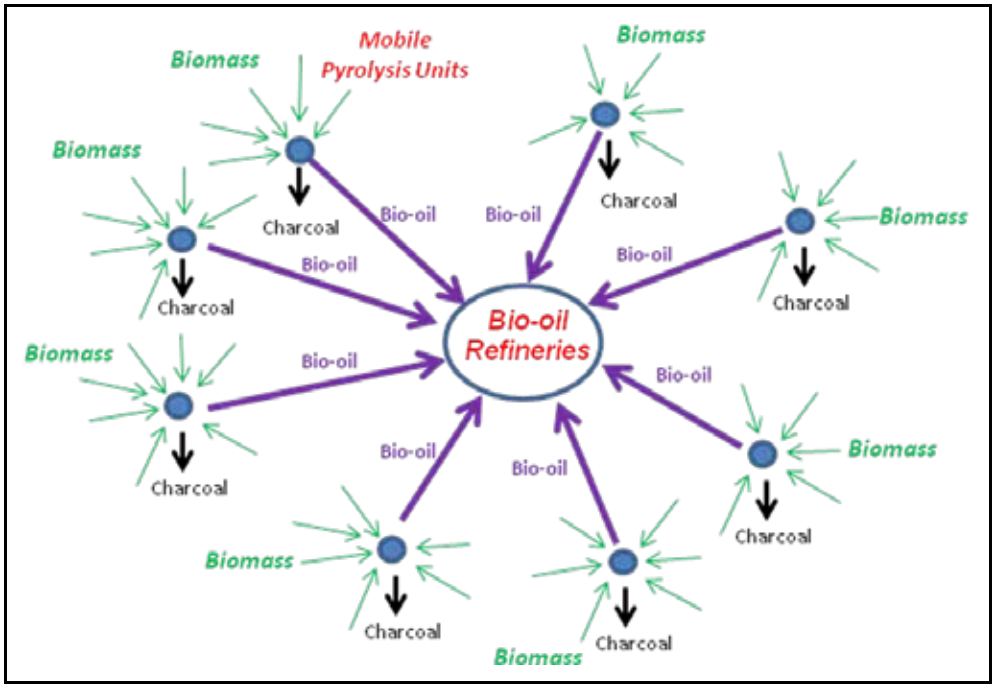

Figure 2.1.-New model of biomass economy formed by distributed pyrolysis units and bio-oil refineries.

[5] Pootakham Y, Kumar A: A comparison of pipeline vs. truck Transport of Bio-oil. ASABE Meeting Minneapolis, 17-20 june 2007, Paper Number: 071602.

[6] Peláez-Samaniego M.R., *Garcia-Perez M.*, Cortez L.B., Rosillo-Calle F., Mesa J.: Improvements of Brazilian Carbonization Industry as Part of the Creation of a Global Biomass Economy. *Renew Sust Energ Rev.* v 12, n 4, May, **2008,** p 1063-1086

This project studies several aspects of a new concept for bio-oil refinery for biomass economy shown in Figure 2.1. The feedstock used to evaluate this concept was softwood bark residues from Washington State.

Pyrolysis is a mature technology that offers a secure platform supporting the biorefinery concept herein proposed. Ensyn, Dynamotive, and ABRI among other companies are commercializing fast pyrolysis units. ABRI is already commercializing mobile units (http://www.advbiorefineryinc.ca/about.html). The reactors most commonly used to carry out biomass pyrolysis studies are: fixed bed batch, transported bed, circulating beds, rotating cone, ablative, vacuum, and Auger Pyrolysis reactors[7,8, 9]. Fixed bed reactors, an Auger Pyrolysis reactor, and a Bubbling Fluidized Bed reactor were used in this project. Some of the most important characteristics of these reactors are:

Fixed bed reactors (slow pyrolysis): The biomass forms a fixed bed inside the pyrolysis reactor which is gradually heated by an external oven. The vapors are evacuated by a carrier gas to cooling traps where the bio-oil is collected. These systems always operate as slow pyrolysis reactors.

Auger Pyrolysis reactor: A screw is used to mix and convey a mixture of biomass and sand providing a very good control of the residence time of solids inside the reactor. The sand is heated in a separate oven and is recycled back as a heat carrier. Reactors operating with hot sand can achieve high heating rates, and can be considered as fast pyrolysis reactors. Systems operating without sand cannot achieve high heating rates of biomass particles, consequently the yield and quality of the products will be similar of those obtained with slow pyrolysis reactors.

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[7] Bridgwater AV, Peacocke GVC: Engineering Developments in Fast Pyrolysis for Bio-oils. In: Proceedings of Biomass Pyrolysis Oil Properties and Combustion meeting. Sept. 26-28, Estes Park, Co. 1994, p. 110-127.

[8] Meier D, Faix O. State of the Art of Applied Fast Pyrolysis of Lignocellulosic Materials- a Review. Bioresource Technology 68, 1999, p. 71-77.

[9] Bridgwater AV, Czernik S, Piskorz J: An Overview of Fast Pyrolysis. In: Progress in Thermochemical Biomass Conversion. IEA Bioenergy. Edited by A.V. Bridgwater, Blackwell Sciences, 2001, pp. 977-997.

Bubbling Fluidized Bed reactor (fast pyrolysis): The biomass is fed to a fluidized bed at temperatures around 500 ^{o}C. Particles with diameters less than 2 mm are required to maintain a fully fluidized bed and to achieve high heat transfer rates (over 300 ^{o}C/s). Dynamotive (http://www.dynamotive.com/) has a 200 t/day plan operational. These systems are also known as fast pyrolysis reactors.

Although some of these reactors can convert up to 70 % of bark free woody biomass into crude bio-oils (up to 60 mass % of bark), several aspects of the existing technologies should be improved, including: **(1)** Existing fast pyrolysis units cannot handle feedstocks with high content of alkalines; **(2)** High contents of acetic acid derived from the hemicelluloses results in corrosive and unstable bio-oils; **(3)** The use of large volumes of inert carrier gases dilutes the pyrolytic gases making it almost impossible to recover their energy; and **(4)** The small condensable molecules with less than 5 carbons have a very limited market. In addition to these shortcomings, the pyrolysis of softwood bark is especially challenging because of the high content of extractives and ash and the low content of methoxyl groups. Since bio-oil properties and yields depend on feedstock composition and pyrolysis conditions it is logical to suppose that the yields and properties of bio-oils derived from softwood bark will be very different to those obtained for bark free woody biomass richer in cellulose, hemicelluloses and lignin.

2.5.- Bio-oil Refineries

Pyrolysis oils are dark brown liquids that can contain between 10 and 25 mass % of water. Because the composition of bio-oil is feedstock dependent, its content of oxygen is similar to that of the feedstock. More than 300 organic compounds have been identified in these oils [10,11,12,13,14,15,16]. Since; pyrolysis oils are not soluble with petroleum and cannot be distilled

[10] Evans, R. J. and Milne, T. A. 1987. Molecular characterization of the pyrolysis of biomass I. Fundamentals. *Energy & Fuels*, 1 (2):123–137.

[11] Evans, R. J. and Milne, T. A. 1987. Molecular characterization of the pyrolysis of biomass II. Applications, *Energy & Fuels* 1 (4):311–319.

[12] Diebold, J. P, Milne, T. A., Czernik, S., Oasmaa, A., Bridgwater, A. V., Cuevas, A., Gust, S., Huffman, D., and Piskorz, J. 1999. Proposed specifications for various grades of pyrolysis oils. In *Fast Pyrolysis of Biomass: A Handbook*. vol. 2. ed. A. V. Bridgwater. Newbury, UK: CPL Press. 102–113

because of the high content of sugars and other reactive fractions, these oils should be refined to produce transportation fuels or chemicals.

The equilibrium between the costs associated to operate mobile pyrolysis units, the costs of transportation and the savings associated with the economies of scale will determine the feasibility of building mobile vs. stationary pyrolysis units and centralized refineries near consumer centers vs. distributed rural refineries closer to the biomass resources. The available volume of the biomass will determine the kind of pyrolysis units and bio-oil refineries to be deployed. In this regard we can identify three groups of pyrolysis – bio-oil refinery concepts (small systems: 10-50 t/day; medium size system: 50-500 t/day; and large systems: over 500 t/day). The concept studied in this proposal can be easily adapted to be used at any of these scales.

Small Pyrolysis Units and Bio-oil Refineries (throughput capacity: 10-50 t/day): This concept conceives the existence of small mobile pyrolysis units located close to the biomass resources and the shipping of resulting bio-oils to a rural refinery or to a revamped petroleum refinery where second generation biofuels and chemicals will be obtained. This concept is particularly suited to convert forest thinnings, agricultural wastes, and other sparsely distributed wastes. The Forest Service and the Department of Interior are seeking more than $ 30 billion in funding over the next ten years for ladder-fuel reduction activities. The cost of mechanical removal can be as high as 1,000 USD per acre. These thinnings will be burned in the field and contaminate the atmosphere if no other end-user is identified[17]. Thus, there is an urgent need to develop mobile pyrolysis units to utilize these thinnings. The mobile pyrolysis units are likely to be set up in appropriate locations close to thinning operations. The thinnings will first be

[13] Boucher, M. E., Chaala, A., Pakdel, H., and Roy, C. 2000. Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid for gas turbines. Part I. Properties of bio-oils and its blends with methanol and pyrolytic aqueous phase. *Biomass & Bioenergy* 19 (5):337–350.

[14] Boucher, M. E., Chaala, A., Pakdel, H., and Roy, C. 2000. Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid for gas turbines. Part II. Stability and aging and its blends with methanol and pyrolytic aqueous phase. *Biomass & Bioenergy* 19 (5):351–361.

[15] Oasmaa A., Kuoppala E., and Solantausta Y. 2003b. Fast pyrolysis of forest residue. 2. Physicochemical composition of product liquid. *Energy & Fuels* 17:433–443.

[16] Czernik, S. and Bridgwater, A. V. (2004) Overview of Applications of biomass fast pyrolysis oil. *Energy & Fuels* 18 (2):590–598.

[17] Polagye B. L. Thermochemical Conversion of Forest Thinnings. MSc thesis. University of Washington, 2005

converted to chips in logging deck and transported to the mobile unit where conversion to bio-oil will occur. The Green biomass will be dried using some of the low quality heat from the pyrolysis unit. The mobile units will have storage tanks able to accumulate the production (bio-char and bio-oil) for at least 10 working days. The concept proposed is shown in Figure 2.2.

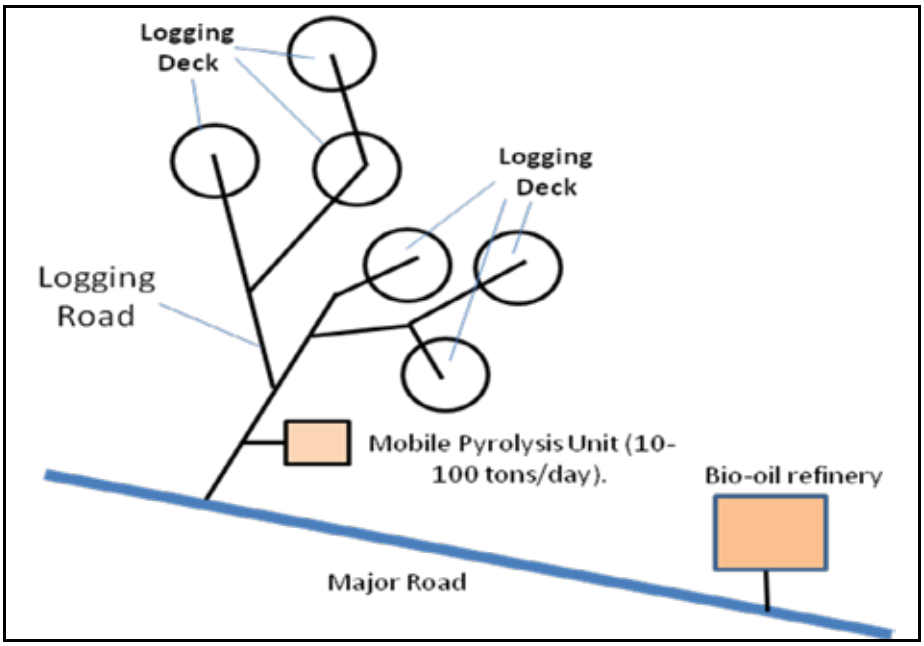

Figure 2.2 Layout of a small mobile pyrolysis to convert forest thinning into bio-oil[15].

Some of the factors that should be taken into account when designing these mobile units are: (1) appropriate logistics are needed to handle, and reduce the size of the thinnings and transport the chips from the logging decks to the pyrolysis unit, (2) module size as dictated by highway transportation regulations, and (3) it is important to coordinate the operation of these plants with a typical forest thinning operation. Because of the small size of the unit, bio-oil upgrading is likely to be limited to a single filtration step to remove charcoal particles.

Figure 2.3 shows a block diagram for a mobile pyrolysis unit to convert biomass into bio-oil. Basically the system will require modular designs easily transportable in trucks for the following components: (1) drier, (2) mill, (3) gasifier, (4) pyrolysis reactor, (5) condensers, and (6) diesel engine.

The viability of this kind of system will depend on the efficiency with which forest thinning and agricultural wastes are harvested and chipped to particle sizes between 3 and 5 cm. Drying the chips in mobile pyrolysis units is likely to happen in batch dryers heated with the exhaust gases from the diesel engine. This diesel engine is needed to generate the electricity consumed by the unit in off grid operations. The dried material will then be fed with a screw feeder into the hammer mill to reduce the particle size to approximately 2 mm. This fine material is then fed to the pyrolysis reactor to obtain charcoal, bio-oil and gases. Our group is proposing to collect the char and gasify it to serve as fuel source for diesel engine. The charcoal could be also used as a soil amendment. The pyrolysis vapors are sent to a two stage condenser. The oil condensed in the first step is formed by precursors of green gasoline, green diesel and ethanol. It should be filtered while it is still hot and stored in a cold container until transportation. The non condensable gases will provide much of the energy needed to run the diesel engine. In the concept proposed the gasifier will act as the energy source for the process. The synthesis gas produced will be used for both the carrier gas in the pyrolysis reactor and fuel for the diesel engine.

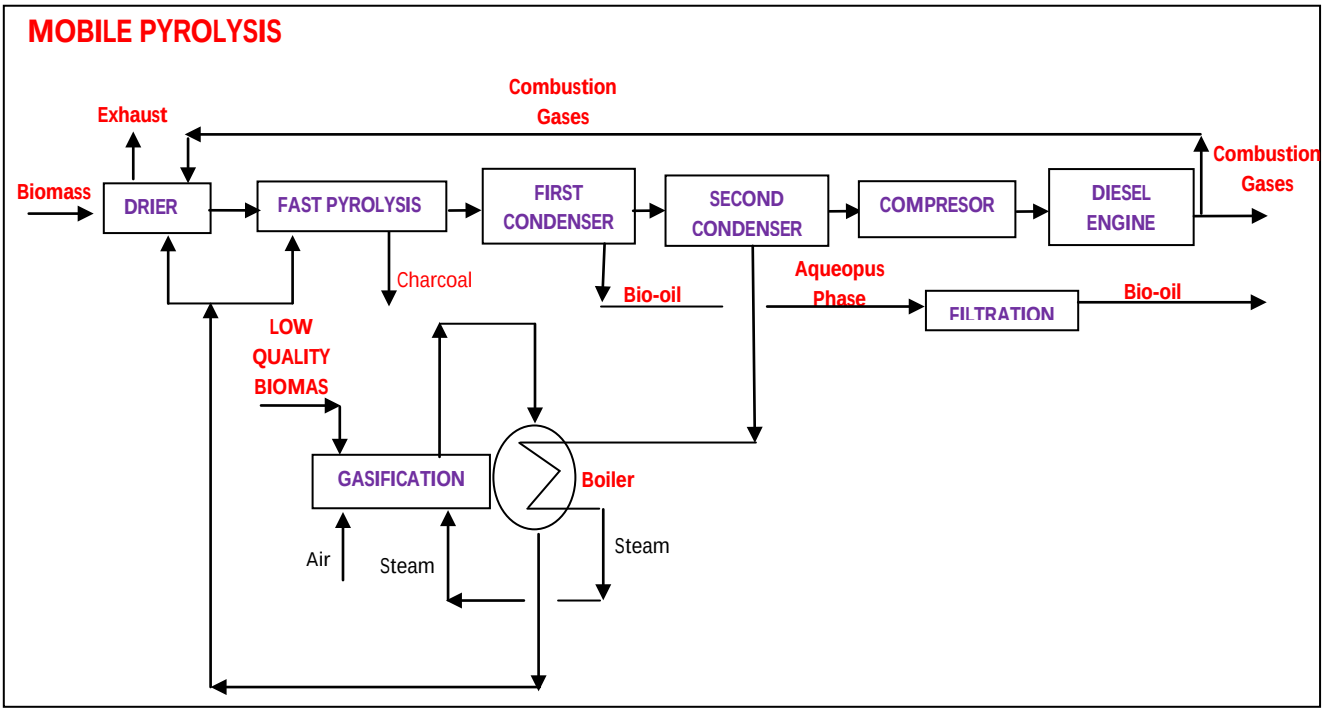

Figure 2.3 Block Diagram of a Mobile pyrolysis unit (10-50 t/d).

The bio-oils produced in mobile units should be further processed in refineries to produce transportation fuels. A block diagram of a bio-oil refinery in which the bio-oil is hydrotreated to produce hydrocarbons (green gasoline and green diesel) is shown in Figure 2.4. The US Department of Energy is currently evaluating this concept.

Briefly, the bio-oil produced in the mobile Pyrolysis units will be stored and pumped through a preheating unit till reaching around 220 ^{o}C. Hydrotreatment should be carried out in two catalytic stages. In the first stage, the bio-oil is stabilized under mild conditions using Co-Mo catalysts. Because of the presence of aldehydes pyrolysis oils cannot be heated to temperatures over 230 ^{o}C without coking. A mild first hydrotreatment step at temperatures between 160 and 230 ^{o}C (30-50 atm) in the presence of acid catalysts is needed to stabilize the aldehydic groups[18]. The resulting oil can then be hydrotreated at higher temperatures (280-320 ^{o}C) and low space

[18] Gagnon J, Kaliaguine S : Catalytic Hydrotreatment of Vacuum Pyrolysis Oils from Wood. Ind. Eng. Chem. Res. 1988, 27, p. 1783-1788.

velocities to hydrogenate phenolic compounds. As a result of these reactions a phase rich in hydrocarbons, an aqueous phase and gases are formed.

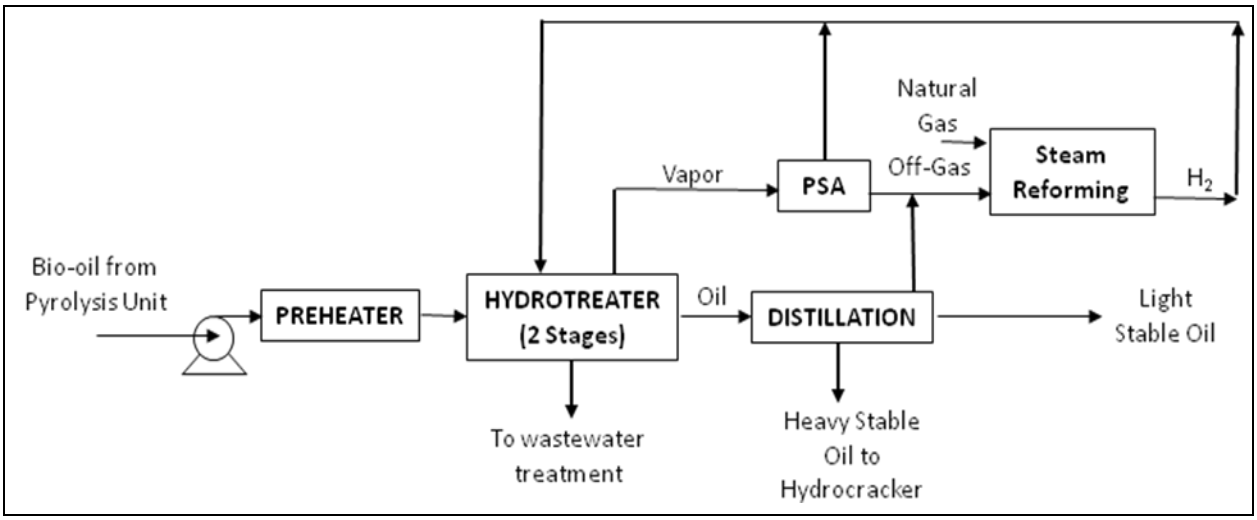

Figure 2.4. Block diagram of a Bio-oil Refinery where bio-oil is hydrotreated to produce green gasoline and green diesel.

The concept shown in Figure 2.4 has been tested by the Department of Energy, UOP and Dynamotive. It is able to convert between 35 and 40 mass % of the bio-oil into green gasoline and green diesel[17]. If we take into account that a typical fast pyrolysis unit yields between 60 and 70 mass % of the biomass into a crude bio-oil, then this overall concept should be able to convert between 21 and 28 % of the biomass into fungible hydrocarbons (Green Gasoline and Green diesel). This technology is currently being tested by PNNL, UOP, and Dynamotive (http://www.dynamotive.com/). Because the calorific value of green gasoline is 1.5 higher than ethanol, we can state that between 31 and 42 mass % of the biomass is converted to ethanol equivalents. These yields are very high, especially if we take into account that current enzymatic hydrolysis technologies can only convert 25 mass % of the biomass into ethanol. No economic assessment is available on the viability of multiple small mobile pyrolysis units (10-50 t/day) and a centralized bio-oil refinery. The tradeoff between the size of the pyrolysis unit, the cost of biomass transportation, and the costs associated with shipping bio-oil to a centralized refinery and the capacity of these refineries should be further investigated. The main limitation of this technology is the formation of coke during hydrotreatment. This phenomenon has been

associated with the presence of sugars. In this project we are proposing the separation and conversion of sugars to ethanol. This will certainly increase the economic viability of this technology.

Medium Size Pyrolysis Units (throughput capacity from 50 to 500 t of biomass/day) As the availability of biomass in a single location grows it become possible to take advantage of the economies of scale and add some new operations to produce stabilized bio-oils in the same unit. The first hydrotreatment step could be carried out in the pyrolysis unit making use of the hydrogen resulting from charcoal gasification and from the steam reforming of small oxygenated molecules with less than 3 carbon atoms (see figure 2.5). Since, medium size pyrolysis units are likely to be coupled with agricultural and forest business, additional economies could be achieved by using the existing infrastructure to produce electricity, steam and water. The main advantage of this concept is that because the biomass is already accumulated in a central location, these units can take advantage of lower feedstock costs.

Obtaining an easily transportable stable product that can be converted to transportation fuel in a large centralized facility should result in lower costs. A typical pulp and paper unit processing between 1000-2000 tons of logs per day and generating between 150 and 400 tons of bark/day could be a good example of a place where this concept could work.

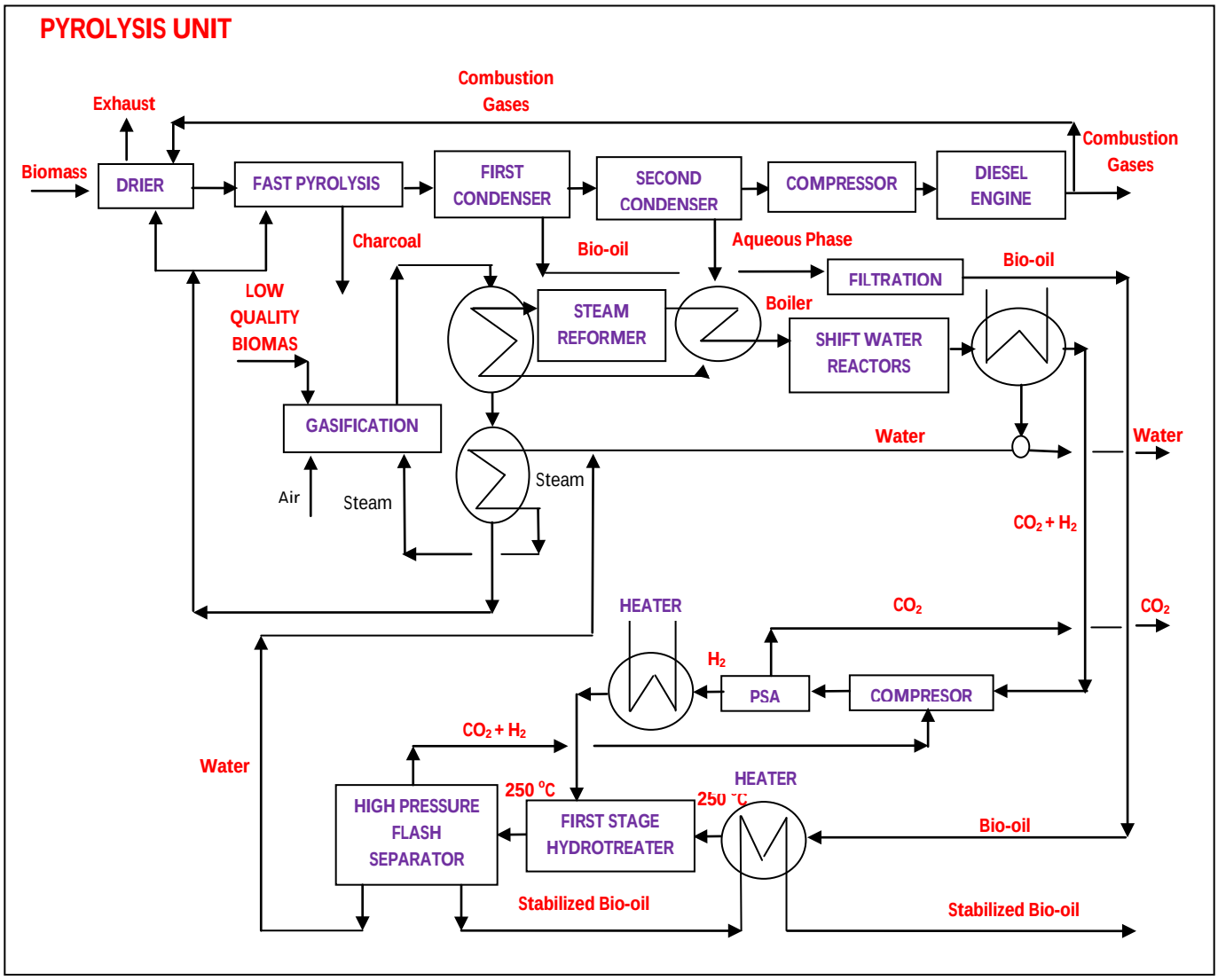

Figure 2.5. Block diagram of a Pyrolysis unit coupled with the first step hydrotreatment unit

The US Department of Energy[19] has evaluated the economic viability of co-locating a 500 t/day pyrolysis unit and the first step of bio-oil hydrotreatment with existing agricultural and forest

[19] Jones SB, Valkenburg C, Walton C, Elliott DC, Holladay JE, Stevens DJ, Kinchin C, Czernik S : Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking : A Design Case. PNNL-18283 Rev.1. Contract DE-AC05-76RL)1830

business and further converting the stabilized bio-oils into green gasoline and diesel in a revamped petroleum refinery. This cost assessment considered four 500 tons/day units feeding a single bio-oil refinery. These pyrolysis units would require the following unit processes: feed preparation, fast pyrolysis, and up-grading (see Figure 1.5). For such a system the minimum fuel selling price was estimated[17] to be $2.04/gal of green gasoline ($1.14 gal ethanol equivalent basis). Producing a fuel fungible with petroleum derived fuels makes this concept very economically attractive.

Large Pyrolysis Units – Bio-oil refineries (throughput capacity over 500 t of biomass/day) The size of some agri-business could be large enough to justify the construction of pyrolysis units and bio-oil refineries in a single location. Sugar mills can process between 4,000-20,000 tons of sugar cane per day. Since 25 mass % of the initial sugar cane is converted into bagasse, between 1,000 and 5,000 tons of bagasse per day can be produced per sugar mill. The Department of Energy has studied the economic viability of a pyrolysis unit-bio-oil refinery complex processing 2000 t/day of hybrid poplar to produce 76 million gallons/year of green gasoline and green diesel. The cost of such a plant was estimated by DOE[17] to be around $ 303 millions. A minimum selling price for gasoline and diesel for this plant was estimated as $2.40/gal ($1.34/gal ethanol equivalent). The increase in the cost of green gasoline and green diesel compared with the previous case was due to the fact that this concept does not make use of existing infrastructure created by the petroleum industry. Building a dedicated bio-oil refinery instead of co-processing bio-oil and petroleum industry increases the overall cost of the resulting fuel.

2.6- Alternative Bio-oil Refinery Proposed

Although hydrotreatment (removal of oxygen and cracking in the presence of hydrogen) of bio-oil to produce green gasoline and green diesel is a very promising concept to convert lingo-cellulosic materials into fungible fuels, converting the whole oil to hydrocarbons may not be the best approach. It is especially true for the fraction rich in sugars. The best type of transportation

fuel obtainable from the sugars is a source of passionate debate[20]. Although there are several new technologies to transform sugars into new fuels (HMF, butanol, green gasoline and green diesel)[21, 22, 23, 24] the fermentation of sugars to produce ethanol is still considered the most viable approach. This is especially attractive for the sugar cane industry because many sugar mills have large infrastructures to convert the molasses to ethanol. In this context separating the sugar rich fractions (pyrolytic molasses) to produce ethanol may be more economically attractive than hydrotreating this fraction to produce green gasoline and diesel. Furthermore, there is evidence suggesting that sugars from cellulose are in fact responsible for coke formation and catalyst deactivation during bio-oil hydrotreatment[25]. Removing the sugars and converting them to ethanol while hydrotreating the phenolic fraction to produce green gasoline and green diesel is a very promising concept because it could drastically reduce the coking problems in hydrotreatment reactors and enhance the yields of transportation fuels produced from bio-oils.

This project is concerned with three main aspects: (1) the production and characterization of bio-oils (2) the separation of these oils into a phase very rich in sugars and a phase rich in phenols and (3) the separation of mono-phenols and the production of ethanol from pyrolytic sugars. The fraction rich in phenols will be evaluated to produce fuel blends with bio-diesel. The concept of bio-oil refinery studied in this proposal is shown in Figure 2.6.

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[20] Huber G, Breaking the Chemical and Engineering Barriers to Lignocellulosic Bio-fuels. Next Generation Hydrocarbon Bio-refineries. Based on the June 25-26, 2007 workshop held in Washington D.C.

[21] Muyafuji H, Nakata T, Ehara K, Saka S: Fermentability of Water-Soluble Portion to Ethanol Obtained by Supercritical Water Treatment of Lignocellulosics. Applied Biochemistry and Biotechnology. Vol. 121-124, 2005.

[22] Helle S, Bennett N.M., Lau K., Matsui J.H., Duff S.J.B. A kinetic model fort he production of glucose by hydrolysis of levoglucosan and cellobiosan from pyrolysis oils. *Carbohydrate Research* 342 (2007) 2365-2370.

[23] Prosen E.M., Radlein D., Piskorz J., Scott D.S., Legge R.L., Microbial utilization of levoglucosan in wood pyrolysate as a carbon and energy source. *Biotechnology and Bioengineering* 42 (1993), pp. 538–541

[24] Yu Z, Zhang H: Pretreatment of cellulose pyrolysate for ethanol production by Saccharomyces cerevisiae, Pichia sp. YZ-1 and Zymamonas mobilis. *Biomass and Bioenergy* 24 (2003) 257-262.

[25] Elliott D.C: Historical Developments in Hydro-processing bio-oils. *Energy & Fuel* 2007, 21, 1792-1815.

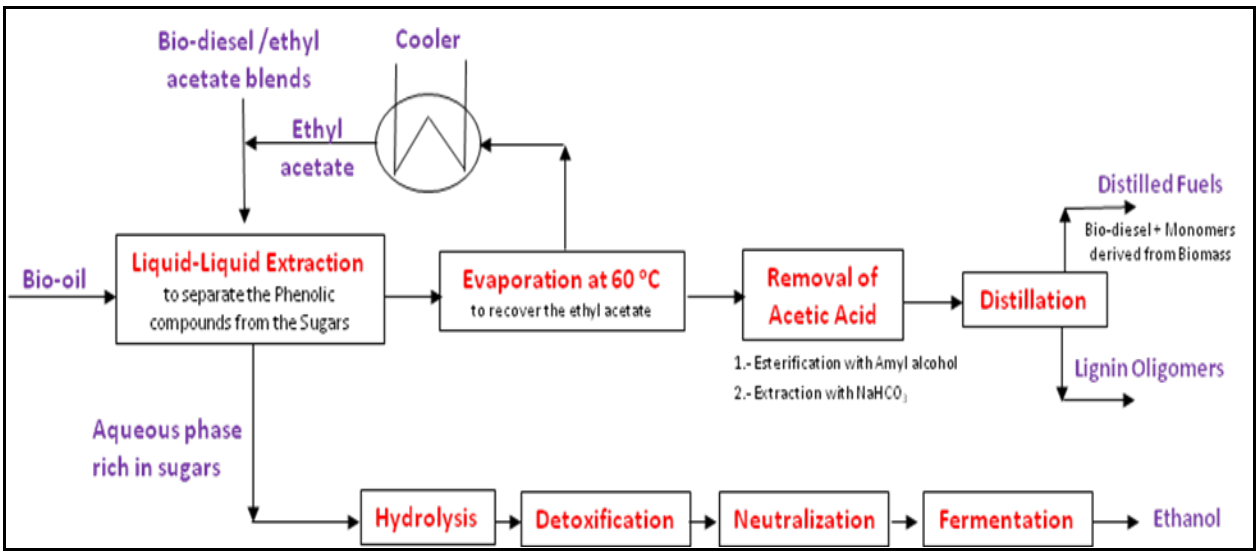

Figure 2.6.- Bio-oil refinery concept proposed

The first step of this concept consists of separating the phenolic fraction, derived from lignin, and the sugars, derived from cellulose, by solvent extraction. One of the main goals of this project is to identify the appropriate bio-diesel/ethyl acetate blends to maximize extraction of phenolic compounds from crude bio-oils. The ethyl acetate (or any other solvent) added to enhance the extraction capability of bio-diesel will be removed by evaporation and re-used in the same process in a closed loop.

Unfortunately, some carboxylic acids are also extracted with the phenols by the organic phase. These acids are responsible for the low pH and corrosiveness of the organic phase. Thus, removal of the acetic acid from the bio-diesel/ethyl acetate blends is an important problem that should be addressed. This project explores two approaches to remove these organic acids. The first approach consists of the extraction of acetic acid from the organic phase with an aqueous solution of $NaHCO_3$. The second approach consists of the esterification of acetic acid with amyl alcohol in the presence of an acid catalyst to form amylacetate. The resulting organic phase will be distilled to obtain a fraction rich in mono-phenols.

The pyrolytic sugars (levoglucosan and cellobiosan) in the aqueous phase resulting from the solvent extraction step will be hydrolyzed to mono-sugars, detoxified (removal of most of the

acids and phenols), neutralized to an appropriate pH, and fermented to produce ethanol. The separation and full utilization of sugars is very important because it will reduce the tendency of the phenolic fraction to form coke while increasing the yield of transportation fuels obtained.

2.7.- Objectives

The main objective of this project is to study at laboratory scale several key steps of a new concept to convert softwood bark from the state of Washington into transportation fuels. Some of the specific aims or tasks accomplished with this project are:

1.- To build new laboratories at Washington State University to produce bio-oil from softwood bark and to analyze and refine the resulting oils.
2.- To determine the yield of bio-oil, charcoal and gases resulting from the pyrolysis of softwood bark in different pyrolysis reactors.
3.- To evaluate the extraction of bio-oils with bio-diesel/ethyl acetate blends and to quantify the distribution coefficients of selected chemical species.
4.- To separate mono-phenols from the bio-diesel rich phase via distillation and to analyze the resulting fractions.
5.- To develop a new scheme to produce ethanol from pyrolytic sugars.
6.- To conduct Pyrolysis - Gas Chromatography/ Mass Spectroscopy (Py-GC/MS) studies to identify the best pyrolysis and pretreatment conditions to enhance the production of anhydro-sugars from softwood bark.
7.- To assess the presence of harmful contaminants (polyaromatic hydrocarbons and dioxins) in bio-oils and charcoals resulting from pyrolysis.

Washington State University and Ecology agree that the implementation of this concept to convert softwood bark into valuable products must be done while ensuring that no new hazardous material is created and that the production will be environmentally friendly. A chapter was added at the end of this report addressing some concerns expressed by Ecology regarding the potential environmental impact of this technology. This task was conducted in collaboration

with the proposal “Use of bio-char from the pyrolysis of waste organic material as a soil amendment” also funded by the Washington State Department of Ecology. An exhaustive literature review to identify the potential development of hazardous or toxic waste elements in the char and oils as the result of biomass pyrolysis reactions and the potential impact of these products on the environment is annexed. The contents of dioxins and polyaromatic hydrocarbons in some of the bio-oils and chars produced in these projects were determined and are reported in the last chapter of this report.

3.- Material and Methods

3.1.- Introduction

One of the major challenges encountered to complete this proposal was the lack of appropriate facilities in the state of Washington to produce, characterize and refine bio-oils. Given these circumstances it was decided to undertake this project with the help of our collaborators from the University of Georgia and from Monash University (Australia) who kindly offered free of charge use of their installations. This chapter describes the construction of a bench-scale Auger pyrolysis reactor at Washington State University (WSU) and the creation of new analytical capabilities to quantify the chemical composition of bio-oils. These installations are part of a strategy to build a thermochemical conversion program at WSU. This program will serve the state to study the viability of converting our organic waste materials from the Pacific Northwest into fuels via pyrolysis and bio-oil refinement. No domestic commercial system is available that can provide the bio-oil and the charcoal needed for our studies. The funds to build our new pyrolysis reactor at WSU were kindly provided by Ecology and by the Agricultural Research Center. The reactors used at the University of Georgia and at Monash University in Australia to produce some of the oils studied in this proposal are also described in this chapter.

3.2.- Auger and Batch Pyrolysis Reactor at the University of Georgia

Dr. Garcia-Perez visited the University of Georgia April 20-30, 2008 with the goal of carrying out some pyrolysis studies using softwood bark from the state of Washington. The University of Georgia has two pyrolysis reactors in operation. The first one is an Auger reactor, the second one is a batch fixed bed system.

Auger Pyrolysis Reactor: As indicated in the contract signed with Ecology, tests were carried out in the Auger reactor available at UGA. This system has been well described elsewhere[26].

[26] *Garcia-Perez M*, Adams T.T., Goodrum J.W., Geller D.P., Das K.C.: Production and Fuel Properties of Pine Chip Bio-oil/Biodiesel Blends. *Energy and Fuels*, ***2007***, 21 (4) 2363.

Briefly, the reactor consisted of a 100 mm diameter stainless-steel tube placed in a Lindberg/Blue M (model HTF55322A) furnace with an Auger driven by a ¼ hp motor. The charcoal was collected in a stainless-steel container located downstream of the Auger. The cooling system in the Auger reactor was formed by a vertical condenser followed by 4 ice-cooled traps. The pressure inside the reactor was maintained a few millimetres of mercury below atmospheric pressure using a vacuum pump with a valve to control the pressure inside the reactor. A total of 3 L/min of nitrogen was used as carrier gas to maintain an inert atmosphere inside the reactor. Condensed liquids were separated into an aqueous and an "oily phase" using separation funnels.

The operation of this reactor with the softwood bark did not work smoothly. The feeding system jammed several times. Although we were able to complete two runs, the system did not operate steadily. After several unsuccessful attempts to stabilize the Auger reactor it was decided to carry out some tests in UGA's batch pyrolysis system and to schedule pyrolysis tests in the fast pyrolysis reactor available at Monash University. The softwood bark remaining from our tests in Georgia was shipped to Australia.

Batch Pyrolysis System: Three Pyrolysis runs (1.8 kg of softwood bark per test) were carried out in the 230 mm long and 255 mm diameter reactor shown in Figure 3.1. The reactor was heated to 500 ^{o}C and maintained at that temperature for 30 minutes using a 30400 Thermolyne furnace. The pyrolysis vapours were rapidly evacuated across the biomass bed using 1.5 L/min of nitrogen as a carrier gas. Four ice-cooled traps connected in series were used as condensers. A trap containing cotton wool and a bubbling trap with water (not shown in Figure 1) were used to remove aerosols from the pyrolysis gases. The charcoal solid residue was left behind in the reactor under nitrogen until the reactor reached room temperature in order to avoid oxidation.

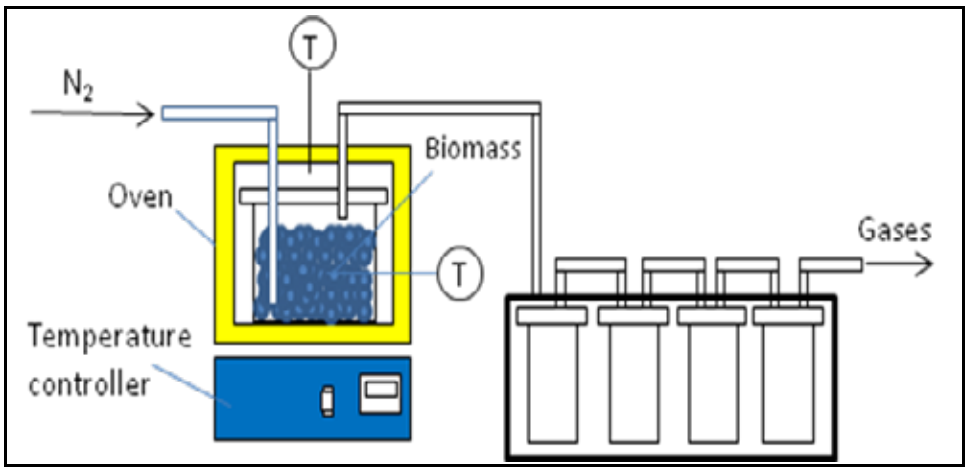

Figure 3.1.- Scheme of the Batch pyrolysis reactor available at UGA.

The temperature profile inside the pyrolysis reactor for two representative tests is shown in Figure 3.2. The S-shape of the heating rate curve is due to the presence of endothermic and exothermic events associated to the thermo-chemical reactions happening inside the reactor. After 270 ^{o}C the reaction becomes exothermic thus the heating rate accelerates. The average heating rate for these runs was 4.5 ^{o}C / min. Clearly this reactor is working in the slow pyrolysis regime.

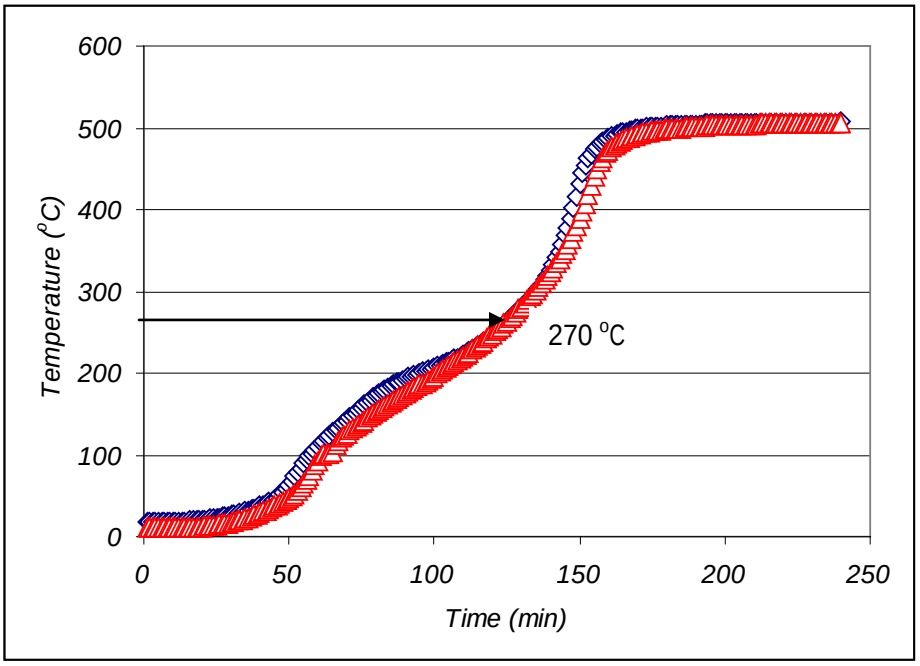

Figure 3.2.- Temperature Profile in batch pyrolysis reactor

3.3.- Fast Pyrolysis reactor at Monash University (Australia)

Between July 22 and August 15, 2008 Dr. Garcia-Perez travel to Monash University (Australia) to conduct fast pyrolysis studies using softwood bark from Washington State. These tests were carried out free of charge as part of our ongoing collaboration with Monash. The fluidized bed pyrolysis unit available at Monash has a normal capacity of 2 kg/h feedstock. Figure 3.3 shows a sketch of this experimental setup. It comprised a fluidized bed reactor and systems for biomass feeding, char collection, vapour condensation, and bio-oil recovery. The feeding system was formed by a sealed hopper of 0.033 m^3 nominal capacity, a stirrer and a screw feeder of adjustable speeds. The auger feeder speed was maintained at 20 rpm to achieve a feeding rate of around 1 kg/h. Approximately 1 kg of biomass was processed per run. The biomass was dried at 105 ^oC (ASTM E871-82) overnight before performing the tests. The reactor consisted of a cylindrical section, 102 mm id and 320 mm long, and a conical part with a height of 198 mm. Silica sand, with a nominal particle size between 351 and 401 mm, was used as inert bed solid. The nitrogen used for fluidization was preheated with a 3 kW inline electrical heater.

The minimum fluidization velocity for the inert bed solids was 0.1 m/s at room temperature. The flow of nitrogen used was two times the minimum fluidization velocity. The corresponding residence time of vapour in the reactor was estimated to be around 1.4 s and around 0.7 s in the cyclone. Temperature in the bed free board and at the exit of the cyclones was continuously monitored. Excellent stability and reproducibility of temperature profiles were achieved. Figure 3.4 shows the temperature profiles for: the nitrogen heater (not shown in Figure 2.3), the fluidized bed reactor, the free board and the cyclones. Operating with Softwood bark presented important challenges for the condensing system installed at Monash. The oils obtained from this feedstock are rich in waxy materials that tend to clog the condensers. The condensing system had to be modified to handle the unique properties of the oils from softwood bark.

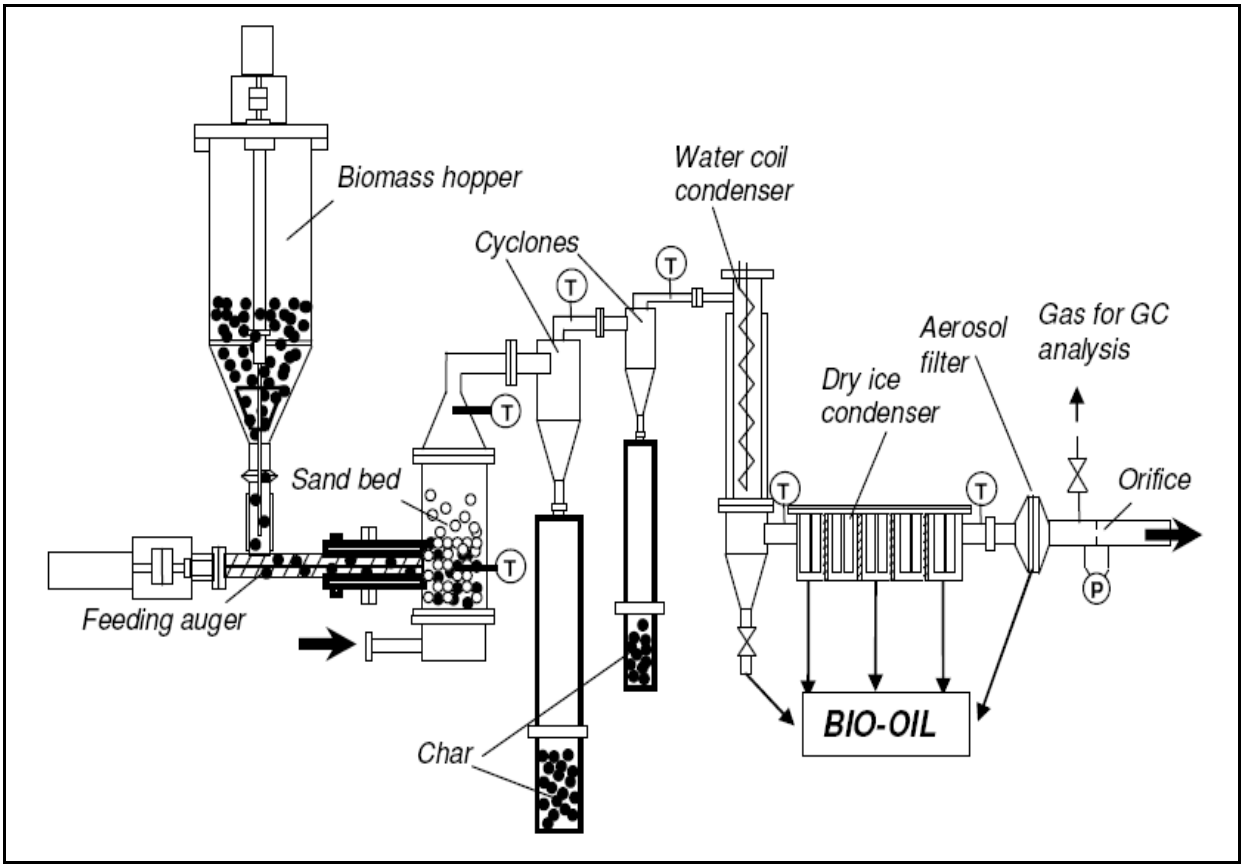

Figure 3.3.- Fast pyrolysis unit available at Monash University[27].

[27] *Garcia-Perez* M, Wang S X, Shen J, Rhodes M J, Tian F-J, Lee W-J, Wu H, Li C-Z: Fast Pyrolysis of Oil Mallee Biomass: Effect of Temperature on the Yield and Quality of Products. *Industrial and Engineering Chemistry Research,* **2008,** 47, 1846-1854

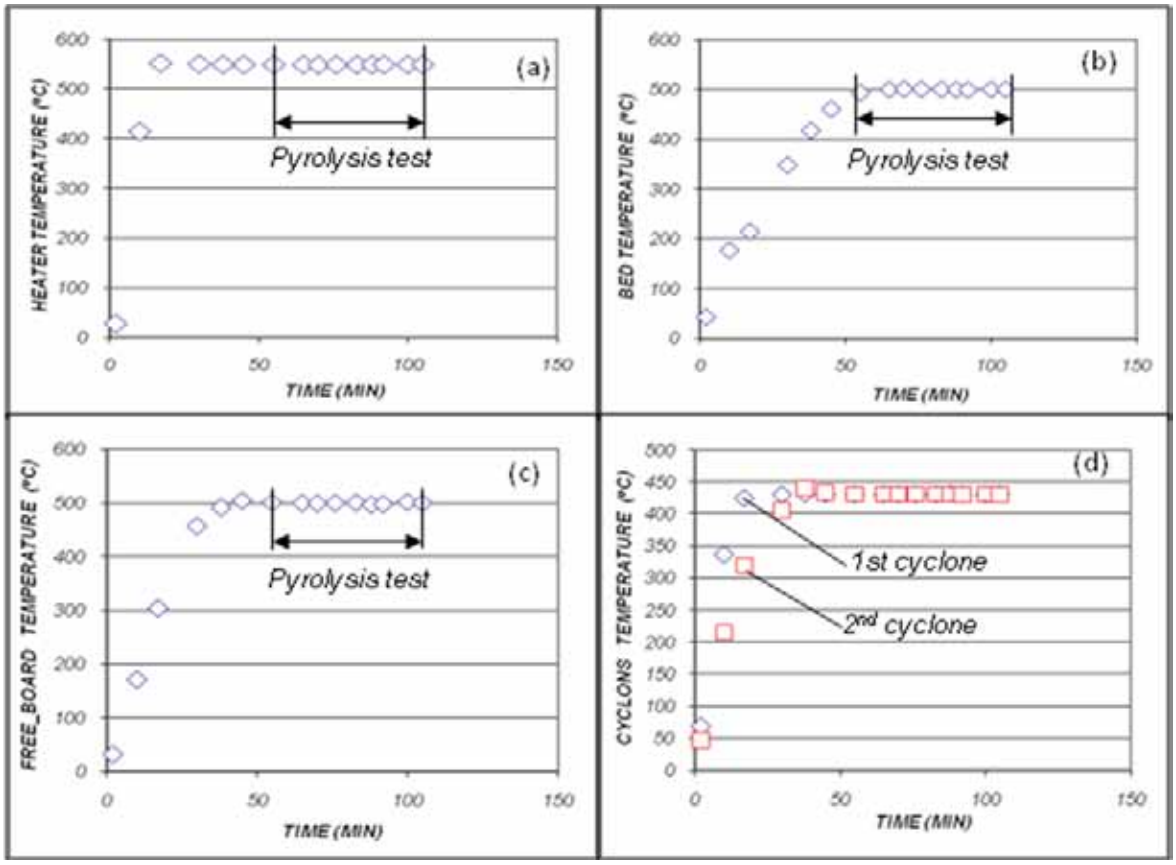

Figure 3.4.- Temperature profiles used to produce the bio-oils from softwood bark.

3.4.- Construction of a New Auger Pyrolysis Reactor at WSU

In order to carry out some of the tasks listed in the contract signed with Ecology it was necessary to build a new pyrolysis reactor at WSU. The mechanical construction and assembly of this system was carried out free of charge by our Engineering Technician (Mr. Wayne Dewitt). Because of the limited availability of funds and the need to produce several kilograms of charcoal in the first six months for the bio-char project (also funded by Ecology), it was decided to build this system in two steps. In the first step a batch pyrolysis system was built with funds provided by Ecology and in the second step this system was further improved to an Auger Pyrolysis reactor using funds provided by the Agricultural Research Center. The batch pyrolysis reactor was operational between June 1st and August 15, 2008 to produce the charcoal committed

to the bio-char project also funded by Ecology. Figures 3.5 and 3.6 show a scheme and a picture of the batch pyrolysis reactor built at Washington State University.

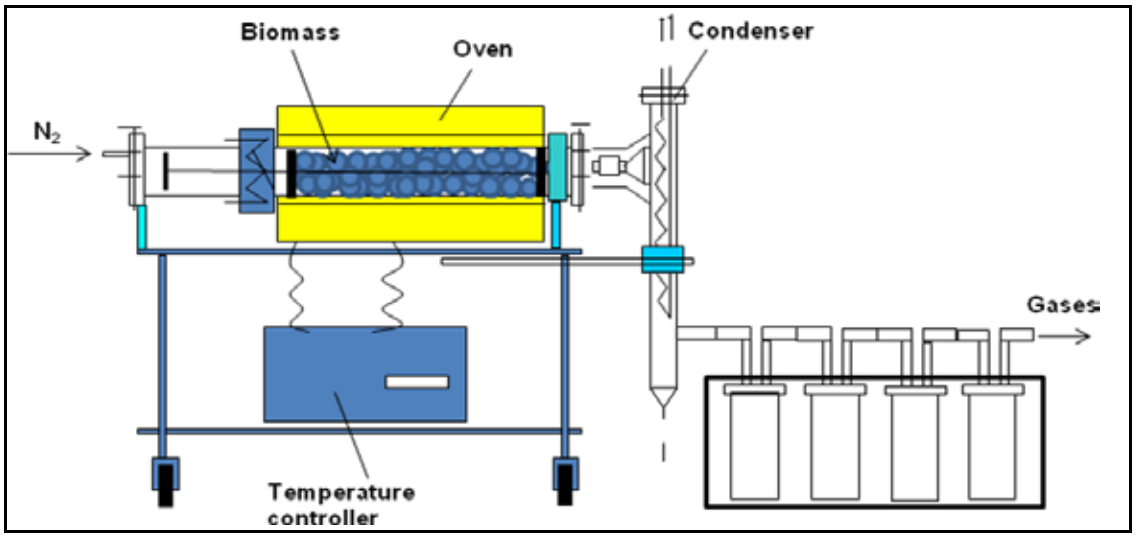

Figure 3.5.- Scheme of the Batch Pyrolysis reactor designed and built at WSU.

Figure 3.6.- Picture of the Batch Pyrolysis Reactor built at WSU (Mr. Wayne Dewitt and Mr. Brandon Kruger).

This system was able to pyrolyze at least 200 g of biomass (pine pellets, switchgrass, digested fiber and softwood bark) per run. It was formed by a 585 mm long and 100 mm diameter horizontal tube inside of which the biomass was pyrolysed. The reactor was heated to temperatures between 250 and 600 ^{o}C and kept at temperature for 30 minutes using a Lindberg/Blue M (model HTF55322A) furnace. The pyrolysis vapors were evacuated from the reactor using 1 L/min of nitrogen as a carrier gas. Four ice-cooled traps connected in series were used as condensers. After each run, the charcoal was left behind in the reactor under nitrogen until it reached ambient temperature in order to avoid oxidation with air. In the initial contract signed with Ecology we were planning to produce all the oils to be used in this project in the Auger Pyrolysis reactor available at the UGA. Due to the unexpected problems faced during the operation of the Auger reactor at UGA in August 2008, and given that we could not solve these problems in short visits of only 10 days, it was decided that it was more cost effective to up-grade our batch pyrolysis reactor at WSU to a continuous system similar to the one at UGA. The WSU Agriculture Research Center kindly provided the extra funds needed to up-grade our system. Having an operational continuous reactor at WSU opened the door to produce larger amounts of charcoal and bio-oils at WSU. Figure 3.7 and 3.8 show a scheme and a picture of the continuous system that is now operational at WSU. This system was built by our Engineering Machinist (Mr. Wayne Dewitt).

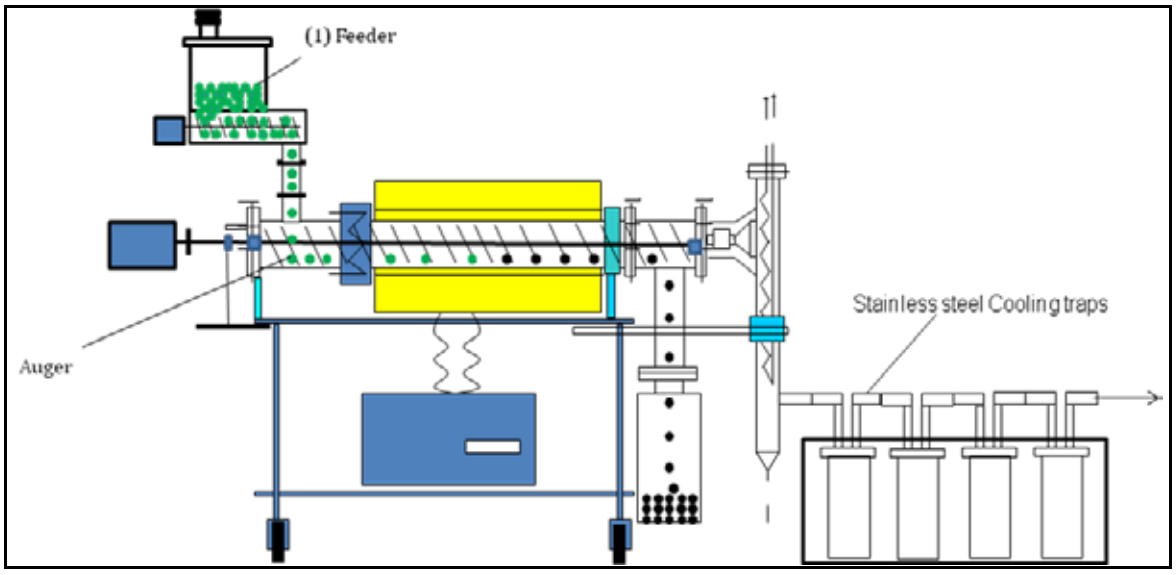

Figure 3.7.- Scheme of the new Auger pyrolysis reactor built at WSU.

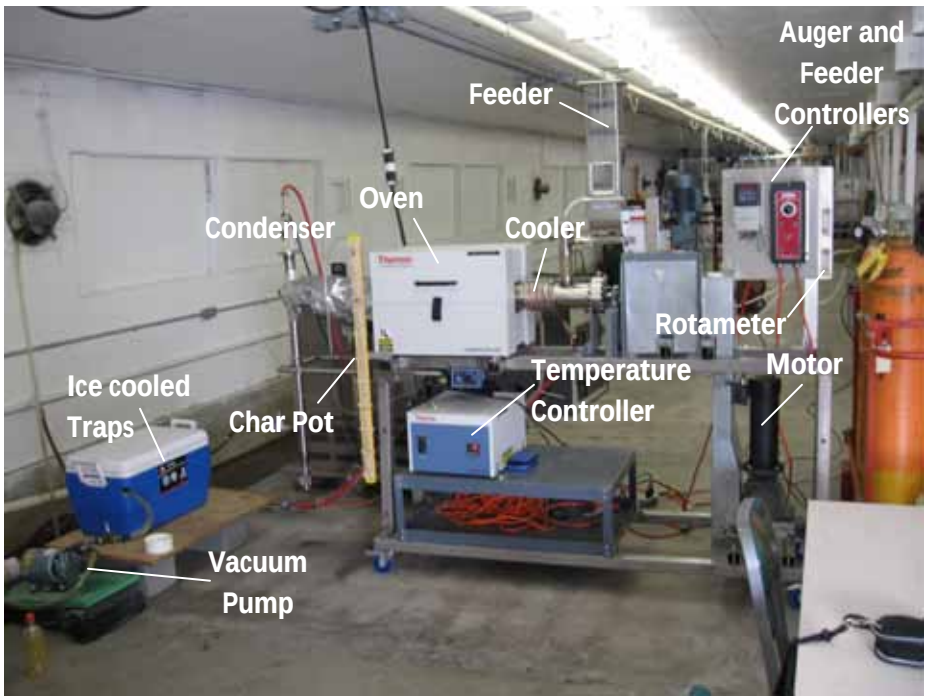

Figure 3.8.- Picture of the new Auger Pyrolysis reactor operational at WSU.

This system has been operated at a throughput capacity between 1 to 2 kg/h of dry biomass. The biomass is fed by a Volumetric Single Screw Stirring Feeder, DSR28 from Brabender Technology. The reactor consists of a 100 mm diameter stainless-steel tube placed in a Lindberg/Blue M (model HTF55322A) furnace with a Auger driven by a1 hp motor (maximum speed: 1725 rpm, 10.9 A). A cooler was installed between the hopper and the furnace to prevent heating the biomass in the hopper. The residence time of the biomass inside the reactor can be controlled varying the speed of the Auger with a manual controller. The charcoal was collected in a stainless-steel container located downstream. A vertical condenser followed by a series of ice-cooled traps was used to condense the pyrolysis vapors. The pressure inside the reactor was maintained a few millimeters of water below atmospheric pressure using a vacuum pump. The flow of nitrogen to the reactor was measured and controlled with two rotameters (one measuring the flow of nitrogen to the hopper and the other to the Auger Reactor). Although the reactor can be operated continuously, the capacity of the current charcoal pot limits the time this system can be operated to only one hour. In total 300 g of charcoal can be produced per run. This time can be easily expanded by enlarging the char pot.

3.5.- New Analytical Laboratory to Study Biomass Thermochemical Reactions and to Characterize Bio-oils

A GC/MS from Agilent, an analytical Pyrolyzer from CDS analytical, a thermogravimetric analyser from Mettler Toledo and a Karl Fisher titrator were purchased and are now fully operational on our laboratories. These equipments and others were used to determine the chemical composition of bio-oils. An analytical pyrolyzer coupled with the GC/MS was also acquired to study the selectivity of thermochemical reactions resulting from pretreatments. This machine was used in this project to identify the best pretreatment and pyrolysis conditions to enhance the production of fermentable sugars from softwood bark. Other equipments used in this project that were already available in our lab include: Ion Exchange Chromatography, and GC-FID. Some of these equipments are shown in Figure 3.9.

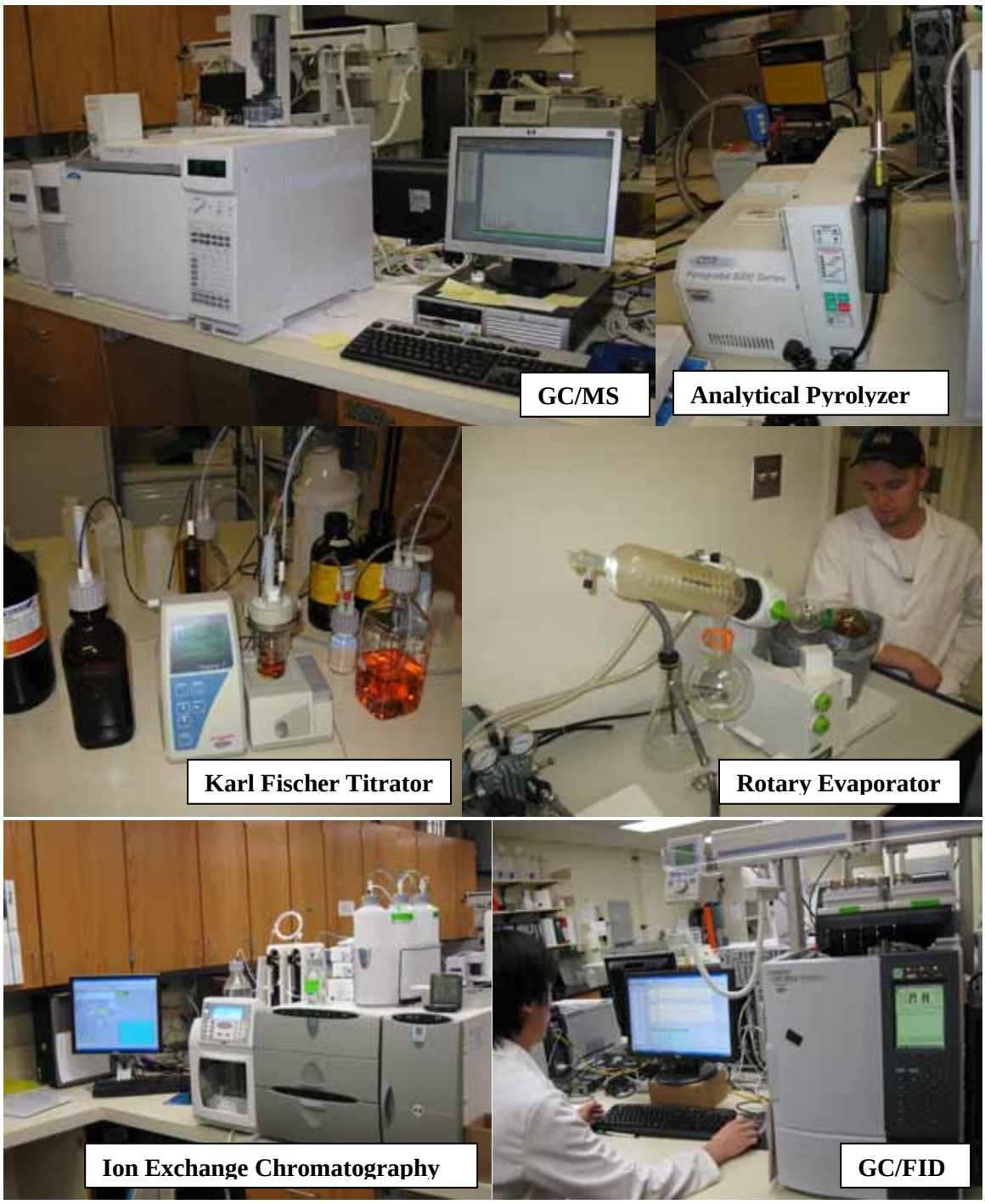

Figure 3.9.- Some of the new analytical equipment purchased by WSU

4.- Production and Characterization of Bio-oils.

The softwood bark studied in this project was pyrolysed in both slow and fast pyrolysis reactors. The yield of products (bio-oil, charcoal and gases) and the compositions of the oils obtained were compared. The composition of some of these oils was contrasted with bio-oils from the fast pyrolysis of hardwood kindly supplied by Dynamotive and by InnovaTek.

4.1.- Composition of Softwood bark

The softwood bark used as feedstock in this proposal was supplied by Jeff Gage from Swanson Bark & Wood Products (240 Tennant Way, Longview, WA). The contents of ash, extractives, cellulose, hemicelluloses, and lignin were determined following the methods ASTM D1102[28], ASTM D1105[29], ASTM E1758[30] and ASTM D1106[31] respectively. The softwood bark composition as received and after extraction in hot water (at 121 ^{o}C, 15 psi for 30 minutes) is shown in Table 4.1. Hot water extraction was used to remove the alkalines known to be responsible for undesirable polycondensation reactions which increase the charcoal yields.

Table 4.1.- Composition of Softwood bark before and after pretreatment in hot water (mass %).

	Extractives	Klason Lignin	Glucose (Cellulose)	Xylose /Mannose	Arabinose	Galactose	Ash	Total
Softwood bark as received	25.89	39.35	12.45	3.13	2.64	1.55	5.64	90.65
Softwood bark after extraction	7.97	49.03	15.66	4.03	3.48	1.92	5.55	87.63

The composition of the bark studied in this project (Table 4.1) corresponds very well with the composition of a typical softwood bark (see Table 2.1). This feedstock contains higher content of

[28] ASTM D1102-84 (2007) Standard Test Method for Ash in Wood
[29] ASTM D1105-96 (2007) Standard Test Method for Preparation of Extractive-Free Wood.
[30] ASTM E1758-01 (2007) Standard Test Method for Determination of Carbohydrates in Biomass
[31] ASTM D1106-96 (2007) Standard Method for Acid Insoluble Lignin in Wood.

extractives and ash than bark free woody biomass. The content of cellulose is very low (less than 12.45 mass %). While the hemicelluloses (Xylose, Mannose, Arabinose and Galactose) account for a small fraction (7.32 mass %), almost 40 % of these materials are reported as lignin like materials (a mixture of true lignin and suberized phlobaphene (cork)). The lack of closure shown in Table 4.1 is due to the limitations of the method used to quantify hemicelluloses and does not account for some modified sugars.

Among the inorganic compounds forming the ash, the alkalines (Na and K), are known to act as strong catalysts for charcoal formation. It was decided to remove most of these alkalines with a pretreatment in hot water at 121 ^{o}C. The composition of the pre-treated softwood bark is also shown in Table 4.1. 75.6 % of the extractives and 35.65 % of the ash were removed by the hot water pre-treatment. The increase in concentration of the other fractions (Lignin, Cellulose and Hemicelluloses) is easily explained by the reduction in the content of extractives and ash.

4.2.- Yield of Products

The yield of products obtained at the University of Georgia using their Auger and batch pyrolysis reactors, at Monash University (Australia) using their bubbling fluidized bed fast pyrolysis reactor, and at Washington State University using our Auger pyrolysis reactor are shown in Table 4.2. All the tests carried out at the University of Georgia were performed using chips. The tests at WSU and at Monash University were performed with particles ground to diameters less than 2 mm.

Table 4.2.- Yield of products obtained in three different pyrolysis reactors (Final Pyrolysis temperature 500 ^{o}C).

	Batch reactor (UGA)*	Auger Pyrolysis (UGA)*	Auger Pyrolysis (WSU)*	Auger Pyrolysis (WSU)**	Bubbling Fluidized bed (Monash University)*
Total Liquid	45	36	32	38	51
Charcoal	40	27	24	22	32
Gases (By difference)	15	37	44	39	17

*Using Softwood bark as received; **Using Softwood bark pre-treated in hot water

As expected the highest yields of bio-oils were obtained at the Bubbling Fluidized bed reactor. The batch pyrolysis reactor from UGA resulted in higher yields of bio-oil than the Auger reactors. This result can be explained by the conversion of important amounts of condensable materials to gases in the Auger reactor due to more severe conditions (higher temperature) in the gas phase. These severe conditions are known to accelerate the secondary extra-particle homogenous reactions leading to the formation of extra-gases. As expected the highest yields of charcoal were obtained in the batch pyrolysis reactor. This is a good indication that the poly-condensation reactions leading to the formation of extra-charcoal were more important in this system. This phenomena can be explained by the lower heating rates achieved by this system (4.5 ^{o}C/min). The higher yields of charcoal obtained in the Fluidized bed reactor (32 mass %) compared with the Auger reactors (24-27 mass %) could be explained by the premature mechanical entrainment of partially converted low density bark particles out of the reactor. The lower yields of gases obtained in the Batch reactor is due to these gases are being exposed to lower temperatures as they are carried away from the pyrolysis reactor. In the case of the fast pyrolysis reactor, although the gases are exposed to relatively high temperatures (over 500 ^{o}C), their residence time in these conditions is so low (less than 2 s) that very little extra gas is formed.

Table 4.3 shows the yield of products obtained in the same reactors but when using softwood (bark free pine). The yield of oil was between 5 and 22 mass % higher than when bark was used. This result can be explained by the higher content of lignin, ash and extractives in bark. The yield of charcoal was in general lower when using bark free materials. The only exception was in the

case of the Auger Pyrolysis reactor when the values were very similar. The yields of gases obtained in the batch and fluidized bed pyrolysis reactors were comparable, but were much lower than in the case of bark free pine converted in the Auger Pyrolysis reactor.

Table 4.3.- Yield of products reported in the literature for the Auger and Fast Pyrolysis of Pine (softwood) .

	Batch Pyrolysis (UGA)[30]	Auger Pyrolysis (UGA)[32]	Bubbling Fluidized bed (Monash University)[33]
Total Liquid	50	58	64
Charcoal	31	30	14
Gases (By difference)	18.4	12.2	22

4.3. Analysis of the Chemical composition of Gases

The gases resulting from the test conducted in the batch pyrolysis reactor at UGA on April 30, 2008 were analysed free of charge, using an Agilent 3000 micro-GC available in the labs of Dr. Das. Sample of gases were taken at different pyrolysis temperatures and analysed. The GC was calibrated using Agilent's gas standards, which included a gas analyser test mixture and a refinery gas test mixture. The results shown in Table 4.4 were obtained after removing the nitrogen used as carrier gas and prorating the pyrolysis gases.

Clearly, the main gas produced during pyrolysis is carbon dioxide. Hydrogen, carbon monoxide, methane and ethane are the main gases that contribute to the calorific values of pyrolytic gases. The content of hydrogen in the gases increases as the pyrolysis temperature increases.

[32] Garcia-Perez M, Adams T.T., Goodrum JW, Geller D, Das KC : Production and Fuel Properties of Pine Chip Bio-oil/Biodiesel blends. Energy & Fuels, 2007, 21, 2363-2372.

[33] Garcia-Perez M, Wang S-W, Shen J, Rhodes MJ, Tian F, Lee W-J, Wu H, Li C-Z: Fast Pyrolysis of Oil Mallee Woody Biomass: Effect of Temperature on the Yield and Quality of Pyrolysis Products. Ind. Eng. Chem. Res., 2008, 47, 1846-1857.

Table 4.4.- Concentration of the gases (vol. %) obtained in the batch reactor at different temperatures (^{o}C) (test carried out on April 30, 2008).

Gas Analyzed	250 ^{o}C	350 ^{o}C	450 ^{o}C
Hydrogen	3.1	3.4	7.9
Carbon Monoxide	33.7	29.2	27.7
Carbon Dioxide	54.5	56.5	55.7
Methane	2.8	2.7	3.6
Ethane	3.2	4.4	3.3
Ethylene	1.4	1.5	0.61
Propylene	0.34	0.56	0.22
Iso-butane	0.11	0.3	0.22
1-butene	0.11	0.19	0.06
iso-butylene	0.23	0.41	0.1
trans-2-butene	0.11	0.24	0.08
cis-2-butene	0.08	0.17	0.06
1,3 butadiene	0.008	0.01	0.01
iso-pentane	0.009	0.02	0.01
n-pentane	0.07	0.18	0.07
1-pentene	0.08	0.03	0.01
cis-2-pentene	0.02	0.05	0.02
Trans-2-pentene	0.04	0.11	0.04
2-methyl-2-butene	0.02	0.05	0.04

4.4.- Bio-oil Characterization

The oils obtained from softwood bark in the batch pyrolysis reactor are formed by two phases (layers) (an aqueous phase and an oily phase) (16.9 mass % oily phase and 27.8 mass % aqueous phase). The aqueous phase was rotary evaporated to remove most of the water and obtain an oily phase herein called “dissolved oil” (22 mass % of the aqueous phase was collected as dissolved oil). While the oily phase was rich in extractive and lignin derived compounds, the dissolved oil contained more compounds derived from cellulose and hemicellulose.

4.4.1- GC/MS Analyses

The content of water was quantified by Karl Fischer Titration. The analysis of bio-oil was carried out using an Agilent 6890 N Gas Chromatographer coupled with an Agilent Technologies Inert XL Mass Spectrometry Detector with a capillary column (Agilent HP-5 MS, HP19091S-433). The following compounds were used for calibration: hydroxyacetaldehyde, acetic acid, acetol, propionic acid, Toluene, cyclopentanone, 2-furaldehyde, furfuryl alcohol, 2-(2H), o-xylene, furanone, phenol, o-cresol, eugenol, vanillin, levoglucosan, stilbene, and syringaldehyde. At least 5 standard solutions for each of these compounds were prepared. The response factor of each of the standards was calculated using phenanthrene as internal standard. It was not possible to obtain standards for all the compounds identified by the GC/MS chromatograms. Consequently the response factors for some compounds were considered equal to that for the standard of the closest chemical structure. Methanol solutions containing 4.5 mass % of bio-oil and 0.2 mass % of phenanthrene as the internal standard were used to quantify the chemical compounds of interest. The particles present in the bio-oil samples were removed with a micro-filter (0.45 mm) prior to injection into the GC-MS. 1 ml sample was injected into the injection port set at 200 ^{o}C with a split ratio of 10:1. The syringe was washed with methanol both before and after each injection. The column was operated in a constant flow mode using 1 mL/min of helium as a carrier gas. The mass spectrometer was operated at the electron ionization mode and scanned from 30 to 400 uma. The identification of each compound was achieved based on retention time and the matching mass spectrum for the standard in the spectral library.

Figure 4.1 shows the GC/MS chromatograms obtained for some of the oils resulting from this project. The name and the content of the compounds characterized in the chromatogram are listed in Table 4.4. Our analyses using GC/MS and Karl Fischer Titration allowed us to quantify between 47 and 63 mass % of the bio-oil. The compositions of oils produced in this project were compared with those of commercial oils kindly provided by Dynamotive and Innovatek.

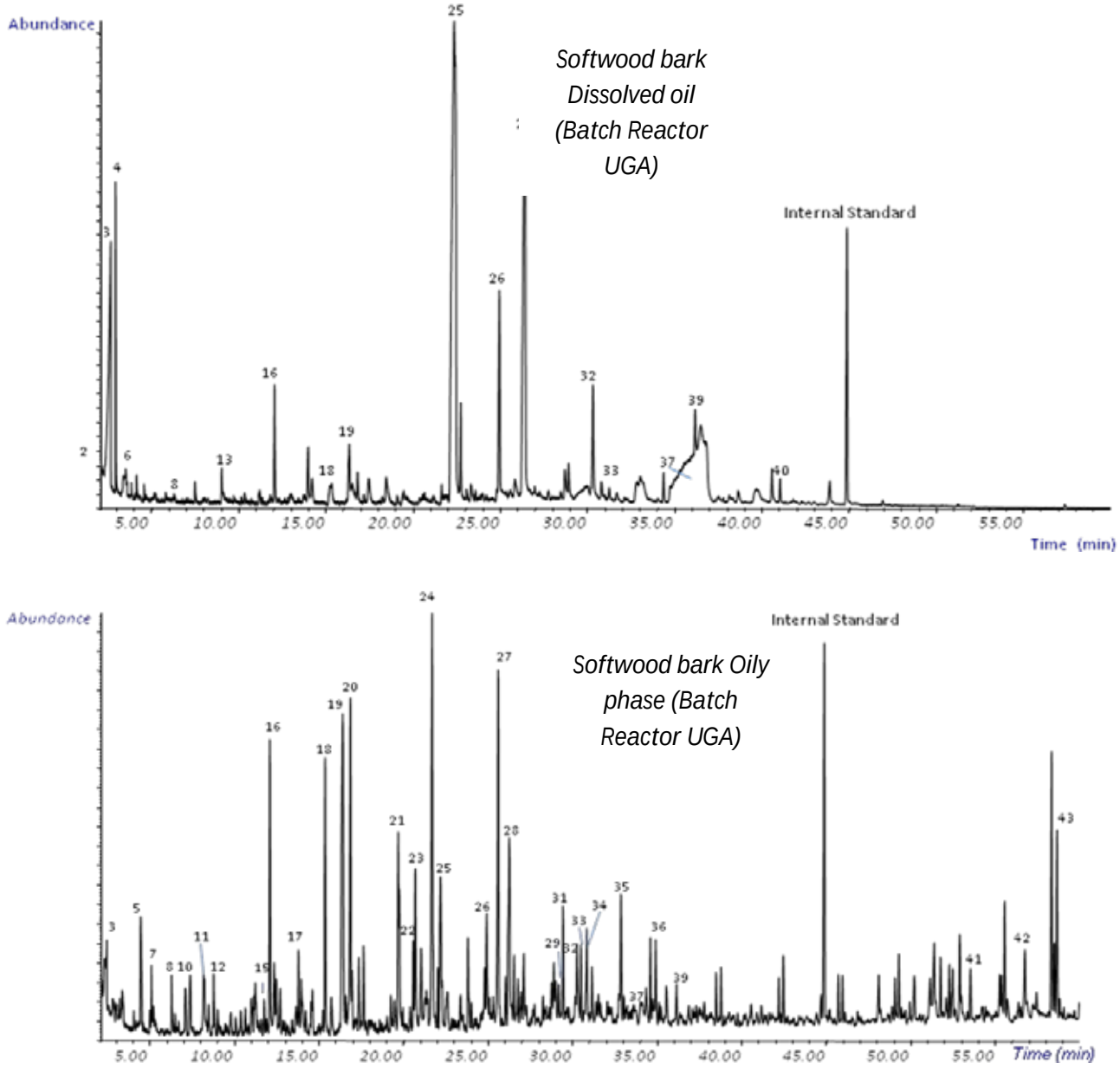

Figure 4.1 Total Ion Chromatogram for the dissolved oil and oily phase obtained from softwood bark.

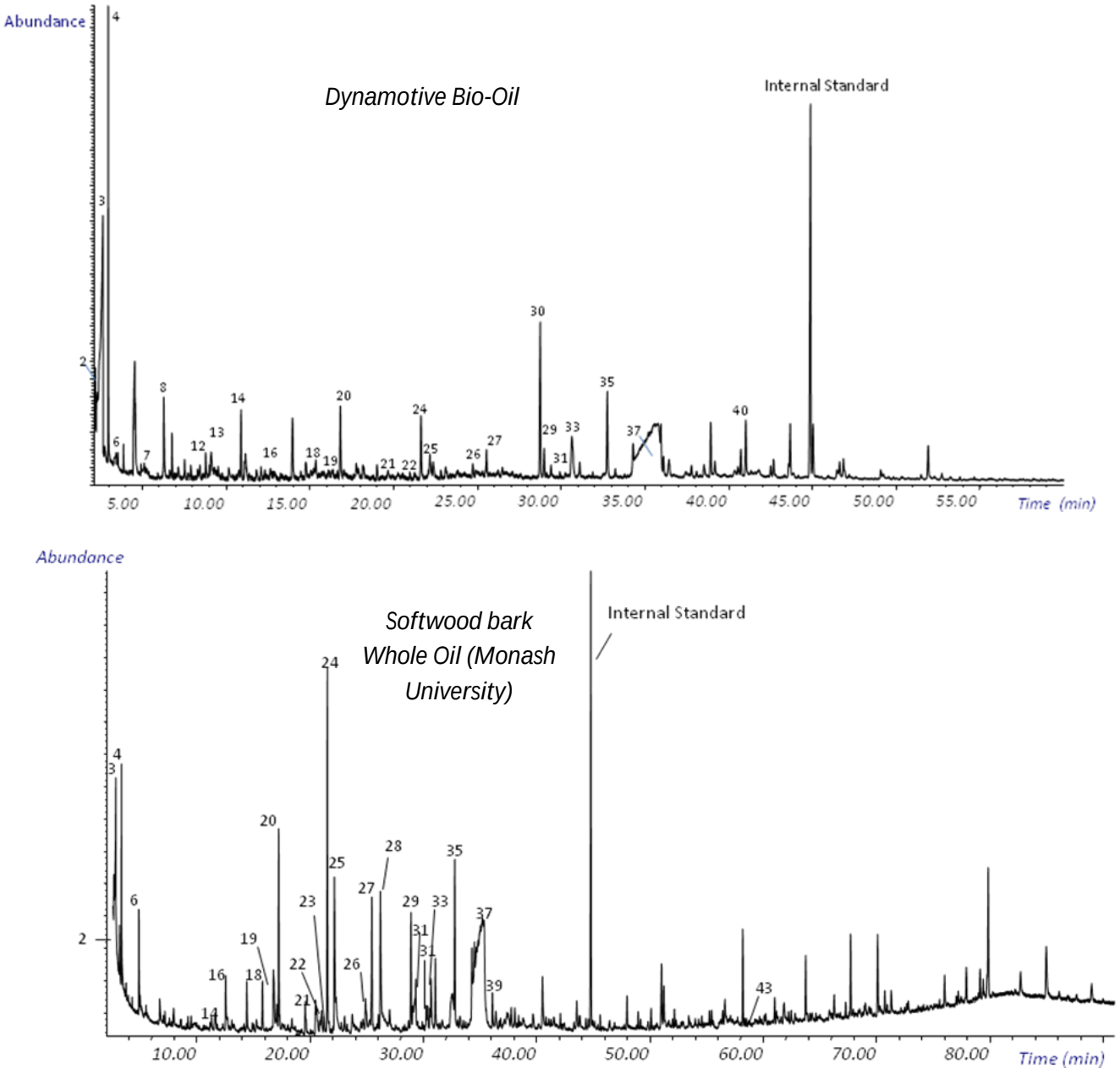

Figure 4.1 Total Ion Chromatogram for the dissolved oil and oily phase obtained from softwood bark (continuation).

Table 4.4 Content of selected chemical species in bio-oils (mass %).

	Compound	Softwood Bark Dissolved oil*	Softwood Bark Oily phase*	Softwood Bark Whole oil**	Dynamotive Oil	InnovaTek, Inc
1	Water	18.50	13.56	13.92	29.35	44.36
2	Glycolaldehyde	1.41	0	1.41	1.62	2.17
3	Acetic Acid	3.92	1.02	1.17	3.30	3.93
4	Acetol	2.43	0	1.56	2.67	3.55
5	Propionic Acid	1.017	0	0	0	0
6	Toluene	0	0.11	0.003	0.001	0
7	Cyclopentanone	0	0.023	0	0.002	0.002
8	2-Furaldehyde	0.10	0.35	0	0.52	0.34
9	Furfuryl Alcohol	0	0	0	0	0
10	p-Xylene	0	2.72	0	0	0
11	o-Xylene	0	1.94	0	0	0
12	2-Cyclopenten-1-one, 2-methyl-	0	0.08	0	0.04	0.060
13	2(5H)-Furanone	0.28	0	0	0.36	0.17
14	2-Furanethanol, b-methoxy-(S)-	0	0	0.35	0.83	0
15	Benzene, 1-ethyl-2-methyl-	0	1.28	0	0	0
16	Phenol	1.12	1.63	0.58	0.29	0.41
17	Benzene, 1-methyl-2-(1-methylethyl)-	0	4.71	0	0	0
18	O-Cresol	0.17	0.91	0.28	0.14	0.19
19	p-Cresol and m-Cresol	0.63	1.66	0.55	0.18	0.25
20	Phenol, 2-methoxy-	0	2.64	1.81	1.07	0.55
21	Phenol, 2,4-dimethyl- and Phenol, 2,5-dimethyl-	0	1.01	0.31	0.12	0.16
22	Phenol, 4-ethyl-	0	0.78	0.26	0.08	0.12
23	Phenol, 3,4-dimethyl-	0	0.87	0.22	0	0
24	Phenol, 2-methoxy-4-methyl-	0	1.22	0.80	0.29	0.13
25	Pyrotechol	5.26	1.62	1.14	0.67	1.01
26	1,2-Benzenediol, 3-methyl-	2.19	1.60	0.71	0	0.95
27	Phenol, 4-ethyl-2-methoxy-	0	0.98	0.43	0.17	0
28	1,2-Benzenediol, 4-methyl-	3.89	2.15	1.56	0	0.79
29	Eugenol	0	0.13	0.31	0.13	0.04
30	Syringol	0	0	0	1.11	0.46
31	Phenol, 2-methoxy-4-propyl-	0	0.39	0.21	0.09	0
32	4-Ethylcatechol	0.56	0.37	0.16	0	0.13

*Oil obtained at UGA with a batch pyrolysis reactor

**Whole Oil obtained with a fast pyrolysis reactor (Monash University)

Table 4.4 Content of selected chemical species in Bio-oils (mass %) (continuation….)

	Compound	Softwood Bark Dissolved oil *	Softwood Bark Oily phase*	Softwood Bark Whole oil**	Dynamotive Oil	InnovaTek, Inc
33	Vanillin	0.34	0.30	0.45	0.30	0.28
34	Tetradecane	0	1.58	0	0	0
35	Phenol, 2-methoxy-4-(1-propenyl)-, (E)-	0	0.47	0.76	0.05	0
36	Pentadecane	0	1.51	0	0	0
37	1,6-Anhydro-b-D-Glucose	6.49	0.49	3.61	4.07	2.78
38	cis-Stilbene	0	0	0	0	0
39	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	0.65	0.48	0.52	0	0
40	Syringaldehyde	0.36	0	0	0.50	0.33
41	Phenanthrene, 2,7-dimethyl-	0	0.05	0	0	0
42	Phenanthrene, 2,3,5-trimethyl-	0	0.10	0	0	0
43	Phenanthrene, 1-methyl-7-(1-methylethyl)-	0	0.20	0.003	0	0
	Total	49.3	48.9	33.09	47.9	63.2

*Oil obtained at UGA using the batch pyrolysis reactor
**Whole Oil obtained at Monash University with a fast pyrolysis reactor

Clearly, there are major differences between the chemical compositions of the oils studied in this proposal. The oily phase tends to contain higher concentrations of phenolic compounds while the dissolved oil has higher concentrations of sugars (see levoglucosan). The concentration of organic compounds in softwood bark oil obtained at Monash University was somewhere between these two extreme cases. This result is an indication that the whole oil obtained by fast pyrolysis is in fact a stable blend of oily phase and dissolved oil.

4.4.2.- Sugar Analyses

The total content of sugars in these oils was quantified following a method developed in our lab. Briefly, the bio-oil was precipitated in cold water (4 ^{o}C) to separate the sugars and the lignin derived oligomers. The sugars solubilise in the water and most of the lignin precipitates. The sugars were hydrolysed and quantified by Ion Exchange Chromatography. The results are shown in Table 3.5. The content of sugars in the oily phase was not reported because of their low content and the difficulties to precipitate this phase rich in extractives, which tend to have a

waxy texture. The extractives tend to stick to the walls of the precipitating container and cannot be easily recovered for further analyses.

Table 4.5.- Quantification of the content of Sugars of some representative oils.

	Softwood bark dissolved oil (mass %)	Dynamotive oil (mass %)	Innovatec Bio-oil (mass %)
Fucose	0.091	0.058	0.077
Arabinose	0.122	0.105	0.066
Galactose	0.811	0.197	0.097
Glucose	7.274	5.028	3.704
Mannose/Xylose	0.661	0.586	0.365
Fructose	---	0.115	0.195
Ribose	---	0.019	0.035
Total sugars	**8.959**	**6.108**	**4.539**

The Glucose detected in bio-oils is derived from the hydrolysis of levoglucosan and cellobiosan present in the oil. The content of glucose (a fermentable sugar) in these oils varies between 3.7 and 7.3 mass %. This range of concentration is suitable for fermentation. The content of other sugars derived from hemicelluloses (Fucose, arabinose, galactose, Mannose/xylose, Fructose, Ribose) is between 17 and 19 mass % of the total amount of sugars produced during pyrolysis.

5.- Bio-oil extraction with Blends of Bio-diesel and Ethyl Acetate

5.1.- Bio-oil Extraction

One of the most common methods to separate bio-oil fractions is with solvent extractions. In this project we studied the separation of bio-oil fractions using blends of fatty acid-methyl esters (biodiesel) and ethyl-acetate. The main goal of these tests was to identify the optimal conditions to selectively remove phenols, furans and carboxylic acids from dissolved oil without extracting the sugars. Figure 5.1 shows that the addition of Ethyl acetate to bio-diesel increases the mass % of bio-oil that can be extracted, and is generally true for all the oils studied. However, the source of the bio-oil dictates the optimum ethyl acetate/blends. For example Dynamotive oils showed a linear relationship between the Bio-oil/Bio-diesel ratio used to prepare the sample and the ratio of Bio-diesel/ethyl acetate and Bio-oil rich phases obtained. Maximum extractions were achieved when using ethyl acetate. In the case of Softwood bark oily phase the relationship between these two parameters is not linear. It reaches a plateau when the bio-diesel-ethyl acetate phase/ bio-oil ratio exceed 4. Blends of Bio-diesel with 50 % of ethyl acetate seem to be optimal to extract softwood bark oily phase. 76.2 mass % of the Bio-oil was extracted with this blend. The behaviour of the whole oil produced from Softwood bark in a fast pyrolysis unit at Monash University is somewhat between the oily phase produced at UGA and Dynamotive oil.

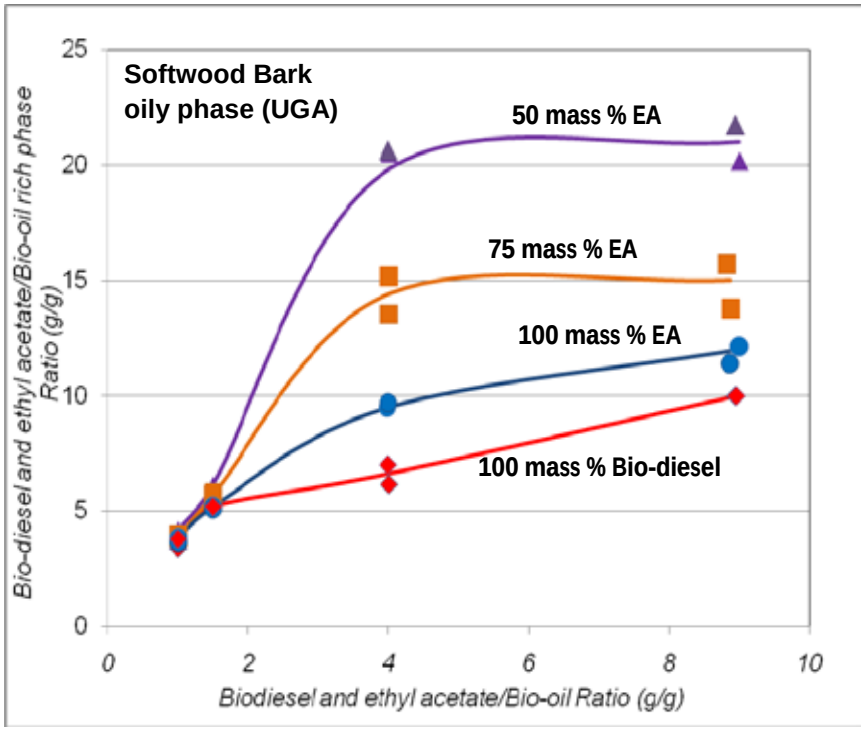

Figure 5.1.- Preparation of Bio-oil Bio-diesel Blends.

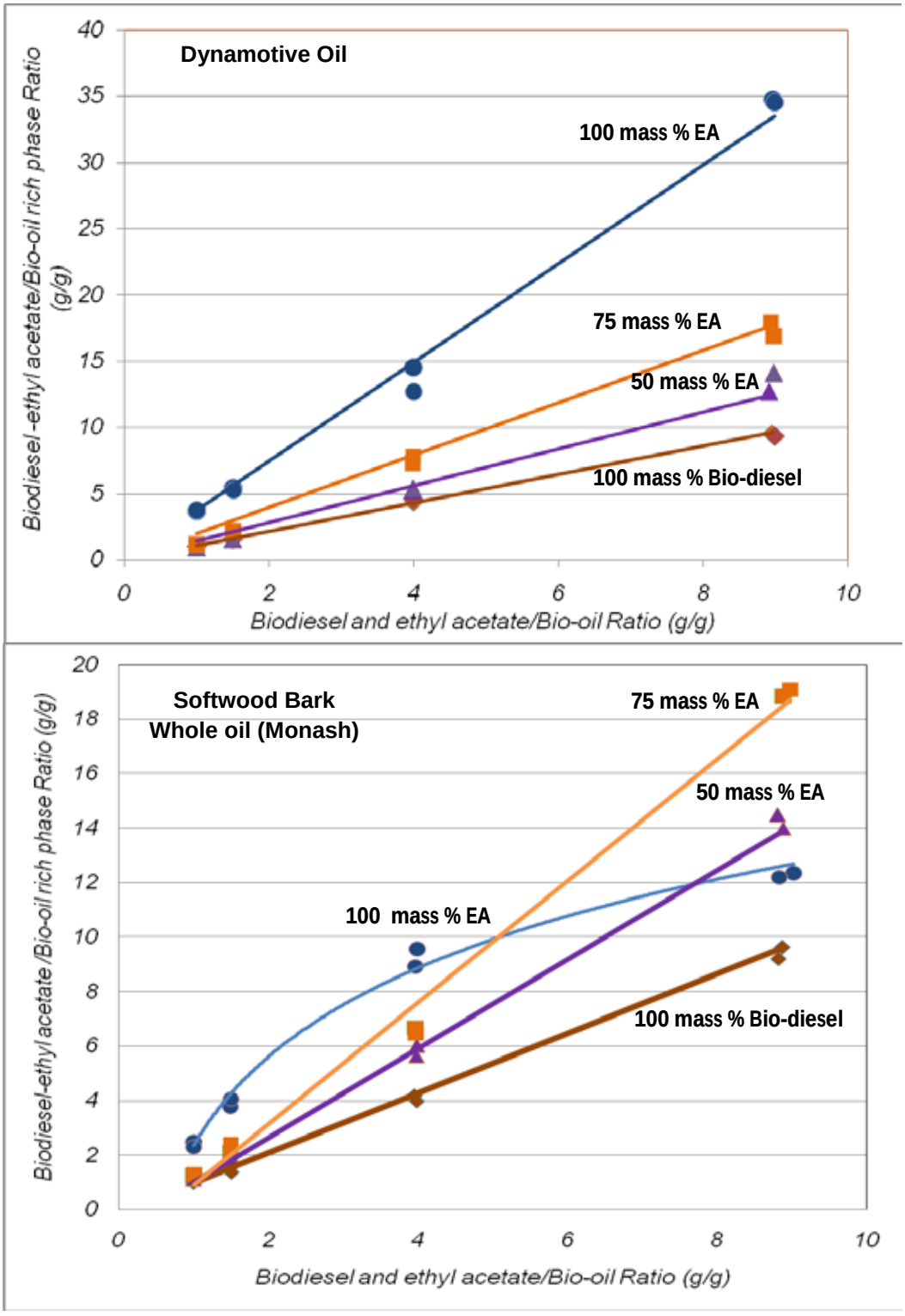

Figure 5.1.- Preparation of Bio-oil Bio-diesel Blends (continuation…)

5.2.- Characterization of Bio-oil/Bio-diesel Blends.

The purpose of this section is to consistently identify what is being extracted with the bio-diesel blends. The bio-diesel rich phase and the bio-oil rich phases obtained from the softwood oily phase produced at the University of Georgia and from Dynamotive oils were analysed by GC/MS. Unfortunately the oils from Australia were received late in the project so a full characterization of the resulting bio-oil and bio-diesel rich fractions was not possible. The results are shown in Tables 4.1 a-g. In general the bio-diesel/ethyl acetate rich phase gets enriched with phenolic and furanic compounds. The aqueous phases get enriched with polar compounds such as acetol, acetic acid, and levoglucosan.

Table 5.1.- Composition of bio-diesel rich phase and bio-oil rich phase obtained from different blends Dynamotive oil with a blend of 0% bio-diesel + 100 % ethyl acetate.

Chemicals	**EARP[1] (50% BO[2] 50% EA[3])**	**EARP (40% BO 60% EA)**	**EARP (20% BO 80% EA)**	**EARP (10% BO 90% EA)**	**BORP (50% BO 50% EA)**	**BORP (40% BO 60% EA)**	**BORF (20% BO 80% EA)**	**BORF (10% BO 90% EA)**
Acetic acid	ND	ND	ND	ND	ND	ND	ND	ND
Acetol	1.5	1.3	0.8	0.5	2.6	2.5	1.9	ND
2-furaldehyde	0.3	0.3	0.2	0.1	0.3	0.2	0.1	ND
Phenol	0.2	0.2	0.1	0.06	0.1	0.1	0.08	ND
o-cresol	0.1	0.1	0.06	0.03	0.06	0.05	ND	ND
m-cresol	0.1	0.1	0.07	0.034	0.06	0.05	ND	ND
Phenol, 2-methoxy	0.9	0.8	0.5	0.3	0.5	0.4	0.2	ND
Phenol, 2,4-dimethyl	0.1	0.1	0.05	ND	0.06	0.04	ND	ND
Phenol, 2-ethyl	0.08	0.06	0.04	ND	0.04	0.03	ND	ND
Phenol, 2-methoxy-4-methyl	0.2	0.2	0.1	0.05	0.14	0.38	0.07	ND
Phenol, 4-ethyl-2-methoxy-	0.1	0.1	0.06	0.03	0.05	0.03		ND
Syringol	4.1	3.5	2.1	1.3	2.7	2.1	1.6	ND
Eugenol	0.1	0.09	0.05	0.03	0.05	0.03	0.02	ND
Phenol, 2-methoxy-4-propyl	0.06	0.05	0.03	ND	ND	ND	ND	ND
Phenol, 2-methoxy-4-(1-propenyl)-(E)	0.07	0.05	0.03	0.01	0.03	0.02	0.01	ND
1,6-Anhydro-b-D-Glucose	1.5	1.2	0.7	0.5	6.2	6.8	9.5	12.2

[1]EARP: Ethyl Acetate Rich Phase, [2]BO: Bio-oil, [3]EA: Ethyl Acetate, [4]BORP: Bio-oil Rich Phase, ND: Non Detected

Table 5.2.- Composition of bio-diesel rich phase and bio-oil rich phase obtained from different blends Softwood bark oily phase with a blend of 0% bio-diesel + 100 % ethyl acetate.

Chemicals	**EARP[1] (50% BO[2] 50% EA[3])**	**EARP[1] (40% BO 60% EA)**	**EARP (20% BO 80% EA)**	**EARP (10% BO 90% EA)**	**BORP (50% BO 50% EA)**	**BORP (40% BO 60% EA)**	**BORP (20% BO 80% EA)**	**BORP (10% BO 90% EA)**
Acetic acid	ND	ND	ND	ND	ND	ND	ND	ND
Acetol	ND	ND	ND	ND	ND	ND	ND	ND
2-furaldehyde	0.3	0.2	0.1	0.08	0.3	0.2	0.1	ND
Phenol	1.3	1.1	0.7	0.5	1.2	1.1	0.8	0.8
O-cresol	0.7	0.6	0.4	0.3	0.7	0.6	0.5	0.5
m-cresol	1.3	1.1	0.8	0.5	1.2	1.1	0.8	0.9
Phenol, 2-methoxy	2.1	1.8	1.2	0.8	1.8	1.7	1.3	1.3
Phenol, 2,4-dimethyl	1.5	1.3	0.8	0.6	1.4	1.2	1.0	1.0
Phenol, 2-methoxy-4-methyl	0.9	0.7	0.4	0.3	0.8	0.7	0.5	0.4
Phenol, 4-ethyl-2-methoxy-	0.8	0.6	0.4	0.2	0.7	0.6	0.5	0.4
Phenol, 2-methoxy-4-propyl	0.3	0.3	0.2	0.1	0.3	0.3	0.2	0.2
Eugenol	0.1	0.1	0.06	0.04	0.1	0.1	0.07	0.06
Phenol, 2-methoxy-6-(1-propenyl)-(E)	0.4	0.3	0.2	0.1	0.4	0.3	0.2	0.2
1,6-Anhydro-b-D-Glucose	ND	ND	ND	ND	0.3	0.3	0.2	0.1

[1]EARP: Ethyl Acetate Rich Phase, [2]BO: Bio-oil, [3]EA: Ethyl Acetate, [4]BORP: Bio-oil Rich Phase, ND: Non Detected

Table 5.3.- Composition of bio-diesel rich phase and bio-oil rich phase obtained from different blends Dynamotive oil with a blend of 25% bio-diesel + 75% ethyl acetate.

Chemicals	**BDRP[1] (50% BO[2] 50% BD[3]-EA[4])**	**BDRP (40% BO 60% BD-EA)**	**BDRP (20% BO 80% BD-EA)**	**BDRP (10% BO 90% BD-EA)**	**BORP (50% BO 50% BD-EA)**	**BORP (40% BO 60% BD-EA)**	**BORP (20% BO 80% BD-EA)**	**BDRP (10% BO 90% BD-EA)**
Acetic acid	1.3	1.0	ND	ND	2.5	2.2	1.4	ND
Acetol	1.0	1.0	0.6	0.4	2.6	2.7	2.1	ND
2-furaldehyde	0.3	0.3	0.2	0.1	0.3	0.3	0.1	ND
Phenol	0.2	0.2	0.1	0.05	0.2	0.1	0.06	ND
o-cresol	0.1	0.1	0.05	0.03	ND	ND	ND	ND
m-cresol	0.2	0.1	0.06	0.03	ND	ND	ND	ND
Phenol 2-methoxy	1.0	0.8	0.4	0.3	0.5	0.4	0.2	ND
Phenol, 2,4-dimethyl	0.1	0.1	0.05	ND	ND	ND	ND	ND
Phenol, 2-ethyl,	0.1	0.07	0.03	ND	ND	ND	ND	ND
Phenol, 2-methoxy-4-methyl	0.2	0.2	0.1	0.05	0.1	0.09	0.07	ND
Phenol, 4-ethyl-2-methoxy	0.2	0.1	0.07	0.03	0.05	0.04	ND	ND
Syringol	4.0	3.4	2.0	1.2	3.1	2.6	1.6	ND
Eugenol	0.1	0.1	0.05	0.03	0.04	0.03	0.01	ND
Phenol, 2-methoxy-4-propyl	0.07	0.05	0.03	ND	ND	ND	ND	ND
Phenol, 2-methoxy-4-(1-propenyl)-(E)	0.08	0.06	0.03	0.02	0.03	0.02	0.01	ND
1,6-Anhydro-b-D-Glucose	0.4	0.4	0.2	0.2	4.4	4.8	5.7	8.8

[1]BDRP: Bio-diesel Rich Phase, [2]BO: Bio-oil, [3]BD: Bio-diesel, [4]EA: Ethyl Acetate, [4]BORP: Bio-oil Rich Phase, ND: Non Detected

Table 5.4.- Composition of biodiesel rich phase and bio-oil rich phase obtained from different blends of Softwood bark oily phase and 25% bio-diesel + 75% ethyl acetate.

Chemicals	**BDRP[1] (50% BO[2] 50% BD[3]-EA[4])**	**BDRP (40% BO 60% BD-EA)**	**BDRP (20% BO 80% BD-EA)**	**BDRP (10% BO 90% BD-EA)**	**BORP (50% BO 50% BD-EA)**	**BORP (40% BO 60% BD-EA)**	**BORP (20% BO 80% BD-EA)**	**BDRP (10% BO 90% BD-EA)**
Acetic acid,	ND	ND	ND	ND	ND	ND	ND	ND
Acetol	ND	ND	ND	ND	ND	ND	ND	ND
2-furaldehyde	0.3	0.2	0.1	0.1	0.2	0.2	ND	ND
Phenol	1.3	1.2	0.7	0.5	1.1	1.0	1.0	0.7
O-cresol	0.7	0.6	0.4	0.3	0.6	0.5	0.6	0.4
m-cresol,(p-)	1.3	1.2	0.8	0.5	1.1	1.0	1.0	0.7
Phenol, 2-methoxy,	2.0	1.8	1.2	0.8	1.7	1.5	1.6	1.2
Phenol, 2,4-dimethyl	1.5	1.3	0.9	0.6	1.3	1.1	1.2	0.9
Phenol, 2-methoxy-4-methyl	0.9	0.8	0.4	0.3	0.7	0.6	0.5	0.4
Phenol, 4-ethyl-2-methoxy-	0.8	0.6	0.4	0.2	0.6	0.5	0.5	0.3
Phenol, 2-methoxy-4-propyl	0.3	0.3	0.2	0.1	0.3	0.2	0.2	0.1
Eugenol	0.1	0.1	0.06	0.04	0.1	0.08	0.07	0.05
Phenol, 2-methoxy-6-(1-propenyl)-(E)	0.4	0.4	0.2	0.1	0.3	0.3	0.2	0.2
1,6-Anhydro-b-D-Glucose	ND	ND	ND	ND	0.7	0.7	1.1	-

[1]BDRP: Bio-diesel Rich Phase, [2]BO: Bio-oil, [3]BD: Bio-diesel, [4]EA: Ethyl Acetate, [4]BORP: Bio-oil Rich Phase, ND: Non Detected

Table 5.5.- Composition of bio-diesel rich phase and bio-oil rich phase obtained from different blends of Dynamotive bio-oil and 50% bio-diesel + 50% ethyl acetate.

Chemicals	**BDRP[1] (50% BO[2] 50% BD[3]-EA[4])**	**BDRP (40% BO 60% BD-EA)**	**BDRP (20% BO 80% BD-EA)**	**BDRP (10% BO 90% BD-EA)**	**BORP (50% BO 50% BD-EA)**	**BORP (40% BO 60% BD-EA)**	**BORP (20% BO 80% BD-EA)**	**BDRP (10% BO 90% BD-EA)**
Acetic acid	ND	ND	ND	ND	2.7	2.5	1.9	2.0
Acetol	0.6	0.6	0.5	0.3	2.7	2.7	2.5	2.5
2-furaldehyde	0.4	0.4	0.2	0.1	0.4	0.3	0.2	0.2
Phenol	0.2	0.2	0.08	0.04	0.2	0.1	0.08	0.07
o-cresol	0.1	0.1	0.06	0.03	ND	ND	ND	ND
m-cresol	0.2	0.1	0.06	ND	ND	ND	ND	ND
Phenol, 2-methoxy	0.9	0.8	0.4	0.2	0.6	0.5	0.3	0.3
Phenol, 2,4-dimethyl	0.1	0.1	0.05	ND	ND	ND	ND	ND
Phenol, 2-ehtyl	0.09	0.07	0.03	ND	ND	ND	ND	ND
Phenol, 2-methoxy-4-methyl	0.2	0.2	0.1	0.05	0.2	0.1	0.07	0.07
Phenol, 4-ethyl-2-methoxy-	0.2	0.1	0.06	0.03	0.05	0.04	0.02	ND
Syringol	3.5	3.2	2.0	1.1	3.7	3.2	2.1	2.1
Eugenol	0.1	0.1	0.05	0.03	0.05	0.04	0.02	0.02
Phenol, 2-methoxy-4-propyl	0.07	0.06	0.03	ND	ND	ND	ND	ND
Phenol, 2-methoxy-4-(1-propenyl)-(E)	0.08	0.09	0.03	0.02	0.03	0.03	0.01	0.01
1,6-Anhydro-b-D-Glucose	ND	ND	ND	ND	4.09	4.3	5.2	5.5

[1]BDRP: Bio-diesel Rich Phase, [2]BO: Bio-oil, [3]BD: Bio-diesel, [4]EA: Ethyl Acetate, [4]BORP: Bio-oil Rich Phase, ND: Non Detected

Table 5.6.- Composition of bio-diesel rich phase and bio-oil rich phase obtained from different blends of Softwood bark bio-oil and 50% bio-diesel + 50% ethyl acetate.

Chemicals	**BDRP[1] (50% BO[2] 50% BD[3]-EA[4])**	**BDRP (40% BO 60% BD-EA)**	**BDRP (20% BO 80% BD-EA)**	**BDRP (10% BO 90% BD-EA)**	**BORP (50% BO 50% BD-EA)**	**BORP (40% BO 60% BD-EA)**	**BORP (20% BO 80% BD-EA)**	**BDRP (10% BO 90% BD-EA)**
Acetic acid	ND	ND	ND	ND	ND	ND	ND	ND
Acetol	ND	ND	ND	ND	ND	ND	ND	ND
2-furaldehyde	0.3	0.2	0.1	0.09	0.3	0.2	ND	ND
Phenol	1.3	1.2	0.7	0.5	1.1	1.1	0.8	0.6
O-cresol	0.7	0.7	0.4	0.3	0.6	0.6	0.4	0.4
m-cresol	1.3	1.2	0.8	0.5	1.1	1.0	0.8	0.6
Phenol, 2-methoxy	2.0	1.8	1.2	0.8	1.7	1.6	1.2	1.0
Phenol, 2,4-dimethyl	1.5	1.3	0.9	0.6	1.1	1.1	0.8	0.8
Phenol, 2-methoxy-4-methyl	0.9	0.8	0.5	0.3	0.6	0.6	0.4	0.3
Phenol, 4-ethyl-2-methoxy	0.7	0.6	0.4	0.2	0.5	0.5	0.3	0.3
Phenol, 2-methoxy-4-propyl	0.3	0.3	0.2	0.1	0.2	0.2	0.1	0.1
Eugenol	0.1	0.1	0.06	0.04	0.09	0.08	0.04	0.04
Phenol, 2-methoxy-6-(1-propenyl)-(E)	0.4	0.4	0.2	0.1	0.3	0.3	0.2	0.1
1,6-Anhydro-b-D-Glucose	ND	ND	ND	ND	0.5	0.4	1.0	0.8

[1]BDRP: Bio-diesel Rich Phase, [2]BO: Bio-oil, [3]BD: Bio-diesel, [4]EA: Ethyl Acetate, [4]BORP: Bio-oil Rich Phase, ND: Non Detected

Table 5.7.- Composition of bio-diesel rich phase and bio-oil rich phase obtained from different blends of Dynamotive bio-oil and 100% bio-diesel + 0% ethyl acetate.

Chemicals	**BDRP[1] (50% BO[2] 50% BD[3]-EA[4])**	**BDRP (40% BO 60% BD-EA)**	**BDRP (20% BO 80% BD-EA)**	**BDRP (10% BO 90% BD-EA)**	**BORP (50% BO 50% BD-EA)**	**BORP (40% BO 60% BD-EA)**	**BORP (20% BO 80% BD-EA)**	**BDRP (10% BO 90% BD-EA)**
Acetic acid	1.0	0.8	0.8	0.6	3.5	3.6	3.1	2.7
Acetol	ND	ND	ND	ND	2.7	3.5	3.2	3.0
2-furaldehyde	0.3	0.2	0.1	ND	0.2	0.5	0.3	0.2
Phenol	0.2	0.1	ND	ND	0.2	0.2	0.1	ND
o-cresol	0.1	0.08	0.04	ND	ND	ND	ND	ND
m-cresol	0.1	0.08	0.04	ND	ND	ND	ND	ND
Phenol,-methoxy	0.7	0.6	0.4	0.2	0.8	0.6	0.4	0.2
Phenol, 2,4-dimethyl	0.1	0.04	ND	ND	ND	ND	ND	ND
Phenol, 2-ethyl,	0.1	0.04	ND	ND	ND	ND	ND	ND
Phenol, 2-methoxy-4-methyl	0.2	0.2	0.1	0.04	0.2	0.2	0.1	0.1
Phenol, 4-ethyl-2-methoxy-	0.1	0.1	0.05	0.02	0.07	0.06	0.03	ND
Syringol	2.2	2.2	1.4	0.8	4.4	4.2	3.1	2.1
Eugenol	0.1	0.09	0.05	0.02	0.08	0.06	0.04	0.02
Phenol, 2-methoxy-4-propyl	0.06	0.05	0.03	0.01	0.04	ND	ND	ND
Phenol, 2-methoxy-4-(1-propenyl)-(E)	0.06	0.05	0.03	0.01	0.05	0.04	0.02	0.02
1,6-Anhydro-b-D-Glucose	ND	ND	ND	ND	4.3	4.3	4.6	4.8

[1]BDRP: Bio-diesel Rich Phase, [2]BO: Bio-oil, [3]BD: Bio-diesel, [4]EA: Ethyl Acetate, [4]BORP: Bio-oil Rich Phase, ND: Non Detected

Table 5.8.- Composition of bio-diesel rich phase and bio-oil rich phase obtained from different blends of Softwood bark bio-oil and 100% bio-diesel + 0% ethyl acetate.

Chemicals	**BDRP[1] (50% BO[2] 50% BD[3]-EA[4])**	**BDRP (40% BO 60% BD-EA)**	**BDRP (20% BO 80% BD-EA)**	**BDRP (10% BO 90% BD-EA)**	**BORP (50% BO 50% BD-EA)**	**BORP (40% BO 60% BD-EA)**	**BORP (20% BO 80% BD-EA)**	**BDRP (10% BO 90% BD-EA)**
Acetic acid,	0.6	0.5	0.2	0.1	1.3	1.2	0.9	ND
Acetol	ND	ND	ND	ND	ND	ND	ND	ND
2-furaldehyde	0.2	0.2	0.1	0.06	0.2	0.2	0.1	ND
Phenol	1.3	1.1	0.7	0.4	1.3	1.1	0.6	0.5
O-cresol	0.7	0.7	0.4	0.3	0.6	0.5	0.3	0.3
m-cresol,(p-)	1.3	1.2	0.8	0.5	1.3	1.1	0.6	0.5
Phenol,2-methoxy	2.0	1.8	1.2	0.9	2.00	1.7	0.9	0.9
Phenol, 2,4-dimethyl	1.5	1.4	0.8	0.6	1.3	1.1	0.7	0.6
Phenol, 2-methoxy-4-methyl	0.3	0.8	0.5	0.3	0.8	0.6	0.3	0.3
Phenol, 4-ethyl-2-methoxy	0.3	0.6	0.4	0.2	0.6	0.5	0.3	0.3
Phenol, 2-methoxy-4-propyl	0.3	0.3	0.7	0.1	0.2	0.2	0.1	0.1
Eugenol	0.1	0.1	0.06	0.04	0.1	0.08	0.04	0.03
Phenol, 2-methoxy-6-(1-propenyl)-(E)	0.4	0.4	0.2	0.1	0.3	0.3	0.2	0.1
1,6-Anhydro-b-D-Glucose	ND	ND	ND	ND	4.2	5.1	5.6	5.1

[1]BDRP: Bio-diesel Rich Phase, [2]BO: Bio-oil, [3]BD: Bio-diesel, [4]EA: Ethyl Acetate, [4]BORP: Bio-oil Rich Phase, ND: Non Detected

5.3.- Distribution Coefficients of Selected Bio-oil Components.

Although most industrial solvents are generally single functionality organic compounds such as ketones, esters, alcohols, or linear or branched aliphatic hydrocarbons, multifunctional solvents are also commonly used. One approach to achieve a multifunctional solvent with properties tailored for a given application is to blend several single functionality organic solvents. In this study we decided to study ethyl acetate/bio-diesel blends.

The distribution coefficient (Partition ratio) and the solute selectivity are some of the main factors that should be taken into account to choose a solvent. The distribution coefficient is defined as the ratio **(**$K_i = Y_i/X_i$), where Y_i is the concentration of solute i in the solvent (in this case the solvent is Bio-diesel-Ethyl Acetate blends) and X_i is the concentration of solute in the feed (in this case the feed is Bio-oil). The solute selectivity is a very important parameter that should be studied to make sure that undesirable solutes (in this case the sugars) are not extracted while recovering the desired solutes from the feed (in this case phenols and furans). The selectivity of a given solvent for solute *i* compared to solute *j* is characterized by the separation $a_{ij} = K_i/K_j$. Values of a_{ij} must be greater than 1 to achieve an increase in solute purity. Often blends are used in industrial processes to provide more selectivity even at the expense of lower distribution coefficients.

Figures 5.2-5.10 show the distribution coefficient for selected compounds found in bio-oils (2-furaldehyde, phenol, phenol 2-methoxy, phenol 2-methoxy 4-methyl, Phenol 2-methoxy 4 ethyl, Eugenol, Phenol 2-methoxy-4-ethyl, , Phenol 2-methoxy, 4-(1-propenyl), Acetol, syringol and Levoglucosan). The values of distribution coefficients were in all cases below 10. Values of K greater than 10 are usually sought for industrial systems to ensure compact designs and the use of small volumes of solvent. Solvent extraction can still be used as a technique to separate solutes from systems with low values of K but larger equipment and solvent-feed ratios are required. Our results clearly show that distribution coefficients behave differently depending on the nature of the bio-oil studied. In general higher concentration of ethyl acetate in bio-diesel increases distribution coefficients for phenols extracted from the Dynamotive oil but reduced the

coefficient for the same compounds when extracted from softwood bark oily phase. This results in extraction conditions that will depend on the characteristics of the bio-oil used.

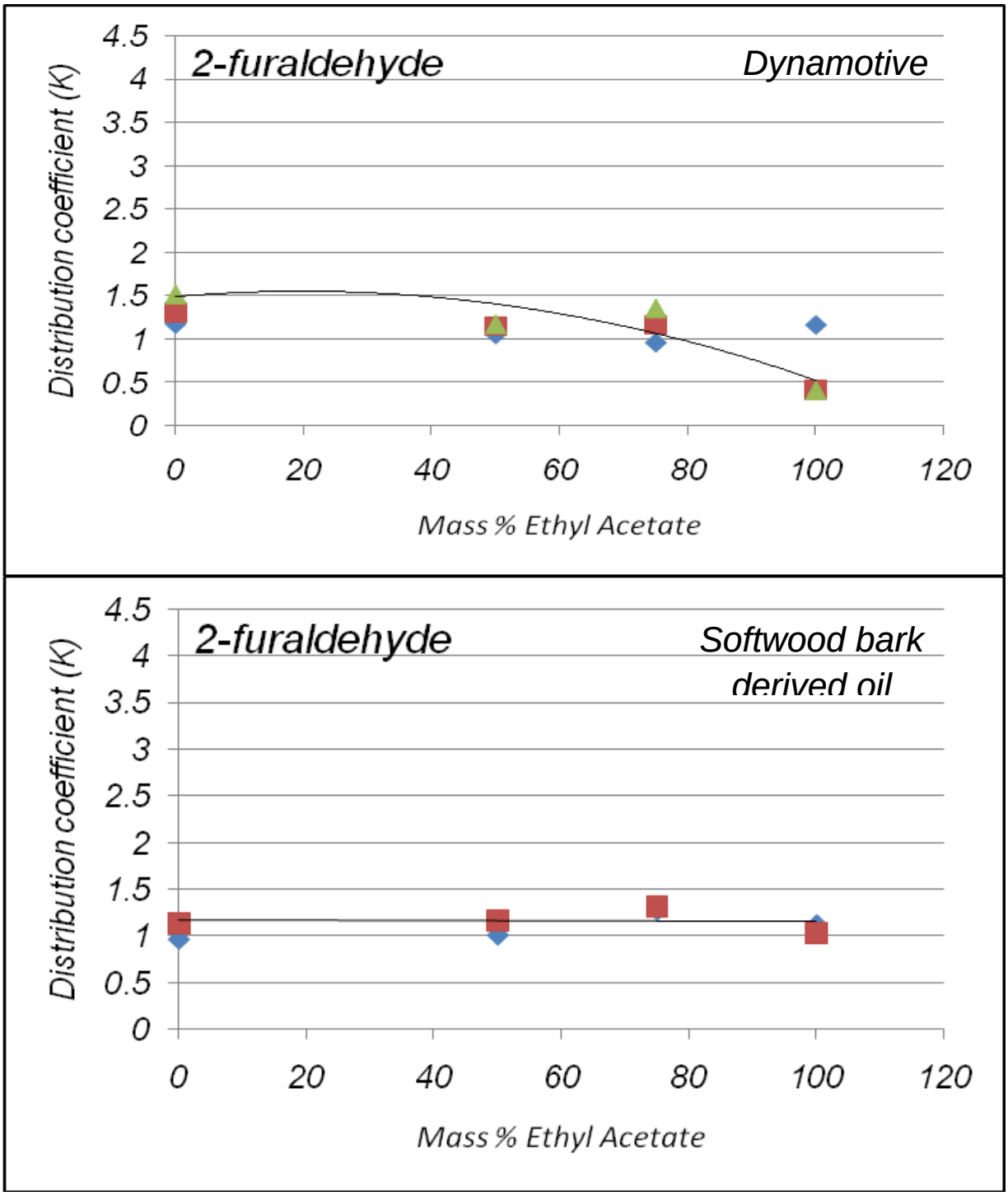

Figure 5.2.- Distribution Coefficient of 2-furaldehyde as a function of ethyl acetate concentrations in ethyl acetate/ bio-diesel blends.

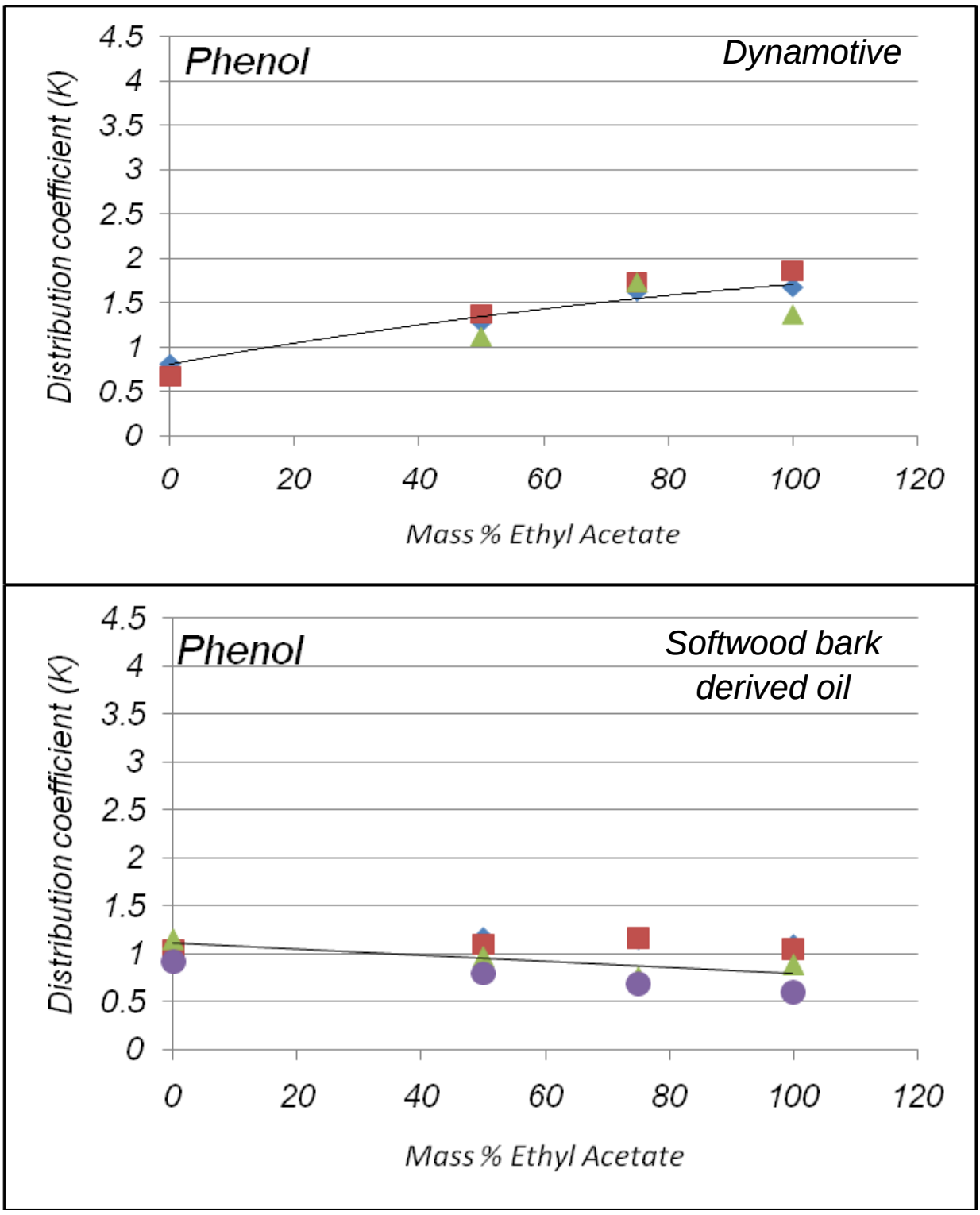

Figure 5.3.- Distribution Coefficient of Phenol as a function of methyl acetate concentration in ethyl acetate/ bio-diesel blends.

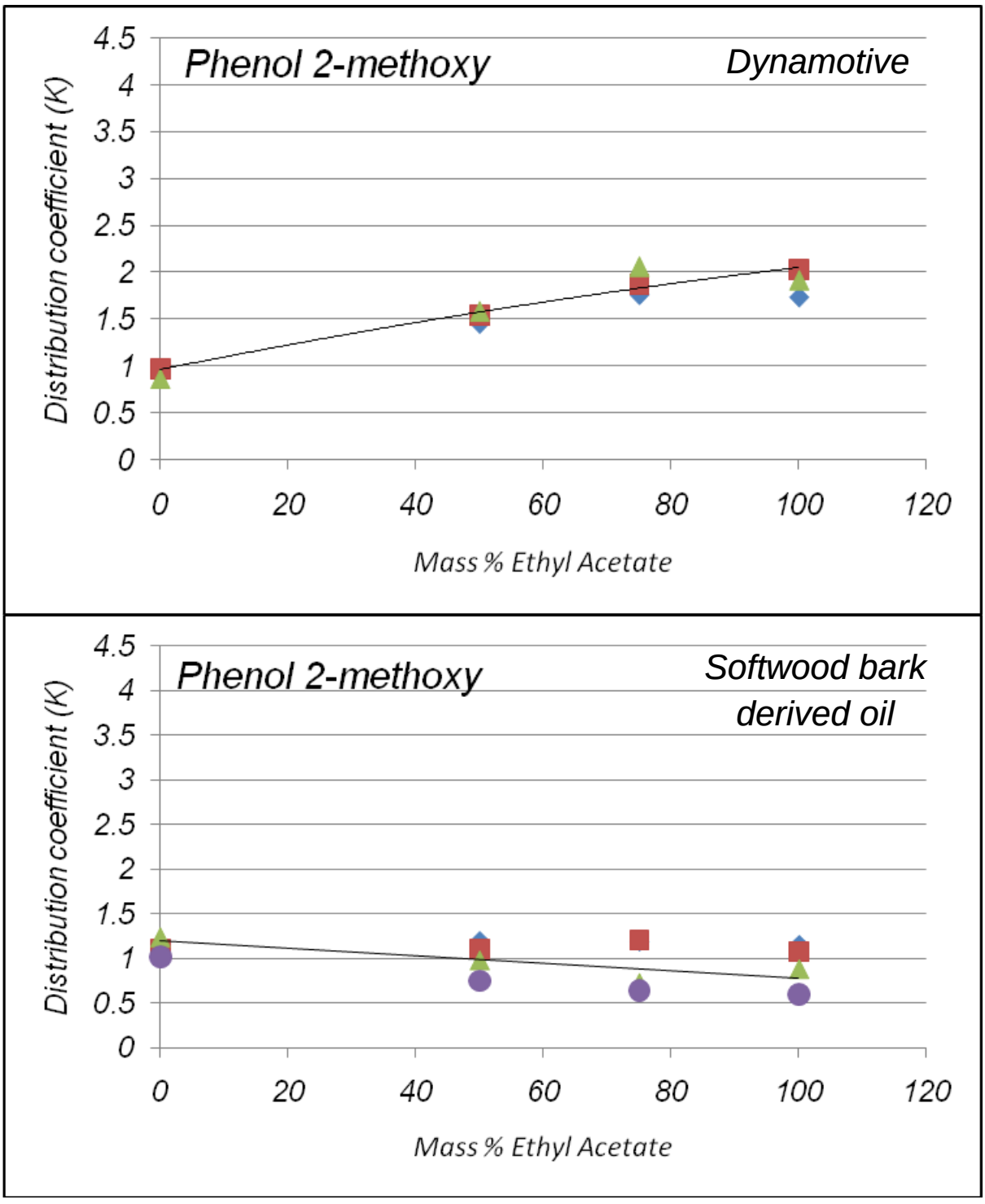

Figure 5.4.- Distribution Coefficient of 2-methoxyphenol as a function of Ethyl acetate concentration in ethyl acetate/ bio-diesel blends.

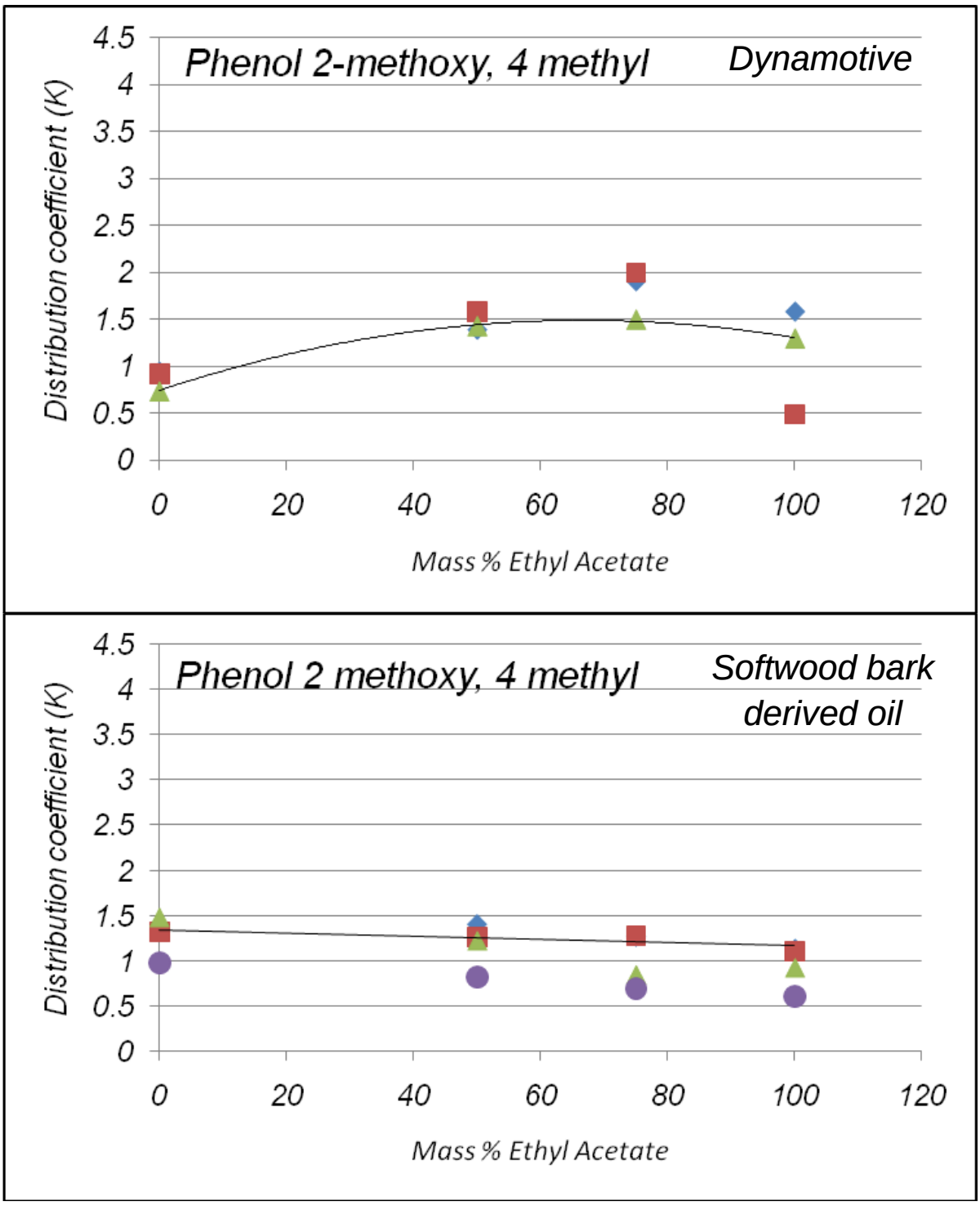

Figure 5.5.- Distribution Coefficient of 2-methoxy, 4 methyl phenol as a function of ethyl acetate concentration in ethyl acetate/ bio-diesel blends.

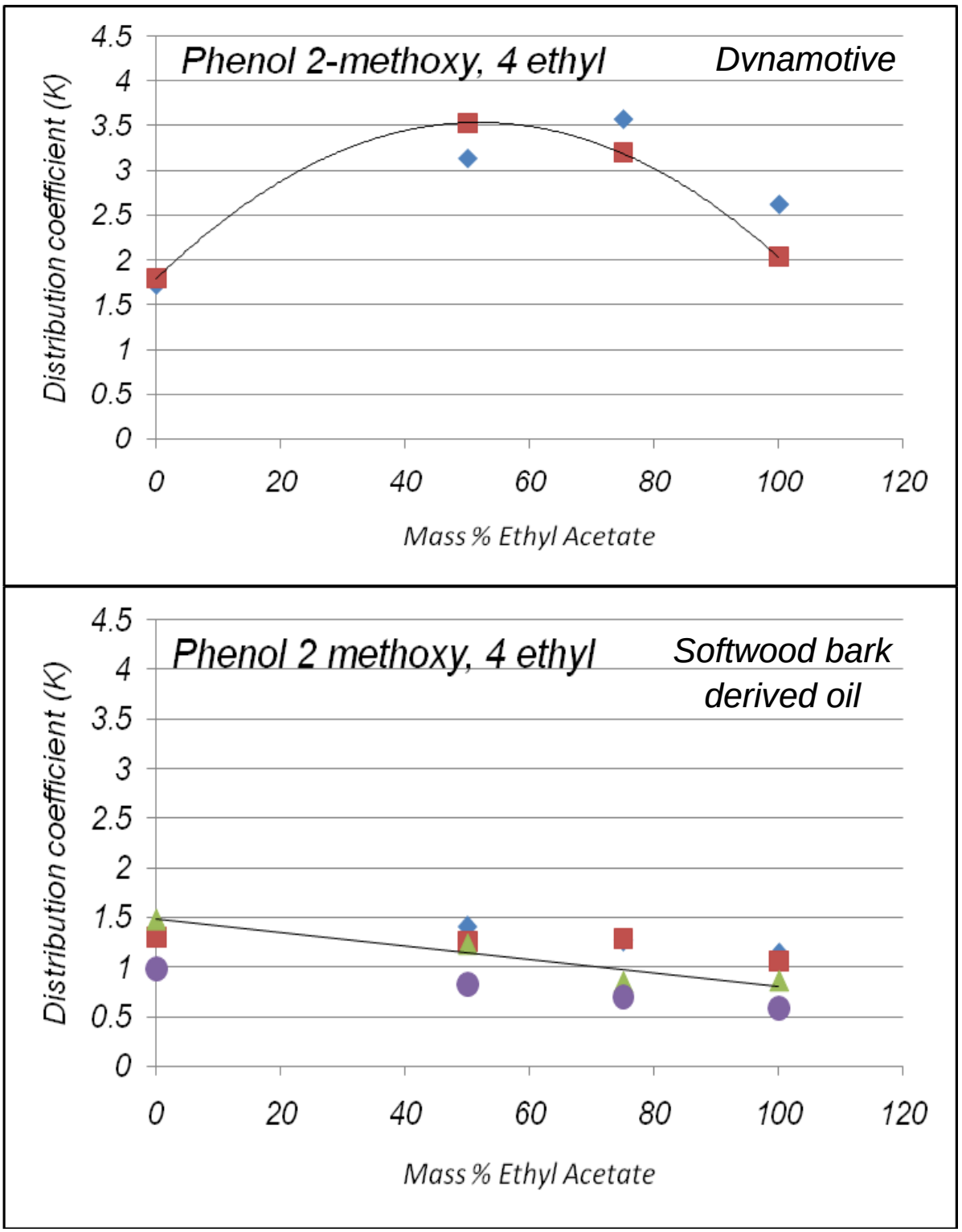

Figure 5.6.- Distribution Coefficient of phenol 2-methoxy, 4 ethyl as a function of Ethyl acetate concentration in ethyl acetate/ bio-diesel blends.

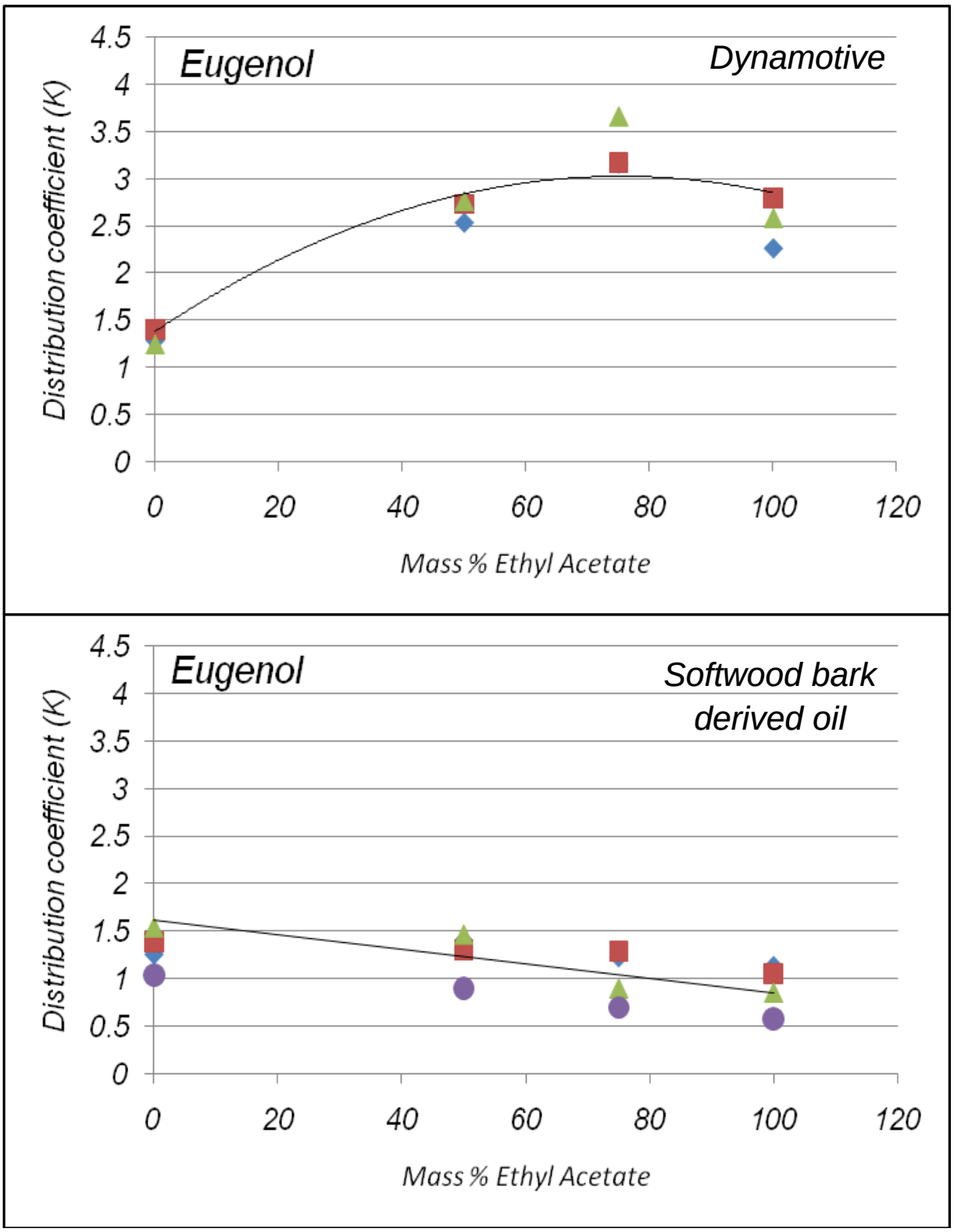

Figure 5.7.- Distribution Coefficient of Eugenol as a function of Ethyl acetate concentration in ethyl acetate/ bio-diesel blends.

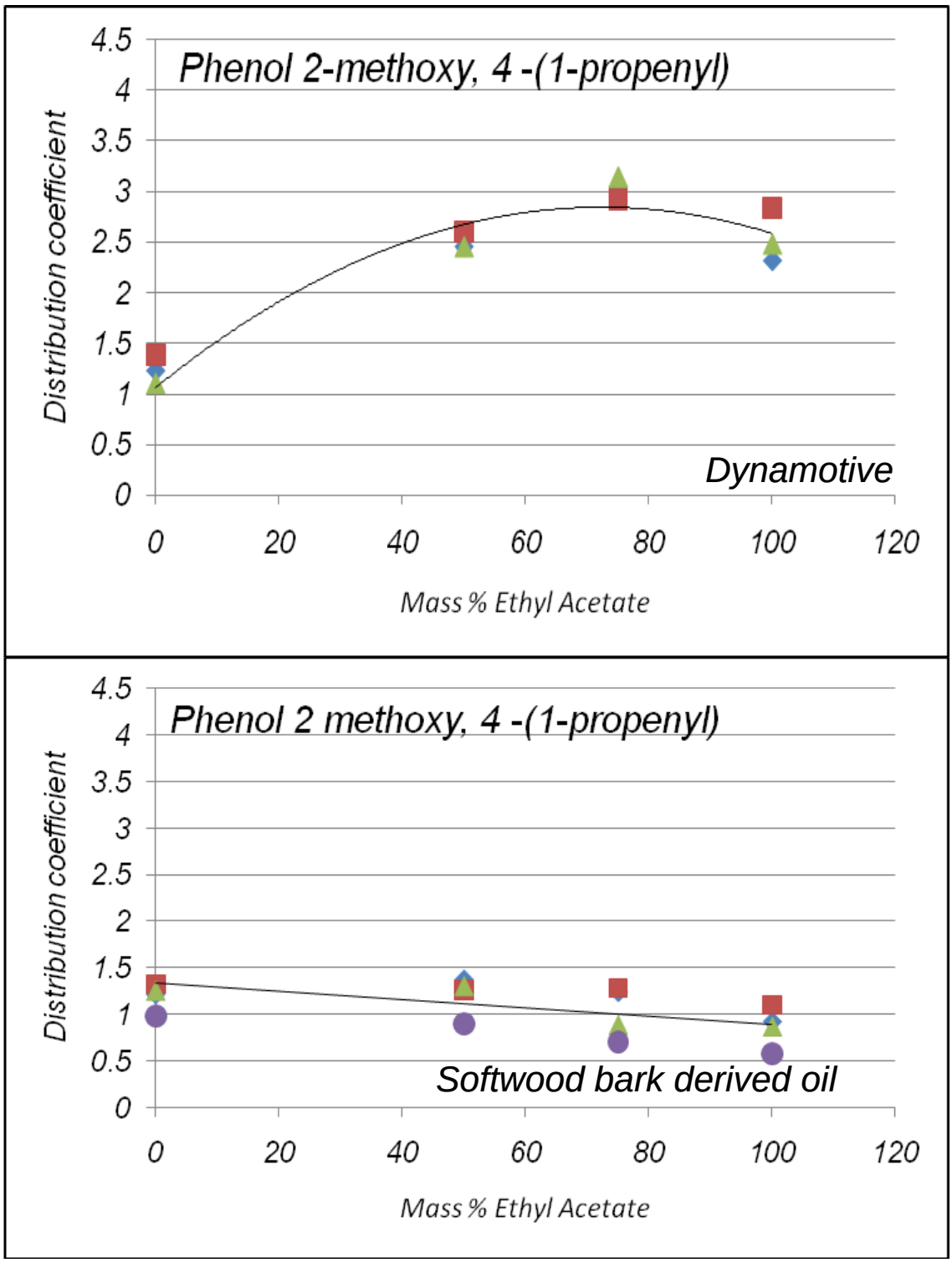

Figure 5.8.- Distribution Coefficient of Phenol 2 methoxy, 4-(1-propenyl) as a function of Ethyl acetate concentration in ethyl acetate/ bio-diesel blends.

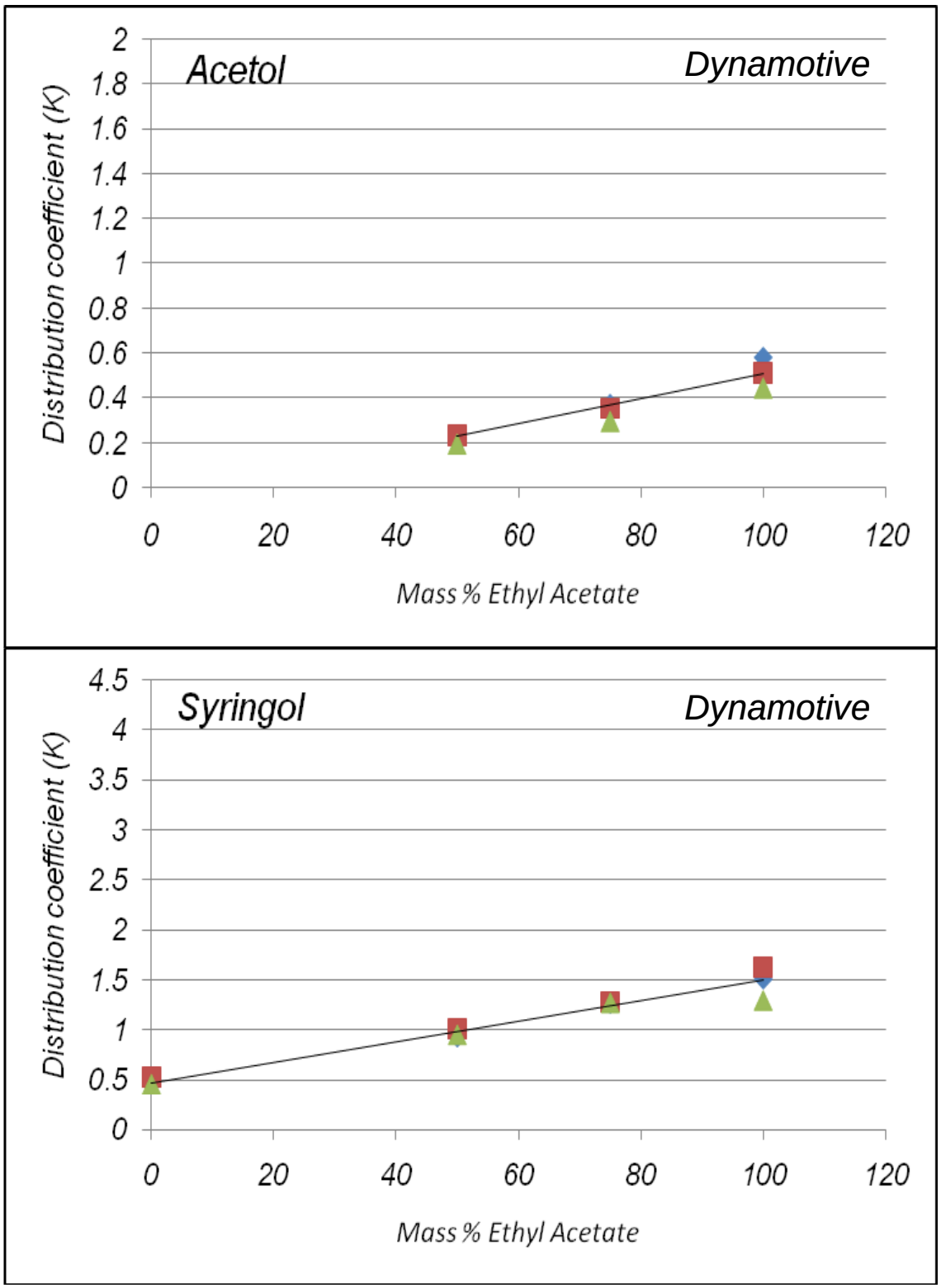

Figure 5.9.- Distribution Coefficient of Acetol and Syringol as a function of Ethyl acetate concentration in ethyl acetate/ bio-diesel blends.

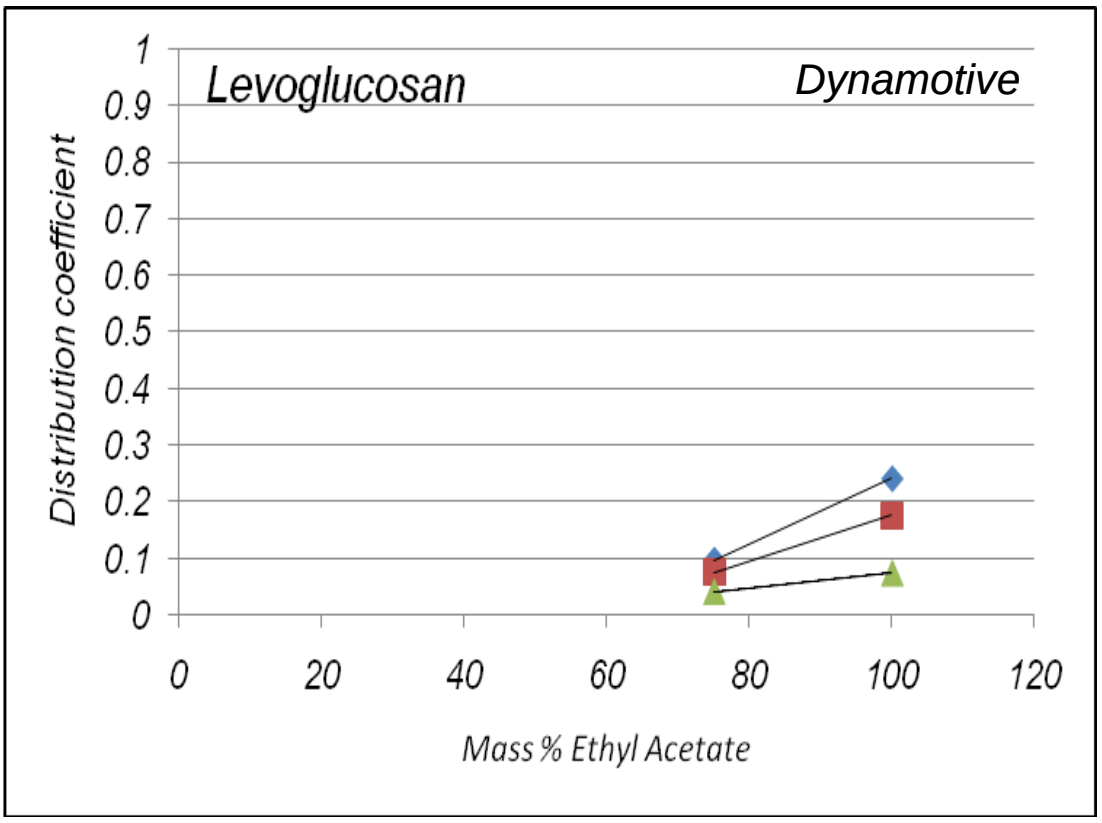

Figure 5.10.- Distribution Coefficient of Acetol and Syringol as a function of Ethyl acetate concentration in ethyl acetate/ bio-diesel blends.

Unfortunately we were only able to quantify the content of Levoglucosan in solutions with ethyl acetate concentrations of over 75 mass %. The selectivity of syringol-levoglucosan extractions decreases from 26 to 8 % as the concentration of ethyl acetate changes from 75 to 100 mass %. A similar trend was observed when comparing other phenols with levoglucosan. This result suggests that in order to minimize the removal of levoglucosan from the aqueous phase it may be desirable to use blends with a lower content of ethyl acetate. Concentrations between 50 and 75 mass % seem to be ideal. Although higher concentrations may result in more compact equipments and the need to use less solvents, higher losses of sugars may occur.

5.4- Removal of acids from the bio-diesel rich phase

Small amounts of acetic acid are also soluble in the ethyl acetate/biodiesel rich phase reducing the pH of this phase. This section is devoted to evaluate two approaches to reduce the content of acids in the bio-diesel rich phase. The first approach studied consists of an extraction with $NaHCO_3$, the second approach studied consists of the esterification of these acids with isoamyl alcohol in the presence of acid catalysts.

5.4.1- Extraction with $NaHCO_3$.

In this study the Bio-diesel rich phase obtained from a blend of 1/1 Dynamotive bio-oil and Bio-diesel was extracted with a solution of $NaHCO_3$ (5 mass %). The ratios of bio-diesel rich phase/$NaHCO_3$ solutions used were 1:1, 3:1 and 6:1.

Figure 5.11 clearly shows that after the first extraction step almost all the acetic acid in the bio-diesel rich phase was removed. In the chromatogram obtained after extraction it was only possible to identify a small peak associated with methanol. This result proves that the extraction with $NaHCO_3$ is an efficient method to remove carboxylic acids from bio-diesel rich phases. Similar results were obtained for other bio-diesel rich phase/$NaHCO_3$ aqueous phase ratios.

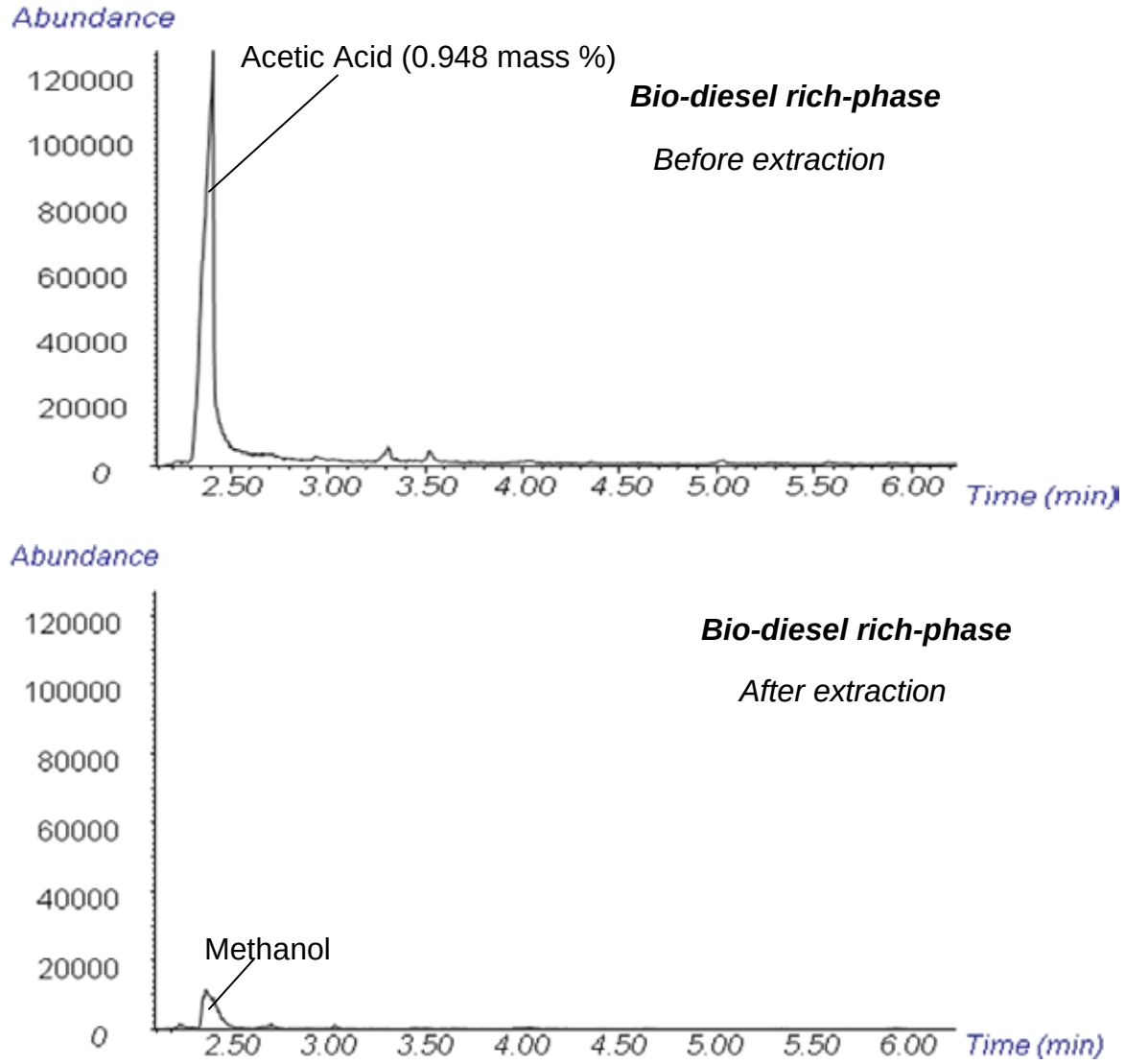

Figure 5.11.- GC/MS chromatograph of a Bio-diesel Rich before and after the extraction with $NaHCO_3$.

5.4.2- Esterification of Acetic Acid with Amyl Alcohol in the Presence of Solid Acid Catalysts.

The second concept to remove the acetic acid from the bio-diesel/ethyl acetate rich phases is esterification with Iso-amyl alcohol in the presence of an acidic ion-exchange resin. The results shown in Figure 5.12 were obtained with a bio-diesel rich phase obtained when 40 mass % of Dynamotive oil was blended with 60 mass % Biodiesel. 25 grams of the biodiesel rich phase was blended with 2 grams of isoamyl alcohol and 1 gram of Amberlyst 15 (solid acidic catalyst). The

reaction was conducted in a closed vial at 75 ^{o}C for 6 hours. The vial was shaken every 15 minutes. These chromatographs show that the concept proposed is technically viable and that most of the acetic acid can be converted into Isoamylacetate.

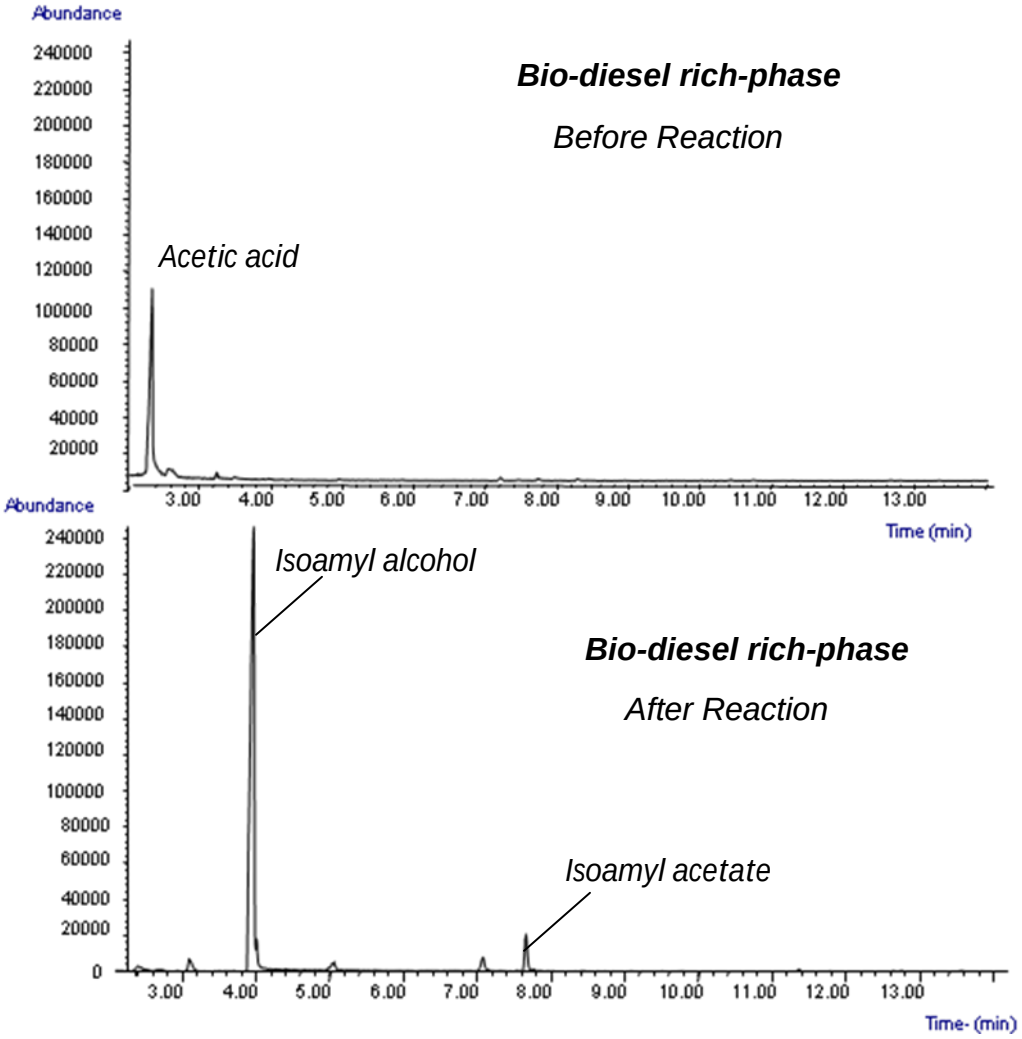

Figure 5.12.- GC/MS chromatograph of a Bio-diesel Rich before and after the reaction with Isoamyl alcohol at 75 ^{o}C in the presence of Amberlyst 15 (Isoamyl alcohol was in excess).

5.5.- Distillation of Resulting Bio-diesel Rich Phase and GC/MS Analysis of Distillation Products.

Table 5.9 shows the mass fraction of a bio-diesel rich phase collected at different distillation temperatures. Only 27.5 mass % of the bio-diesel rich phase was distilled at temperatures below 250 ^{o}C, the rest remain as in bottom.

Table 5.9.- Distillation Curve of Bio-oil/Bio-diesel Blend

Temperature °C	Distilled fraction (mass %)
0-100	2.7
100-150	2.9
150-200	8.8
200-250	13.2
Bottom (>250)	72.5

The distilled fractions were analyzed by GC/MS. The chromatograms obtained are shown in Figure 5.13. It is evident that the distilled fraction obtained between 70 and 100 ^{o}C is enriched with bio-oil derived compounds, as the temperature increases the concentration of bio-oil derived compounds starts to decrease.

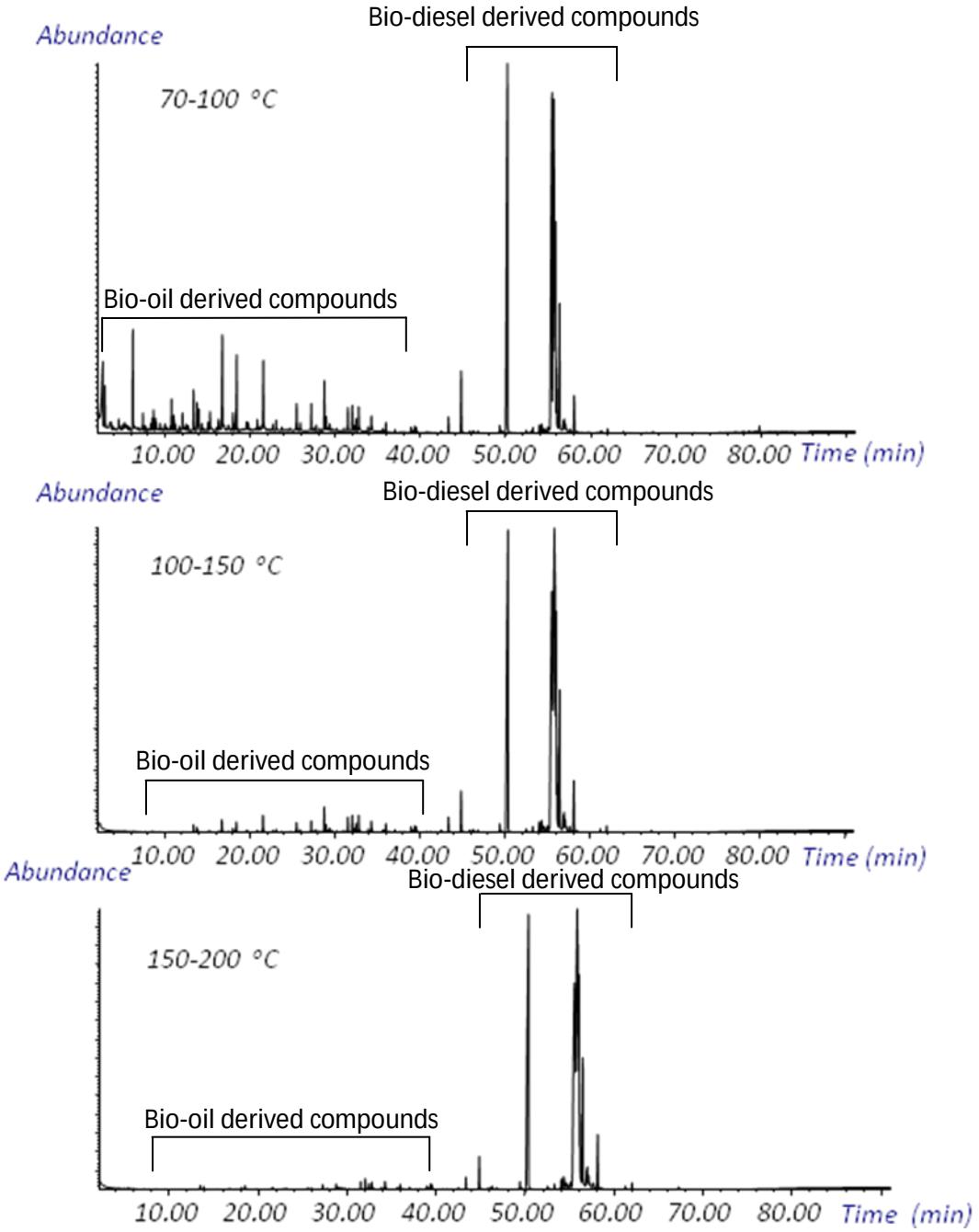

Figure 5.13.- GC/MS chromatograph of the fractions distilled from Bio-diesel Rich phases.

6.- Fermentation of Pyrolytic Sugars.

6.1.- Identifying yeast toxic compounds in bio-oils

Understanding which bio-oil compounds are toxic to the organisms used for fermentation of pyrolytic sugars is critical to develop rational strategies to detoxify these oils. The toxic effects on *Saccharomyces cerevisiae* for some of the most important compounds found in bio-oils (see table 6.1) was studied.

Saccharomyces cerevisiae cultures were stored in aliquots supplemented with 15% glycerol at -80°C and were revived by growth in YPD medium (glucose 2%, yeast extract 1%, peptone 2%) at 30 ^{o}C under normal atmospheric pressure and agitation (120 rpm). The concentration of each of the compounds tested was 25, 50, 75 and 100% of the typical concentrations in bio-oils[34]. The concentrations used for each of the compounds evaluated in this study are shown in Table 6.1.

Table 6.1.- Concentration of compounds studied (mass %)

No	Compounds	25% of CFBO[1]	50% of CFBO[1]	75% of CFBO[1]	100% of CFBO[1]
1	Acetic acid	1.43	2.86	4.30	5.73
2	Propanoic acid	0.455	0.91	1.36	1.82
3	Cyclopentanone	0.03	0.06	0.09	0.12
4	2-furaldehyde	0.08	0.16	0.25	0.33
5	Furfuryl alcohol	0.01	0.01	0.01	0.02
6	Phenol	0.14	0.28	0.42	0.57
7	Eugenol	0.12	0.25	0.38	0.51
8	Acetol	0.62	1.25	1.88	2.51
9	2-(5H)-furanone	0.01	0.01	0.02	0.03
10	Stilbene	0.03	0.06	0.09	0.12
11	Vanillin	0.36	0.73	1.09	1.46
12	Syringaldehyde	0.29	0.58	0.87	1.16
13	O-Cresol	0.01	0.01	0.01	0.02

[1]CFBO: Concentration found in bio-oils

[34] *Garcia-Perez* M, Wang S, Shen J, Rhodes MJ, Lee W-J, Li C-Z: Effects of Temperature on the Formation of Lignin Derived Oligomers during the Fast Pyrolysis of Mallee Woody Biomass. *Energy and Fuels* **2008,** 22, 2022-2032.

Cell growth was monitored spectrophotometrically by determining the optical density (OD) (at 600 nm) of the cultures in the fermentation flask at a specific time (30hr). The values of optical density (OD) were used to calculate inhibition rates compared with controls. The results obtained are shown in Table 6.2. The carboxylic acids and phenols were the most toxic compounds.

Table 6.2.- Inhibition rate estimated from the reduction in the growth of yeast obtained when some of the most important species found in bio-oil were added to the fermentation broth (mass %)

N°	Compound	25% of CFBO[1]	50% of CFBO[1]	75% of CFBO[1]	100% of CFBO[1]
1	Acetic acid	**97.75**	**97.75**	**97.96**	**98.24**
2	Propanoic acid	**97.01**	**97.54**	**97.82**	**98.00**
3	Cyclopentanone	-22.07	-5.26	-4.41	21.73
4	2-furaldehyde	7.81	7.98	11.03	95.89
5	Furfuryl alcohol	5.94	6.90	7.81	7.81
6	Phenol	**76.95**	**96.95**	**97.45**	**97.67**
7	Eugenol	**97.04**	**97.22**	**96.64**	**97.04**
8	Acetol	**44.17**	**77.80**	**78.93**	**80.07**
9	2-(5H)-Furanone	3.057	5.89	8.83	10.42
10	Stilbene	9.17	32.62	37.89	45.07
11	Vanillin	**81.54**	**82.45**	**81.77**	**81.88**
12	Syringaldehyde	**71.68**	**79.95**	**81.54**	**81.99**
13	O-cresol	2.61	14.16	23.38	31.22
14	O-xylol	5.01	5.23	5.33	5.44
15	Pyrocatechol	**84.53**	**90.48**	**91.67**	**92.10**
16	Palmitic acid	2.63	0.36	-2.02	-4.19
17	Toluene	-0.72	1.00	1.66	2.09
18	Tetradecane	1.11	4.68	10.53	10.64
19	Petadecane	4.68	7.39	8.90	9.78

[1]CFBO: Concentration found in bio-oils

The effect of each of these compounds and their concentrations on the production of ethanol was expressed in terms of inhibition rate shown in Table 6.3. These studies also confirmed that the phenols and the carboxylic acids are the main family of toxic compounds which inhibit growth of *Saccharomyces cerevisiae* cultures and therefore limit the production of ethanol. These results allow us to propose a rational approach to detoxify these oils to make possible ethanol fermentation. We are proposing a detoxification concept in which the phenols will be removed by adsorption on activated carbon and the toxic effect of acids will be mitigated by neutralization.

Table 6.3.- Inhibition rate obtained from the concentration of ethanol produced when some of the most important species found in bio-oil were added to the fermentation broth (mass %)

N°	Name	25% of CFBO[1]	50% of CFBO[1]	75% of CFBO[1]	100% of CFBO[1]
1	Stilbene	-7.21	-11.20	-44.95	-15.31
2	Acetic acid	**78.90**	**91.40**	**93.91**	**89.70**
3	Cyclopentanone	16.05	-4.32	90.76	15.17
4	Pentadecane	3.70	-15.84	7.60	-9.39
5	Phenol	11.84	91.25	96.26	97.93
6	propanoic acid	**51.15**	**77.81**	**82.66**	**93.95**
7	Acetol	**98.75**	**99.17**	**98.74**	**99.08**
8	Eugenol	**87.45**	**93.70**	**89.42**	**88.99**
9	Tetradecane	8.26	3.93	-11.86	43.49
10	Toluene	10.60	1.16	-12.33	4.17
11	palmitic acid	2.11	5.18	4.55	4.15
12	o-xylol	13.68	4.07	-3.33	-4.18
13	furfuryl alcohol	-0.07	16.01	2.14	29.75
14	2-(5H)-furanone	11.19	17.01	6.54	18.39
15	Vanillin	**98.19**	**98.72**	**99.07**	**99.16**
16	2-furaldehyde	-3.84	-12.33	3.09	35.65
17	Syringaldehyde	**78.83**	**98.30**	**98.71**	**98.41**
18	Pyrocatechol	**90.46**	**98.40**	**98.97**	**99.17**

[1]CFBO: Concentration found in bio-oils

6.2.- Hydrolysis, Detoxification and Fermentation of Pyrolytic Sugars.

A method to separate, hydrolyze, detoxify and ferment pyrolytic sugars is proposed for the first time. The method consists of the following steps:

1.- Separation of bio-oil in an aqueous phase rich in sugars and an organic phase rich in phenols.

The difference between the separation concept here in proposed and the patents reported in the literature[35] is that instead of precipitating the pyrolytic lignin with water, we proposed to extract the phenolic fractions with organic solvents (in this case ethyl acetate). This method is very similar to the one patented by NREL to separate the phenols for the production of resins[36]. The advantage of this approach over the concept patented by UOP is that the concentration of sugars

[35] Marker T.L, Petri J.A. Gasoline and diesel production from pyrolytic lignin produced from pyrolysis of lignocellulosic waste materials. USPTO Patent Application 20080053870. Agent Honewell Intelectual Property Services, Morritown NJ, US.

[36]Chum, H.L.; Black S.K.; Diebold J.P.; and Kreibich R.E. "Phenolic Compounds Containing/Neutral Fractions Extract and Products Derived Therefrom from Fractionated Fast Pyrolysis Oils," U.S. Patent 5,223,601. (1993).

in the resulting aqueous phase is still high enough to ferment. Thus, conversion to ethanol is economically viable. The results described in this section were obtained with the oil from Dynamotive and with the softwood bark obtained by fast pyrolysis at Monash University. Ethyl acetate/bio-oil ratios (g/g) of 1 were used in their extraction. The blend was shaken for 10 minutes at 30 ^{o}C and was left to equilibrate for over 6 hours.

The organic phase rich in ethyl acetate was removed. The remaining ethyl acetate soluble in the aqueous layer was removed via evaporation under vacuum at 80 ^{o}C. The resulting solution rich in sugars was used for hydrolysis.

2.- Hydrolysis and hydration of pyrolytic sugars (levoglucosan) to produce glucose.

A sample of approximately 10 grams of an aqueous phase rich in sugar was hydrolyzed using a 1 N sulfuric acid solution under reflux for 4 hours. Glucose was formed from the hydrolysis of pyrolytic sugars (chiefly levoglucosan and cellobiosan). The method used to hydrolyze the pyrolytic sugars was similar to that described by Helle et al.[37]

3.- Detoxification of aqueous solution with activated carbon followed by Neutralization with Barium hydroxide.

The hydrolyzed solution obtained in the previous step contains phenols and acetic acid which were proven to be toxic to yeast. The phenols are removed by adsorption on the surface of activated carbon. The activated carbon was added to the solution and the flask shaken and kept in the refrigerator overnight at 4 ^{o}C. The activated carbon was then separated by filtration and the resulting liquid neutralized with Barium hydroxide. The goal of this step is to neutralize the sulfuric acid and the acetic acid present in the aqueous phase which will adjust the pH of the solution from 1.3 to 6. The precipitate formed was separated from the liquid by filtration. The content of sugars in the liquid collected was quantified by Ion Exchange Chromatography. The detoxified aqueous phase rich in sugars was then fermented.

4.- Fermentation of pyrolytic sugars

The YPD media (Y: yeast extract, P peptone and D dextrose) was prepared by taking 25 ml of the solution obtained in the previous step, 2 mass % yeast extract and 1% mass peptone. 10 vol % of Saccharomyces cerevisiae seed culture media were then inoculated in the YPD media. The media was cultured at 30 ^{o}C and the micro-organism growth, sugar consumption and ethanol production was monitored. The new method proposed in this project was tested with the oil kindly provided by Dynamotive and with the fast pyrolysis bio-oil produced at Monash University using softwood bark from the state of Washington. The initial content of glucose in

[37] Helle S, Bennett N.M., Lau K., Matsui J.H., Duff S.J.B. A kinetic model fort he production of glucose by hydrolysis of levoglucosan and cellobiosan from pyrolysis oils. *Carbohydrate Research* 342 (2007) 2365-2370.

the detoxified aqueous phases from the Dynamotive oil and from the oil produced in Monash University were 2.6 and 2.0 mass % respectively. Control solutions were prepared with pure glucose. The results are shown in Figures 6.1-6.3.

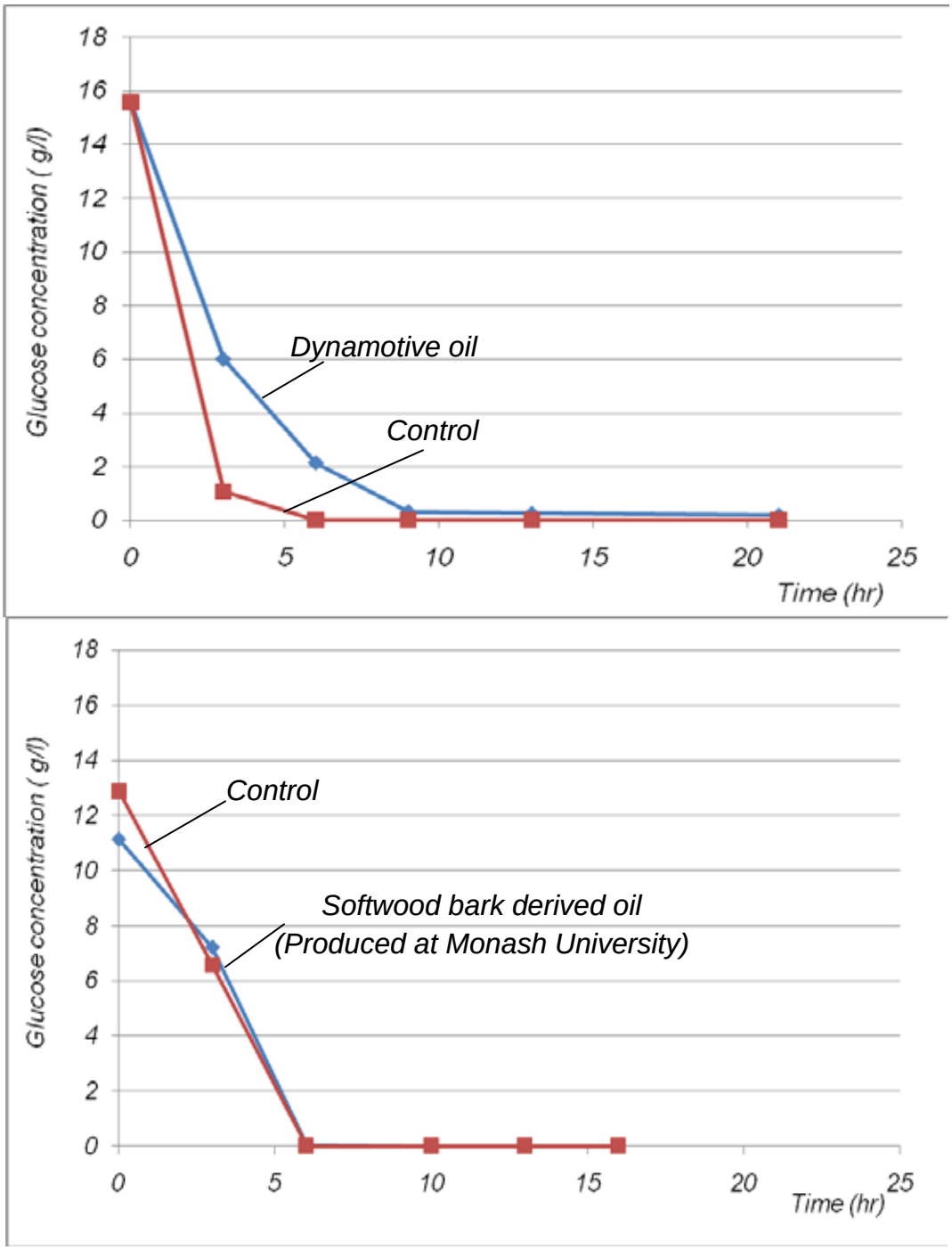

Figure 6.1.- Consumption rate of Glucose During the Fermentation of Pyrolytic sugars and the controls.

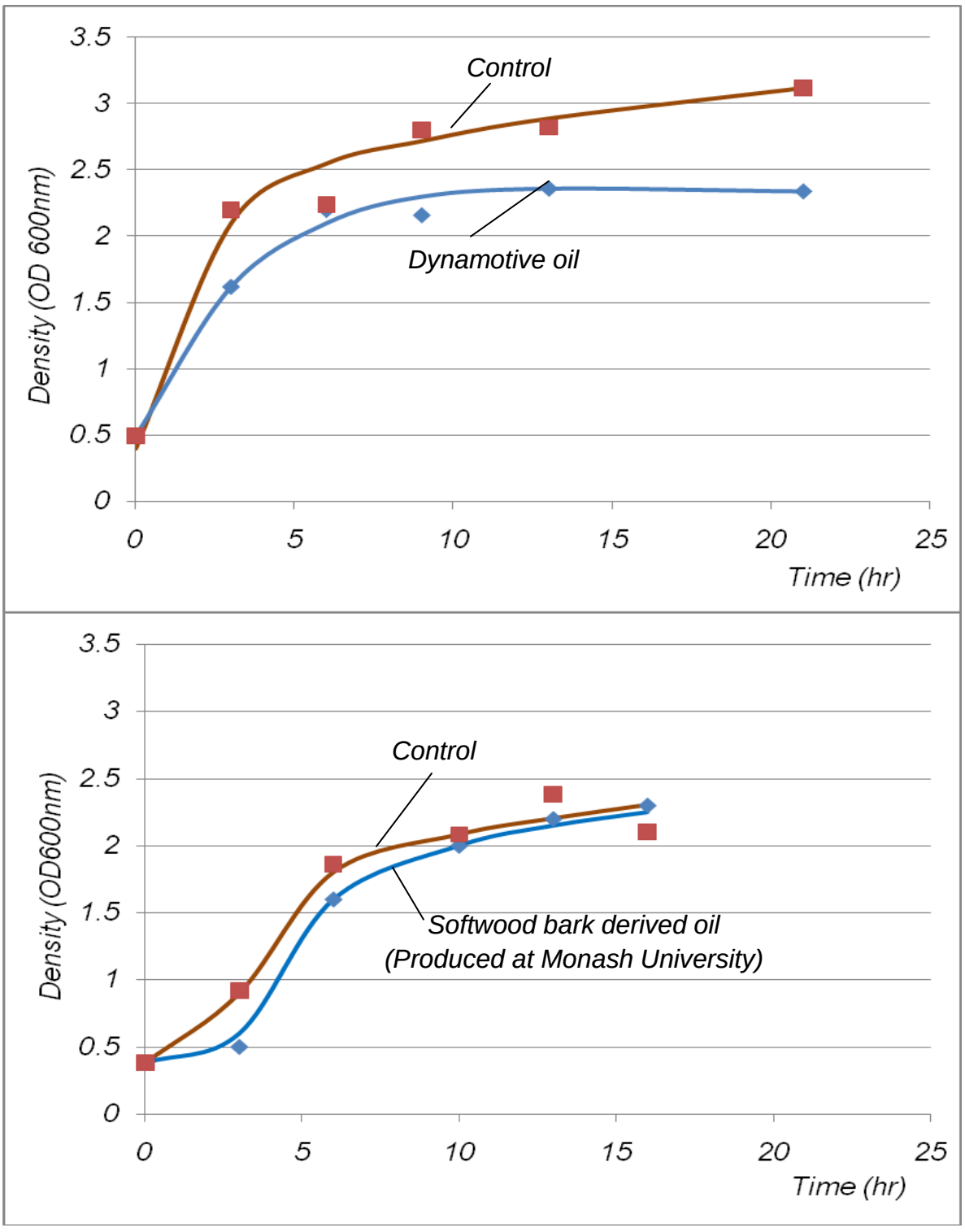

Figure 6.2.- Microbial growth during the fermentation of pyrolytic sugars and the controls.

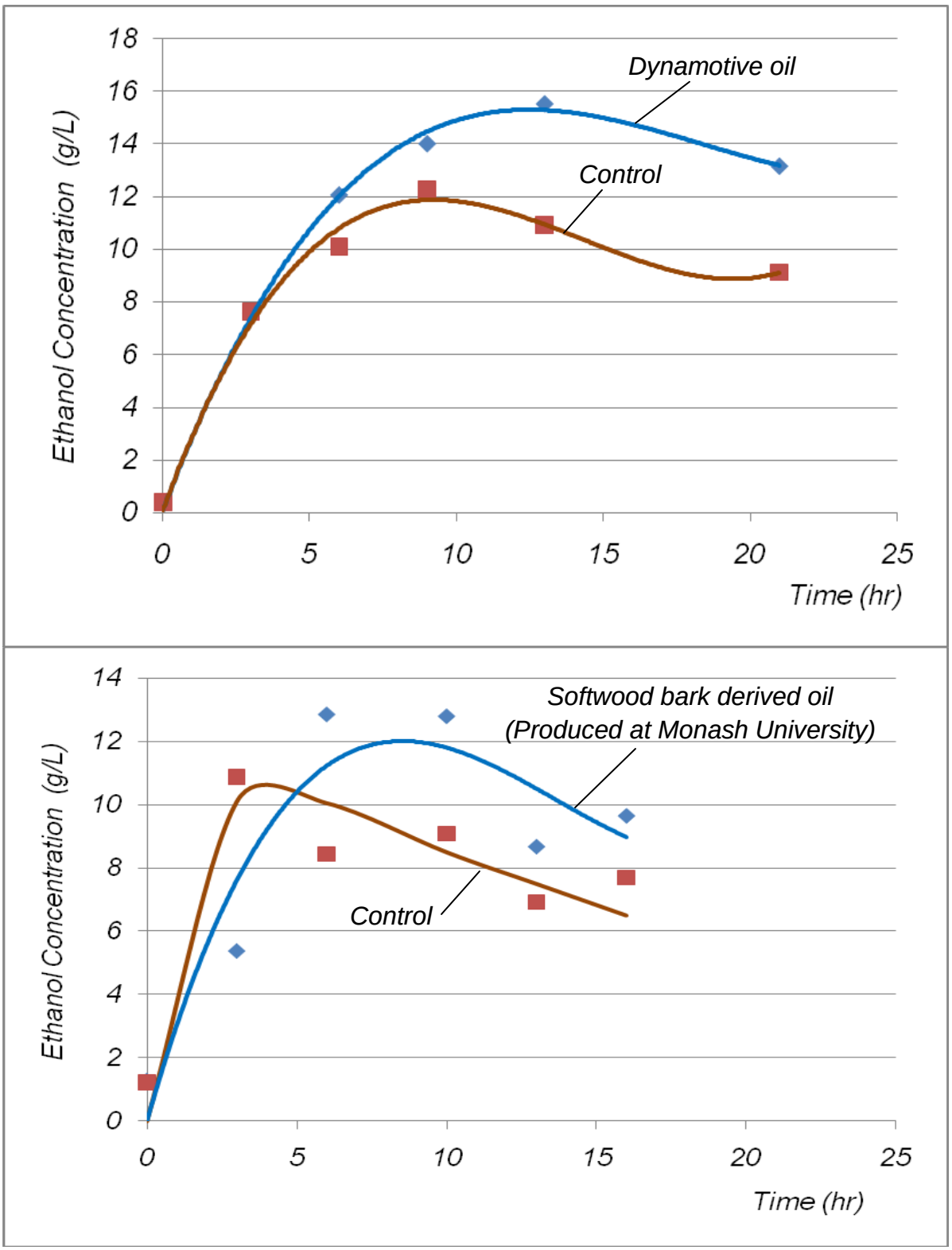

Figure 6.3.- Evolution of Ethanol concentration as a function of fermentation time.

The results obtained in this project have proven for the first time that the pyrolytic sugars resulting from the pyrolysis of lignocellulosic materials can be easily converted to ethanol in yields comparable to those obtained from pure glucose under equivalent fermentation conditions. Since current yields of sugars obtained from pyrolysis are very low, the next chapter of this report is fully devoted to develop new approaches to enhance the yields of pyrolytic sugars.

7.- Enhancing the Formation of Pyrolytic Sugars through Pretreatment

7.1.- Py-GC/MS studies to Evaluate different pretreatment strategies to enhance the formation of anhydro-sugars during biomass pyrolysis.

Although the fast pyrolysis of lignocellulosic materials and bio-oil hydrotreatment have proven to be a very good alternative to convert lignin into resins, green gasoline and green diesel, existing thermochemical technologies are not optimized to achieve high conversion of cellulose into precursors of transportation fuels. Cellulose can be converted by thermal depolymerization into anhydro-sugars however competitive fragmentation reactions result in losses of sugar yields with the consequent formation of low molecular weight compounds with little economic value. Enhancing the selectivity of thermochemical reactions toward depolymerization is critical to maximize the conversion of cellulose into fuels. This chapter will be devoted to identify the best pretreatment and pyrolysis conditions maximizing the yield of levoglucosan from softwood bark.

These studies were carried out using a CDS pyroprobe 5000 connected in-line to an Agilent GC-MS. Samples were loaded into a quartz tube and gently packed with quartz wool prior to pyrolysis. The samples were kept briefly in the oven to ensure adequate removal of oxygen prior to pyrolysis. Samples were pyrolyzed by heating nearly instantaneously to the desired final temperatures and held at this temperature for 3.0 minutes. The inlet temperature was maintained at 250^{o}C. The resulting pyrolysis vapors were separated by means of a 30m x 0.25um inner diameter (5%-phenyl)-methylpolysiloxane non-polar column, with a split ratio of 50:1. The gas flow rate was 1 ml/min and helium was the carrier gas. Linear heating (3°C/min) from 40–280°C was designated for the oven program, and to ensure that no residuals were retained, the oven was held at 280°C for 10 minutes. The gas was then sent into a mass spectrometer (Agilent Technologies Inert XL MSD). The mass spectra of predominant peaks were then compared to an NBS mass spectra library to establish which compound was predominant in a given peak. Typical mass spectrometer conditions were: transfer line 150°C, ion source 230°C, and electron energy 70 eV. The peak area values reported were calculated from the summation of the

predominant ion peaks in the mass spectrum for the given compound. Most of the studies were performed with samples subjected to hot water pretreatment at 150 ^{o}C to remove the alkalines. Three major groups of experiments were carried out:

1.- Effect of pretreatment temperature (between 200 and 300 ^{o}C) on the selectivity towards levoglucosan production.
2.- Effect of Pyrolysis temperature (between 400 and 600 ^{o}C) on the selectivity of cellulose conversion toward levoglucosan.
3.- Effect of alkaline removal in hot water on the selectivity towards levoglucosan production

To determine which pretreatment and pyrolysis conditions resulted in greater selectivity towards fragmentation reactions, the areas of levoglucosan were divided by the area of the peak associated with the most important peaks. Levoglucosan is the main product of depolymerization reactions; consequently, the ratio between the area of these peaks and the area of the peaks of compounds resulting from fragmentation reactions (e.g., hydroxyl-acetaldehyde) can be used as a good indicator of the selectivity achieved.

The results shown in Figures 7.1 and 7.2 indicate that pre-treating the softwood bark at temperatures close to 250 ^{o}C under an inert atmosphere could be a promising strategy to increase the yield of pyrolytic sugars (levoglucosan).

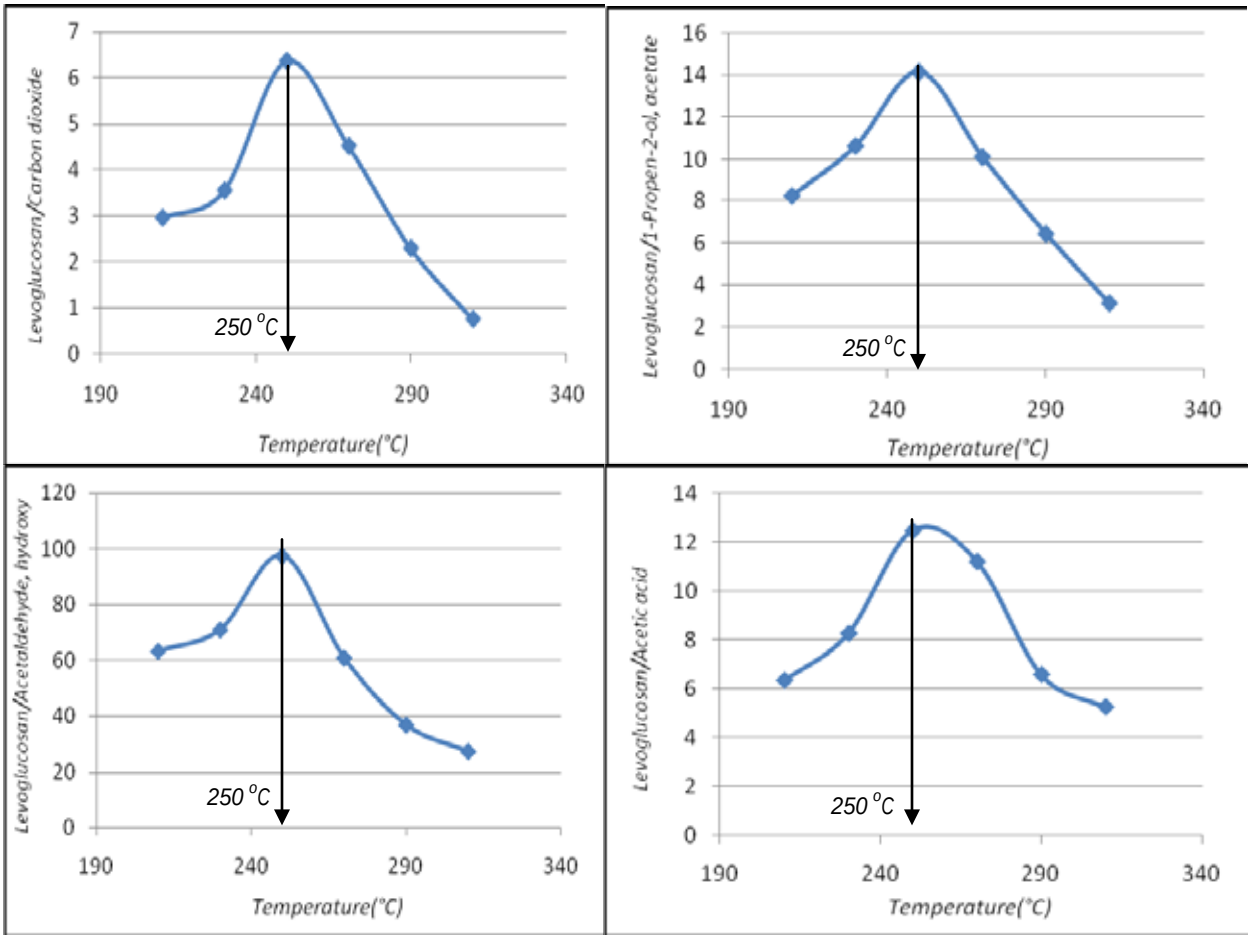

Figure 7.1.- Effect of Pretreatment Temperature on the ratio between Levoglucosan and other compounds resulting from the pyrolysis of softwood bark (Pretreatment time: 60 min, Pyrolysis temperature 500 ^{o}C, bark treated at 150 ^{o}C in hot water to remove the alkalines).

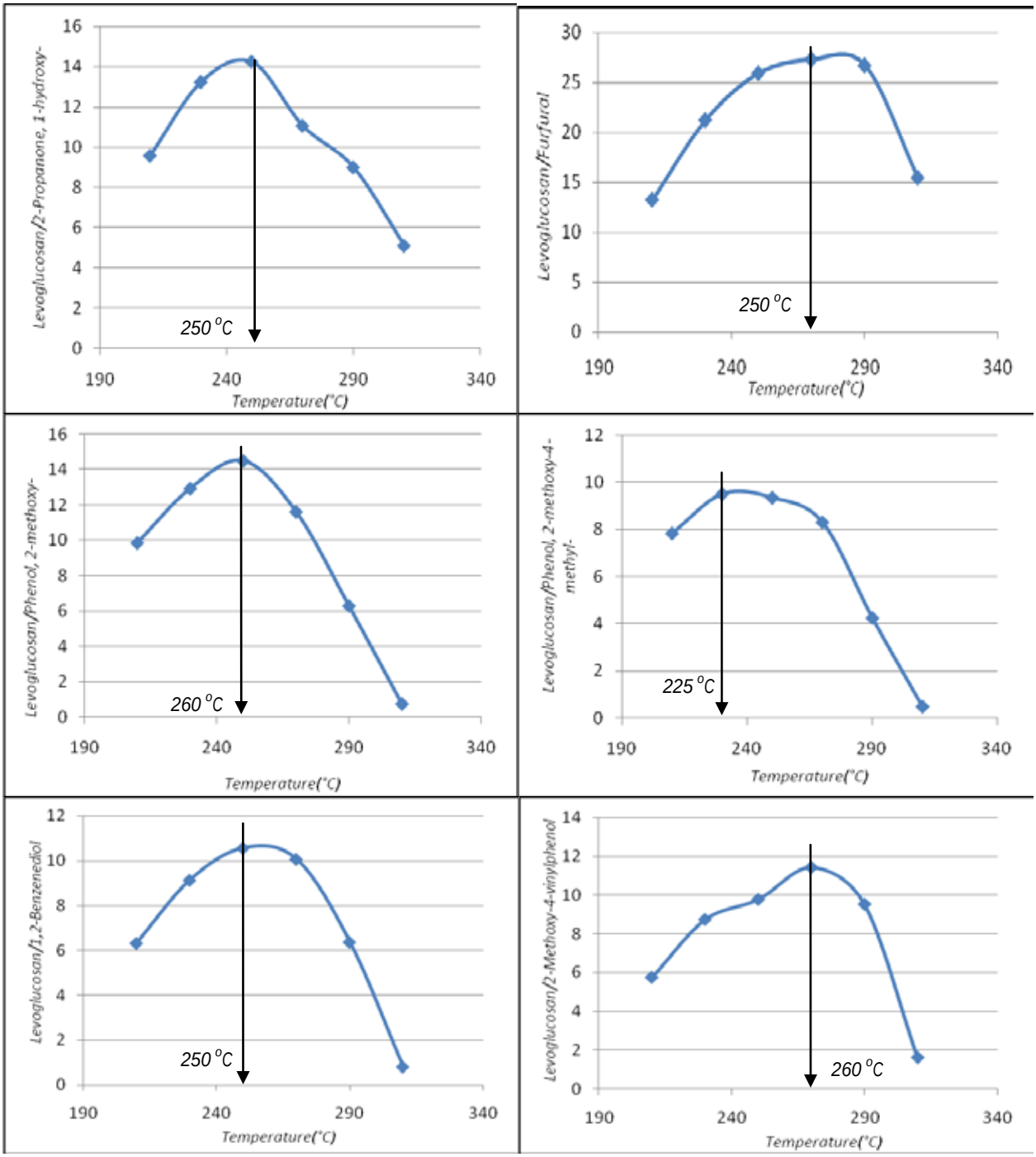

Figure 7.2.- Effect of Pretreatment Temperature on the ratio between Levoglucosan and other compounds resulting from the pyrolysis of softwood bark (pretreatment time: 60 min, pyrolysis temperature 500 °C, bark treated at 150 °C in hot water to remove the alkalines).

The existence of a maximum in the yield of levoglucosan at temperatures around 250 ^{o}C can be explained by the formation of modified cellulose (also called active cellulose) in the temperature ranges between 200 and 250°C. At temperatures over 250 ^{o}C cross linking reactions leading to the formation of charred products predominate.

Pretreatment at temperatures below 250 ^{o}C causes a breaking of hydrogen bond networks that hold the material in a rigid form. The loosened polymers then depolymerize at the disordered regions every 200–300 units. This project has established for the first time that there is a clear relationship between pretreatment conditions and the selectivity of thermochemical reactions responsible for the production of pyrolytic sugars from softwood bark. This relationship can lead to the development of new technologies to enhance the yield of anhydro-sugars from softwood bark.

Figures 7.3 and 7.4 show the dramatic reductions in the selectivity towards the production of levoglucosan when the pyrolysis temperature increases from 400 to 500 ^{o}C. Undesirable fragmentation reactions leading to the formation of levogluocosan are favored at these temperatures. These results suggest that the yields of anhydro-sugars can be maximized if the pyrolysis is carried out at temperatures close to 400 ^{o}C. It is important to point out that most of the pyrolysis units in operation today work at temperatures close to 500 ^{o}C to maximize the yields of oil. At this temperature the production of lignin derived oligomers are maximized.

Further investigations are needed to elucidate whether the losses in the yield of ethanol resulting from the fragmentation of pyrolytic sugars at temperatures over 500 ^{o}C can be compensated with the gains in the production of green gasoline and green diesel due to the increase in the yields of lignin derived oligomers.

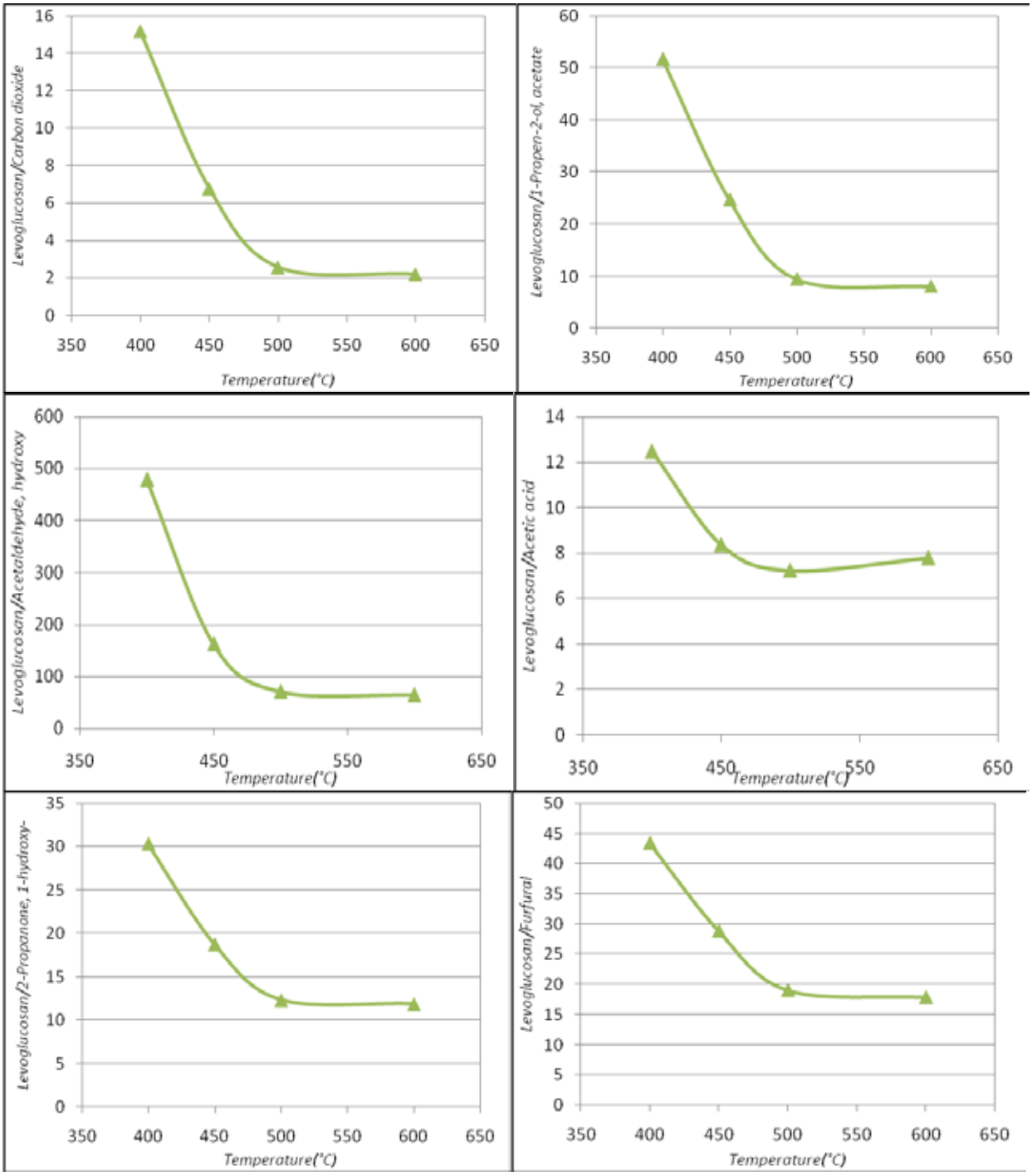

Figure 7.3.- Effect of Pyrolysis temperature (Softwood bark pretreated in hot water at 150 ^{o}C to remove the ash followed by a pretreatment at 250 ^{o}C for 20 minutes).

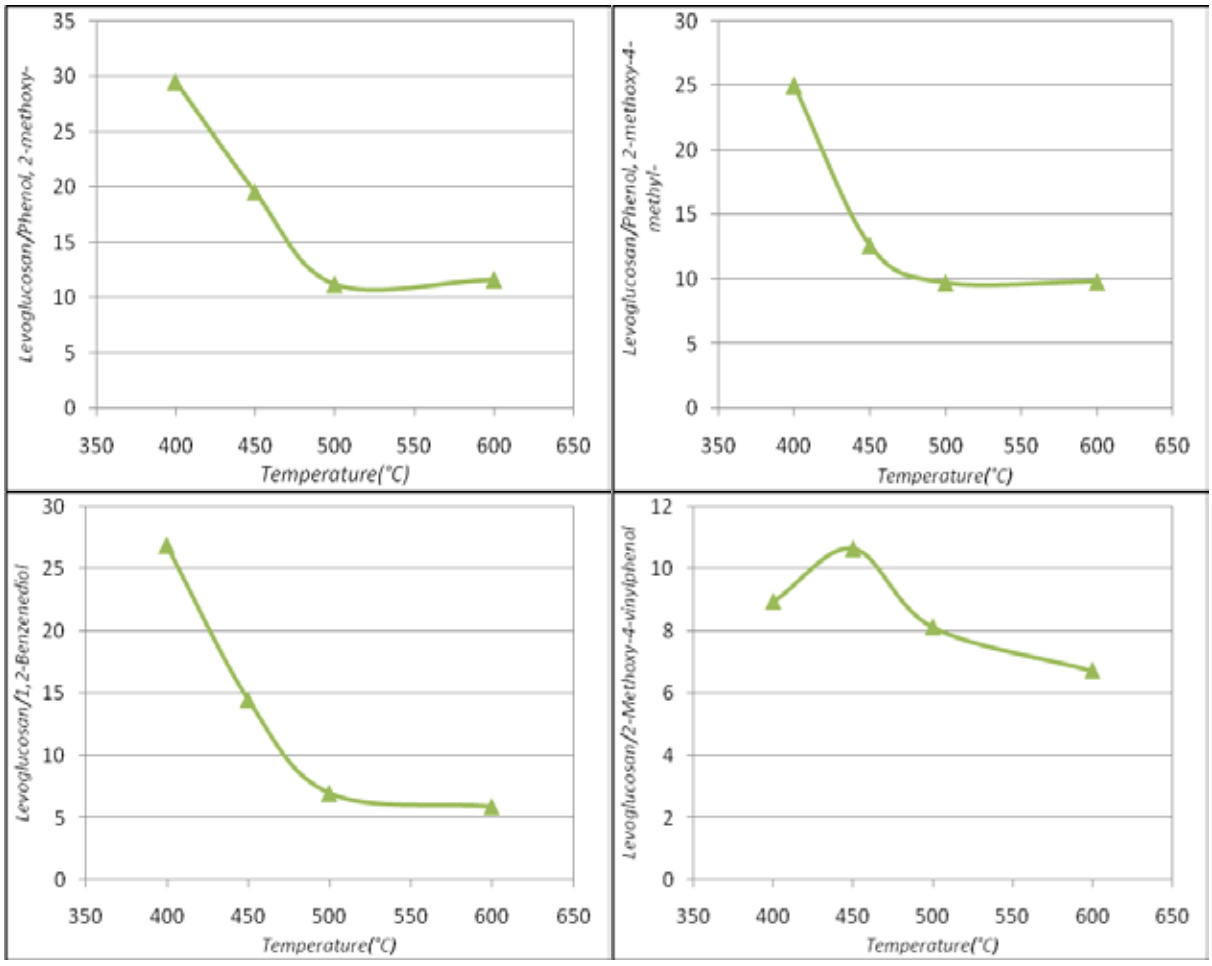

Figure 7.4.- Effect of Pyrolysis temperature (Softwood bark pretreated in hot water at 150 ^{o}C to remove the ash followed by a pretreatment at 250 ^{o}C for 20 minutes).

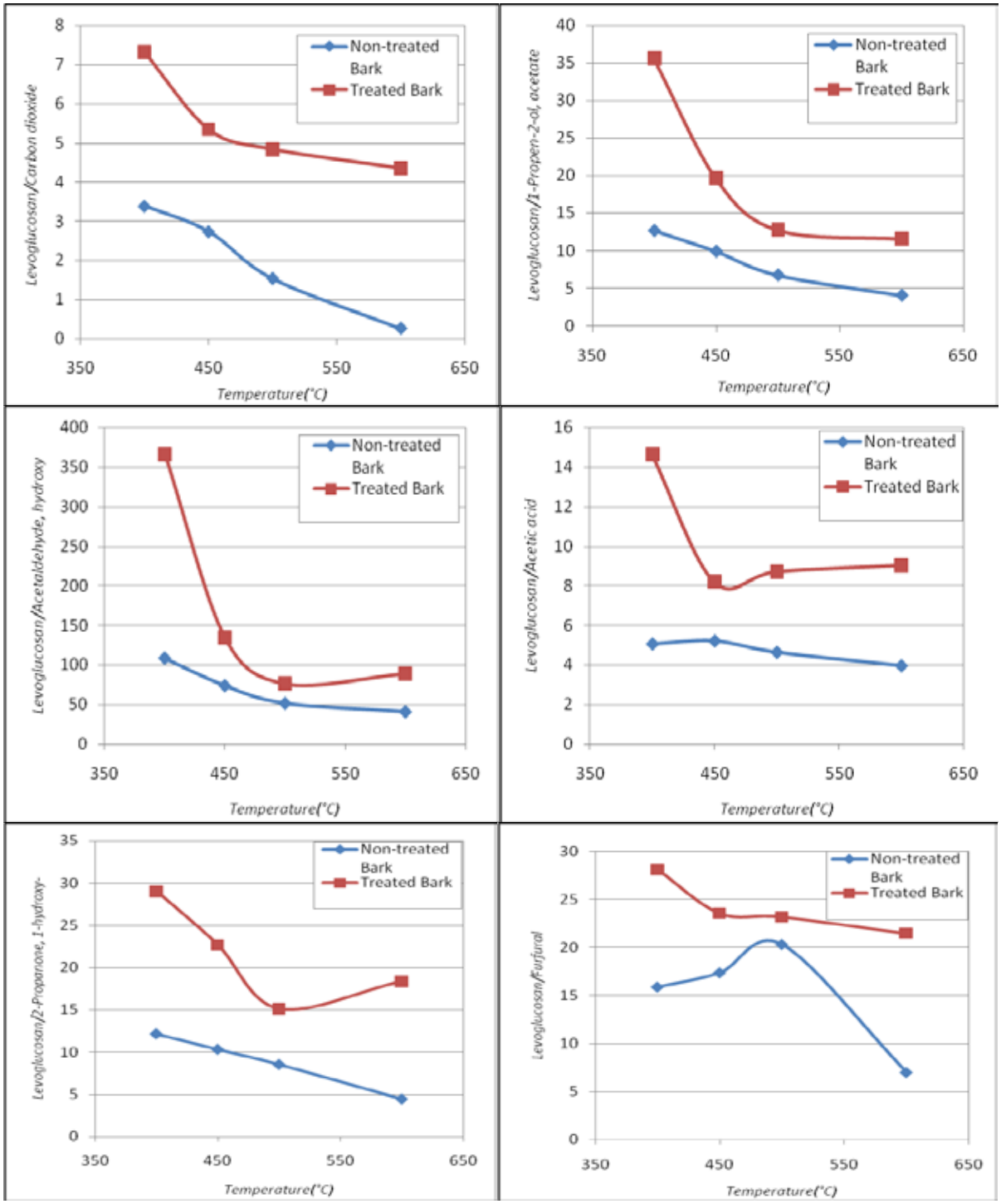

Figure 7.5.- Effect of Removing the alkalines from the softwood bark through a hot water pretreatment (150 ^{o}C in hot water) (Pretreatment conditions 210 ^{o}C, 20 min).

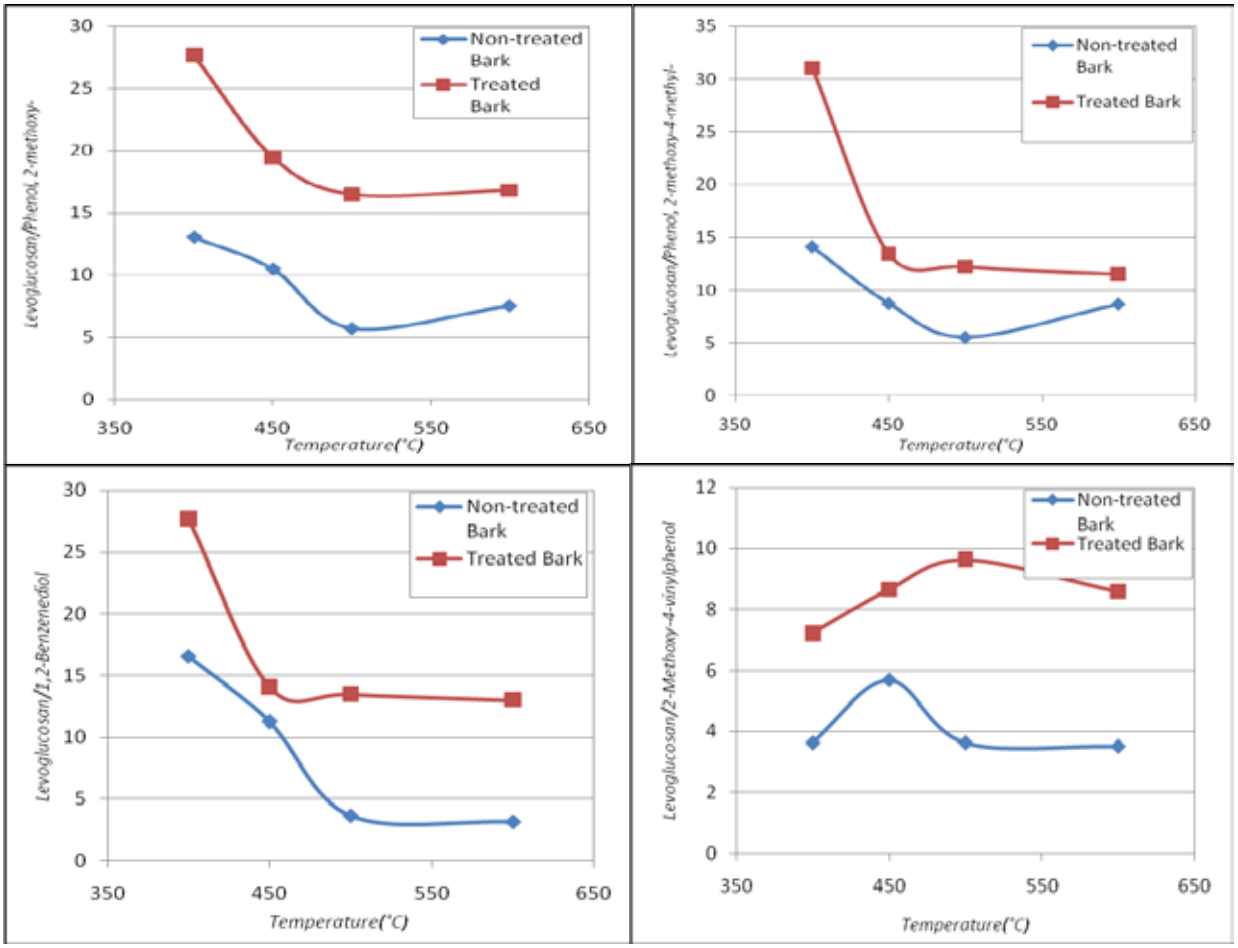

Figure 7.6.- Effect of Removing the alkalines from the softwood bark through a hot water pretreatment (150 ^{o}C in hot water) (Pretreatment conditions 210 ^{o}C, 20 min).

The results shown in Figures 7.5 and 7.6 clearly indicate the importance of removing the alkalines (chiefly Na and K) before pyrolysis. These alkalines act as catalysts of poly-condensation and fragmentation reactions, leading to the formation of extra charcoal and small molecules of little economic value.

All the experimental results obtained in this section suggest that the yields of pyrolytic sugars can be enhanced if:

1.- The softwood bark is pretreated in hot water at temperature close to 150 ^{o}C to remove the alkalines.

2.- The resulting solid is pretreated under an inert atmosphere at temperatures between 230 and 250 ^{o}C to convert the cellulose into active cellulose

3.- The pyrolysis tests are carried out at temperatures close to 400 ^{o}C.

Further studies using fast pyrolysis reactors are needed to confirm these results.

8.- Environmental Impact of Bio-char

8.1.- Introduction

WSU and the Department of Ecology both recognize the need to understand whether there is potential for toxic emissions to the environment from pyrolysis and biochar use. Therefore, it was decided to conduct a literature review on this topic and to identify if there were any references on the potential development of hazardous toxic wastes elements in the bio-char resulting from biomass pyrolysis reactions and the potential impact of these products on the environment. The review focused on the likelihood that the reactions leading to the formation of dioxins, chlorinated furans and poly-aromatic hydrocarbons occur during biomass pyrolysis in the range of temperature between 350 and 600 ^{o}C. Qualitative and Quantitative tests on bio-oil and biochar samples were carried out to prove if PAHs and dioxins were present in the char. The main goal of this chapter is to describe the results obtained in this task. This is a joint task with the project "Use of bio-char from the pyrolysis of waste organic material as a soil amendment" (Interagency agreement: No: C0800248) also funded by the Washington State Department of Ecology.

8.2.- Literature Review

Ms. Judy Metcalf and Dr. Garcia-Perez completed the literature review focusing on the potential development of hazardous or toxic elements in the char and bio-oils as the result of biomass pyrolysis reactions. The final report is available to the general public at the WSU energy program website (http://energy.wsu.edu).

It was considered convenient to add several sections to the review devoted to describing biomass composition, fast pyrolysis technologies and thermo-chemical reactions in order to create a self-contained document that could offer a more complete overview of the complex phenomena associated with the formation of these undesirable compounds.

The review started with a brief introduction describing some basic elements of biomass composition and existing pyrolysis technologies, and goes on to focus on known pathways for the formation of polyaromatic hydrocarbons (PAHs) and dioxins, their toxicity, and ways to control their production during pyrolysis. The possible relationships between the composition of the biomass, the reaction conditions and the presence of PAHs and dioxins in bio-oils and chars were discussed.

It was not possible to find any experimental evidence suggesting the presence of dioxins or chlorinated furans in pyrolysis-oil or bio-char. The main two mechanisms proposed to explain the formation of dioxins during incineration of municipal solid wastes, pyrosynthesis (or precursor mechanism) and de novo synthesis, do not apply to pyrolysis. Both mechanisms occur simultaneously and/or independently and result in the formation of compounds with unique finger prints:

(1) The pyrosynthesis (also known as precursor mechanism) supposes that the dioxins are formed by the polycondensation of precursors (e.g. polychlorophenols, polychlorobenzenes, PCBs) which are formed at temperatures around 1000 ^{o}C. This mechanism occurs in the gas phase when the precursors are quenched to temperatures between 300 and 600°C.

(2) The de novo synthesis involves the presence of carbon as the solid phase. O_2 is also essential for the de novo formation. This mechanism occurs at temperatures between 200 and 400°C.

The lack of oxygen inside pyrolysis reactors, the very low content of chlorine in the biomass and the fact that the precursors of dioxins formation should be generated at temperatures as high as 1200 ^{o}C could explain why it was not possible to find any reference on the presence of dioxins and chlorinated furans in bio-char.

Likewise, the literature does not report any evidence of leachable polyaromatic hydrocarbons (PAHs) in the bio-char produced from biomass fast pyrolysis. Very low content of PAHs (less than 10 ppm) have been reported for fast pyrolysis oils. These concentrations are one order of

magnitude lower than for slow pyrolysis oils (exceeding 100 ppm) and several orders of magnitude below those obtained for gasification tars (over 80 mass %). The PAHs identified in fast pyrolysis oils (concentration below 10 ppm) are highly branched in nature. These branched compounds are known to have lower environmental and toxicological impacts compared with the tars obtained at higher temperatures (through gasification or combustion), which tend to have more condensed structures and contain less oxygen. Conversely to biomass combustion processes where the PAHs are released to the atmosphere, the small amounts of PAHs found in bio-oils will not find their way to the environment, since these compounds will be converted to gasoline or will result in coke during bio-oil hydrotreatment in petroleum refineries.

8.3.- Qualitative Analyses

The qualitative analyses of dioxins and PHAs in bio-char were carried out using CH_2Cl_2 to extract the compounds strongly adsorbed on the bio-char surface. All the tests were carried out using 1 gram of bio-char per 30 g of CH_2Cl_2 overnight. The bio-char was removed by filtration and the resulting liquids were analyzed by an Agilent 6890 Gas Chromatographer coupled with an Inert XL mass spectrometer. 1 micro liter of the liquid was injected and the inlet temperature was maintained at 250 ^oC. A split ratio of 10:1 and a solvent delay of 5 minutes were used. The vapors were separated by means of a 30 m x 0.25 mm (film thickness) non-polar column coated with 5 % phenyl methyl-polysiloxane. 1 ml/min of helium was used as carrier gas. The chromatography column was heated from 40 to 280 ^oC at a heating rate of 3 ^oC / min and held at the final temperature for 10 minutes. Typical conditions used in the mass spectrometer are the following: line transfer temperature 150 ^oC, ion source 230 ^oC, electron energy 70 eV. The chromatograms obtained (see appendix 1) confirm that concentrations of leachable PAHs and dioxins in the CH_2Cl_2 solution are below 10 ppm (limit of detection of our GC/MS).

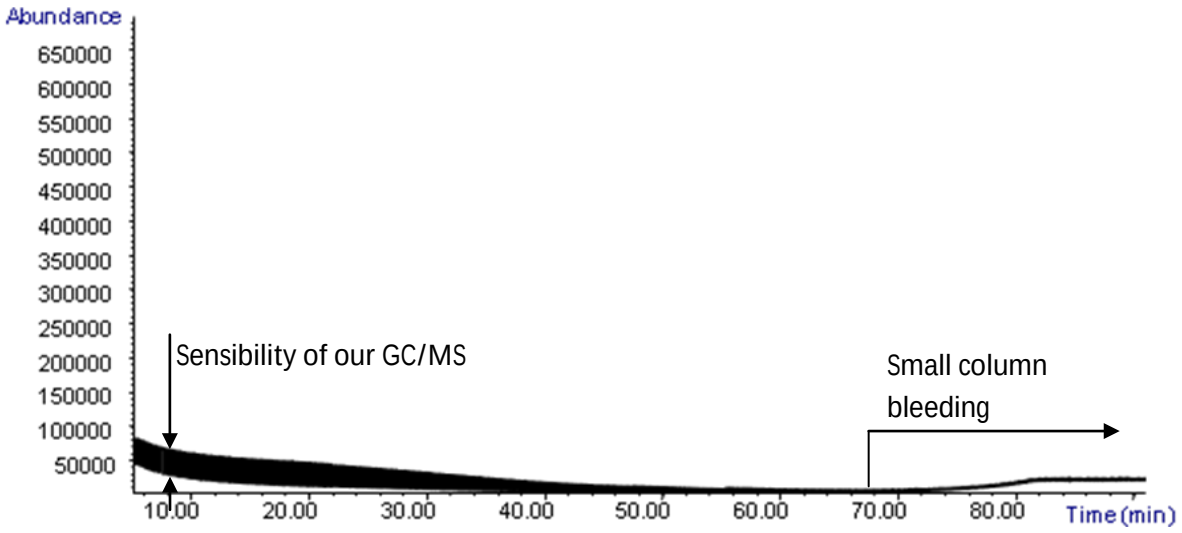

Figure 8.1.- Total Ion Chromatogram of CH_2Cl_2 solutions resulting from the extraction of bark derived bio-chars produced in this project (Pyrolysis temperature 500 ^oC).

A limited bleeding of the column was observed at residences times over 70 min. For any practical purpose our preliminary qualitative results suggested that the bio-char produced in our laboratories from softwood bark, switchgrass, digested fiber and pine pellets (in the batch pyrolysis reactor) at temperatures between 350 and 600 ^oC do not contain leachable PAHs and dioxins detectable by GC/MS.

8.4.- Quantitative Analyses

It was decided to send bio-char and bio-oil samples to a certified analytical lab (Summit Environmental Lab (Cuyahoga Falls, OH)) to confirm the results obtained in our qualitative analyses. The analyses of dioxins and PAHs were carried out following the methods 8290 and 8270 respectively.

Dioxins and Furans

Six bio-char samples were analyzed for Dioxins and Furans (Method 8290). The samples were named as: **Sample 1** (Bio-char from Softwood bark, 500 ^{o}C), **Sample 2** (Bio-char from Pine Pellets, 500 ^{o}C), **Sample 3** (Bio-char from Digested Fiber, 500 ^{o}C), **Sample 4** (Bio-char from Switchgrass, 500 ^{o}C), **Sample 5** (Water soluble fraction of bio-oil from softwood bark, 500 ^{o}C) and **Sample 6** (Oily phase of bio-oil from softwood bark, 500 ^{o}C).

The results shown in Table 8.1 confirmed our qualitative analyses. The content of dioxins and furans in the bio-chars produced in this study were extremely low. Although the aqueous phase from Softwood bark contains measurable contents of OCDD, these small concentrations cannot be considered as environmental hazards because the aqueous phase will not be applied to soils. This phase will be further processed to produce transportation fuels.

Summit Environmental Laboratory was able to detect the presence of 1,2,3,4,6,7,8-HpCDD and OCDD in several of the bio-char produced but in all cases the concentration was below the calibration limits. It was decided to evaluate the toxicity and carcinogenic risk for the mixtures of Dioxins and Furans following the procedure recommended by the Washington Department of Ecology considering that the actual concentration of these two dioxins/furans was equal to the calibration limit reported by the lab. This is a very conservative approach but allowed us to obtain an estimate of the health risks posed by dioxins and chlorinated furans in these charcoals.

TEF methodology proposed by EPA and recommended by the Washington Department of Ecology was use to evaluate the toxicity and assess the risks associated with exposure to dioxin and furan mixtures. The mathematical expression to determine the toxicity equivalent concentration is provided below:

$$\text{Total Toxicity Equivalent Concentration (TTEC)} = \sum C_n \cdot TEF_n$$

The Department of Ecology suggests that when establishing and determining compliance with cleanup levels and remediation levels the mixtures of CDDs and CDFs shall be considered as a single substance. For mixtures of dioxins/furans the reference chemical is **2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD).** It is the most toxic and best studied of the 210 CDDs and CDFs. The values of TEF are 0.0001 for the OCDD and 0.01 for the 1,2,3,4,6,7,8-HpCDD. In our calculations we will suppose the calibration limit for OCDD as 99.9 ng/kg and the calibration limit for 1,2,3,4,6,7,8-HpCDD as 50 ng/kg. The total Toxicity Equivalent Concentration (TTEC) for these bio-chars will be: **0.51 ng/kg**.

Table 8.1.- Content of dioxins and Furans (Method 8290)

Parameter	Range of Calibration Limit (ng/kg)	Sample (ng/kg)					
		1	**2**	**3**	**4**	**5**	**6**
2,3,7,8-TCDF	0.47-1.1	ND	ND	ND	ND	ND	ND
1,2,3,7,8-PeCDF	0.59-1.5	ND	ND	ND	ND	ND	ND
2,3,4,7,8-PeCDF	0.47-1.2	ND	ND	ND	ND	ND	ND
1,2,3,4,7,8-HxCDF	0.27-0.64	ND	ND	ND	ND	ND	ND
1,2,3,6,7,8-HxCDF	0.24-0.51	ND	ND	ND	ND	ND	ND
2,3,4,6,7,8-HxCDF	0.25-0.59	ND	ND	ND	ND	ND	ND
1,2,3,7,8,9-HxCDF	0.27-0.62	ND	ND	ND	ND	ND	ND
1,2,3,4,6,7,8-HpCDF	0.33-0.72	ND	ND	ND	ND	ND	ND
1,2,3,4,7,8,9-HpCDF	0.42-0.9	ND	ND	ND	ND	ND	ND
OCDF	0.81-1.5	ND	ND	ND	ND	ND	ND
2,3,7,8-TCDD	0.52-1.2	ND	ND	ND	ND	ND	ND
1,2,3,7,8-PeCDD	0.47-1.8	ND	ND	ND	ND	ND	ND
1,2,3,4,7,8-HxCDD	0.41-1.0	ND	ND	ND	ND	ND	ND
1,2,3,6,7,8-HxCDD	0.57-1.4	ND	ND	ND	ND	ND	ND
1,2,3,7,8,9-HxCDD	0.46-1.1	ND	ND	ND	ND	ND	ND
1,2,3,4,6,7,8-HpCDD	0.54-50.0	ND	ND	ND	6.79J (SSCL-50.0)	6.21J (SSCL-30.3)	6.49J (SSCL-33.2)
OCDD	1.4-99.9	ND	15.38J (SSCL-65.6)	14.53 J (SSCL-94.5)	21.64J (SSCL-99.9)	**61.61 (SSCL-60.6)**	30.8J (SSCL-66.4)
Total TCDF	2.4-4.0	ND	ND	ND	ND	ND	ND
Total TCDD	2.4-4.0	ND	ND	ND	ND	ND	ND
Total PeCDF	3.0-5.0	ND	ND	ND	ND	ND	ND
Total PeCDD	3.0-5.0	ND	ND	ND	ND	ND	ND
Total HxCDF	3.0- 5.0	ND	ND	ND	ND	ND	ND

J means: Conc. < Calibration Range; ND not detected, SSCL-Sample Specific Calibration Limit.

According to the data available at the Cleanup Level and Risk Calculation (CLARC) website (https://fortress.wa.gov/ecy/clarc/CLARCHome.aspx), the 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) equivalents permissible for unrestricted soil use (method B) is 1.1E-5 mg/kg (**11**

ng/kg). For protection of ground water it is **2.9 ng/kg** and for wildlife it is **2 ng/kg**. We can conclude that the TTEC for the bio-chars studied are several times lower than the required cleanup levels. If we take into account that the bio-char will be added to soils in a range of 1-10 mass %, then TTEC levels will be even smaller: (**0.0051-0.051 ng/kg**). We can conclude that the small content of furans and dioxins that could be present in the bio-chars produced by this study will not represent a hazard when this material is used as a soil amendment. It clearly meets the cleanup standards for dioxins /furans established by the state of Washington.

Polyaromatic Hydrocarbons

Ten bio-char samples were analyzed for PAHs. The samples were named as: **Sample 7** (Bio-char from Softwood bark, 350 ^{o}C), **Sample 8** (Bio-char from Softwood bark, 425 ^{o}C), **Sample 9** (Bio-char from Softwood bark, 500 ^{o}C), **Sample 10** (Bio-char from Softwood bark, 600 ^{o}C), **Sample 11** (Bio-char from Pine Pellets, 350 ^{o}C), **Sample 12** (Bio-char from Pine Pellets, 600 ^{o}C), **Sample 13** (Bio-char from Grass, 350 ^{o}C), **Sample 14** (Bio-char from Grass, 600 ^{o}C), **Sample 15** (Bio-char from Digested Fiber, 350 ^{o}C), and **Sample 16** (Bio-char from Digested Fiber, 600 ^{o}C).The results obtained are shown in Table 2.2.

The only PAH detected was phenanthrene (between 0.5 and 4.3 ppm). The toxicity and risk assessment of this compound was carried out also using the toxicity equivalent factor (TEF) developed by the Environmental Protection agency and recommended by the Washington State Department of Ecology. When establishing and determining compliance with cleanup levels and remediation levels for mixtures of carcinogenic polyaromatic hydrocarbons under the Model Toxics Control Act Cleanup Regulation (WAC 173-340-708 (8)(e)), Ecology advises the mixture to be considered as a single hazardous substance. This means that a target cancer risk level of one in one million (10^{-6}) is used when calculating cleanup levels under Method B. (https://fortress.wa.gov/ecy/clarc/ CLARCHome.aspx). For mixtures of cPAHs the reference is **benzo(a)pyrene**. Benzo(a)pyrene was chosen as the reference chemical because its toxicity is well characterized. The toxicity equivalent factor for each cPAHs is an estimate of the relative toxicity of the cPAH compound compared to benzo(a)pyrene. Although phenanthrene is not

listed as one of the PAH required by the state of Washington (WAC 173-340-708 (e)), we decided to include phenanthrene in our assessment because Ecology suggests taking into account this compound if it is found in the material studied (Table 708-3-MTCA Rule adopted 2007).

Table 8.2.- Content of leachable PHAs (Method 8270)

Parameter	Reported Limit (mg/kg)	Sample (mg/kg)									
		7	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
Acenaphthylene	0.21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acenaphthene	0.21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Anthracene	0.21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(a)anthracene	0.15-0.16	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(a)pyrene	0.052	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(b)fluoranthene	0.21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(ghi)perylene	0.21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(k)fluoranthene	0.21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chrysene	0.21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibenzo(a,h)anthracene	0.052	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Fluorene	0.21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Fluoranthene	0.21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Indo(1,2,3-cd)pyrene	0.15-0.16	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Naphthalene	0.21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Phenanthrene	0.21	**4.3**	**0.8**	**3.3**	**1.5**	**0.6**	**0.5**	**3.0**	**3.6**	**3.4**	**1.7**
Pyrene	0.21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Methylnaphthalene	0.21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1-Methylnaphthalene	0.21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Chloronaphthalene	0.21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbazole	0.21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Phenanthrene, 3,6dimethyl	TIC	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Retene	TIC	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Perylene	TIC	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
C3-Phenanthrenes/Anthracenes	0.21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
C4-Phenanthrenes/Anthracenes	0.21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
C1-Fluororanthene/Pyrene	0.21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

It was not possible to find the cancer potency-equivalent factor for the phenanthrene at the Department of Ecology web site. The value used for our analyses (TEF = 0.001) was obtained from the paper of Chalbot et al[38].Considering the concentration of phenanthrene in bio-char to be as high as (4.3 ppm), the Total Toxicity Equivalent Concentration (TTEC) will be 0.0043 ppm. According to the data available at the cleanup level and Risk Calculation (CLARC) website (https://fortress.wa.gov/ecy/clarc/CLARCHome.aspx), the level of benzo(a)pyrene equivalents

[38] Chalbot M-C, Vei I, Lykoudis S, Kavouras I.G: Particulate polycyclic aromatic hydrocarbons and n-alkanes in recycled paper processing operations. Journal of Hazardous Materials A137 (2006) 742-751.

permissible for unrestricted soil use (method B) is **0.14 mg/kg** (ppm). Levels of **2.33 mg/kg** are required for protection of groundwater and **12 mg/kg** for wildfire. We can conclude that the TTEC for the levels of phenanthrene measured in bio-char (**0.0043 ppm**) is 32 times lower than the required cleanup levels for benzo(a)pyrene. If we take into account that the bio-char will be added to soils in a range of 1-10 mass %, then TTEC levels will be 100 to 10 times smaller: (**0.000043-0.00043 ppm**). Using bio-char as a soil amendment does not represent a hazard. It clearly meets the cleanup standards for cPHAs established by the state of Washington.

8.5.- Conclusions

The literature review conducted by our team supports the view that available data indicate no human health or environmental hazards from bio-char, with the caveat that the literature on the subject is not expansive. The results of this study together with the literature review conducted suggest that under the pyrolysis conditions studied it is possible to produce bio-chars with concentrations of PAHs and dioxins/furans several times lower than current clean up levels required by the Washington State Department of Ecology. Since our conclusions are based on a reduced number of samples (5 samples for dioxins/ furans and 10 samples for PAHs), readers are advised not to generalize these results to other feedstocks and pyrolysis reactors. Additional studies of bio-char produced with other technologies and feedstocks are needed to confirm our findings. Although we do not have any evidence suggesting the existence of other families of pollutants in biomass derived bio-chars, extending our studies to other groups of compounds (for example, heavy metals) is recommended to ensure that the use of bio-char as soil amendments will not create human health concerns or harm the environment. We recommend that all pyrolysis and biochar studies including commercial scale production activities include assessment of human health risk from toxic organic compounds created during pyrolysis and metals concentrated in pyrolytic reduction of the biomass.

9. - Conclusions

9.1. - Overall Conclusions

This project proves the technical viability of a new bio-refinery concept to convert softwood bark generated in the state of Washington into transportation fuels. A new Auger pyrolysis reactor and new analytical capabilities to characterize bio-oils were developed for this project, and are now fully operational at WSU. Having a new thermochemical laboratory in the state of Washington is critical to develop new technologies to produce high value added products from the waste materials available in our state.

Washington State generates over 14.2 million tons of woody biomass annually. The fast pyrolysis of 75 % of all the unutilized lignocellulosic materials available in the state could yield 5.4 million tons of crude bio-oils every year. This value is similar to the capacity of an average petroleum refinery. Bio-oil refineries based on hydrotreatment (which are currently being developed by the US Department of Energy and by the petroleum industry) could convert up to 40 mass % of the whole bio-oil into green gasoline and green diesel. Using this technology the state has a potential to produce 2.2 million tons of green gasoline and green diesel annually. This represents 15 % of the current consumption of transportation fuels in Washington State. It is noteworthy that although these refineries are very efficient at converting lignin derived compounds into green gasoline and green diesel, they do not make good use of the pyrolytic sugars. In fact, there is evidence suggesting that the pyrolytic sugars are responsible for an important part of the severe coking problems and fast deactivation of catalysts observed during hydrotreatment. This project proves for the first time that it is possible to convert the pyrolytic sugars from bio-oil into ethanol.

The concept proposed consists on the separation of phenolics from sugars using solvent extraction and the further conversion of these sugars into ethanol. We found that it is possible to use ethyl acetate and its blends with bio-diesel to separate fast pyrolysis oils into an aqueous phase rich in sugars and an organic phase rich in phenols. For the first time, the pyrolytic sugars

from bio-oils were hydrolyzed, detoxified and fermented to produce ethanol. The yield of ethanol obtained from these pyrolytic sugars was comparable to those obtained with glucose. Additional bench scale studies are needed to generate more data for the scale up and the full economic evaluation of this technology.

Our Py-GC/MS results suggest that the yield of pyrolytic sugars (levoglucosan) from lignocellulosic materials can be enhanced if the biomass is pretreated to remove the alkalines and the structure of cellulose is conveniently modified at temperatures close to 250 ^{o}C. Moreover, our studies also found that reducing the pyrolysis temperature from 500 to 400 ^{o}C will drastically increase the yield of pyrolytic sugars (levoglucosan). It is important to remember that most fast pyrolysis reactors do not pre-treat the biomass and operate at temperatures close to 500 ^{o}C. Under these conditions, the conversions of cellulose to pyrolytic sugars are very low (typically around 20 mass %). We believe that the thermal pretreatment concept proposed here could result in yields of sugar similar to those reported by sulfuric acid pretreatment[39, 40](59 to 80 mass % of cellulose). If this proves to be the case, then it may be possible to dramatically increase the yields of transportation fuels from bio-oils from 40 mass % to perhaps over 50 mass %. More extensive pretreatment and pyrolysis studies at bench scale are needed to produce enough bio-oil to estimate the actual increase in sugars yields obtained with the pretreatment proposed. The development of new methods to enhance the production and uses of pyrolytic sugars warrants further investigation.

Our literature review on the formation of polyaromatic hydrocarbons (PHAs) and dioxins during pyrolysis and the experimental results obtained by a certified analytical lab on our charcoals suggest that bio-char addition to soils is a safe practice and that the levels of dioxins and polyaromatic hydrocarbons measured are well below the current environmental specifications of Washington State. More extensive studies are needed to confirm our results.

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[39] Shadezadeh F, Stevenson TT: Saccharification of Douglas Fir Wood by Combination of prehydrolysis and Pyrolysis. Journal of Applied Polymer Science, Vol. 27, 4577-4585 (1982)

[40] Radlein D, Piskorz J, Grinshpun A, Scott DS: Fast Pyrolysis of pretreated wood and cellulose. American Chemical Society, Division of Fuel Chemistry, v. 32, n 2., 1987, p. 29-35.

9.2.- Technical Conclusions

In addition to the general conclusions mentioned in the previous section, the following more specific technical conclusions also resulted from this project:

1.- The chemical composition of softwood bark is not ideal for the production of ethanol. Bark has low content of cellulose and high contents of ash and cork. Still the conversion of these materials to fuels and chemicals is technically viable.

2.- Among the technologies studied in this project, fast pyrolysis resulted in the highest yield of bio-oils.

3.- In order to maximize the yields of pyrolytic sugars from bark it is necessary: a) to remove the alkalines, b) to convert the cellulose into active cellulose in a pretreatment step at around 250 ^{o}C, and c) to reduce the pyrolysis temperatures from 500 ^{o}C to around 400 ^{o}C. This topic warrants further investigation.

4.- The extraction of bio-oils with ethyl acetate/bio-diesel blends is a viable approach to obtain an organic fraction rich in phenols and an aqueous phase rich in sugars; however, the distribution coefficients obtained with these solvents were generally low. New investigations are needed to evaluate the potential of other solvents to achieve higher distribution coefficients.

5.- The acetic acid present in the phenol rich organic phase is responsible for the low pH and corrosiveness of this phase and can be removed by extraction with $NaHCO_3$ or by esterification with Isoamyl alcohol in the presence of acid catalysis. The mono-phenols can be further recovered by distillation.

6.- Although the idea of converting pyrolytic sugars to ethanol was proposed a while ago by other investigators, this is the first time that this concept has been proven experimentally. We can confirm that it is possible to convert the pyrolytic sugars from bio-oils into ethanol. The method proposed consists on the hydrolysis of pyrolytic sugars, followed by detoxification with activated carbon, a neutralization step and a typical fermentation step with yeasts.

7.- The literature review on the formation of polyaromatic hydrocarbons (PHAs) and dioxins during pyrolysis and our experimental results confirm that the concentration of these

pollutants in biochar is lower than the clean up limits established by the Washington State Department of Ecology.

Overall, we can state that this project allowed us to study at laboratory scale several key components of a bio-refinery concept to convert softwood bark into transportation fuels. Our results confirm that the yields of pyrolytic sugars can be enhanced if the alkalines are removed, the biomass is pretreated at temperatures close to 250 ^{o}C, and the pyrolysis tests are carried out at temperatures close to 400 ^{o}C. This study proves that the conversion of pyrolytic sugars to ethanol is technically viable. Implementing these results will contribute to the enhanced overall conversion of lignocellulosic materials, readily available in our state, into transportation fuels. We believe that enhancing the production of pyrolytic sugars during pyrolysis and further converting this fraction into ethanol while converting the phenols into green gasoline and green diesel could result in overall bio-oil conversions to transportation fuels (green gasoline equivalents) close to 50 mass % (current refinery concepts evaluated by the US Department of Energy can convert up to 40 mass % of bio-oil into transportation fuels).This means that the yield of transportation fuels that could be obtained by this technology utilizing 75% of the available woody biomass in the state represents 21 mass % of the current consumption of transportation fuels in our state. Additional studies are needed to optimize and scale up the concept proposed.

Appendix A: Total ion chromatograph for all the liquids resulting from the CH_2Cl_2 extraction of produced bio-chars.

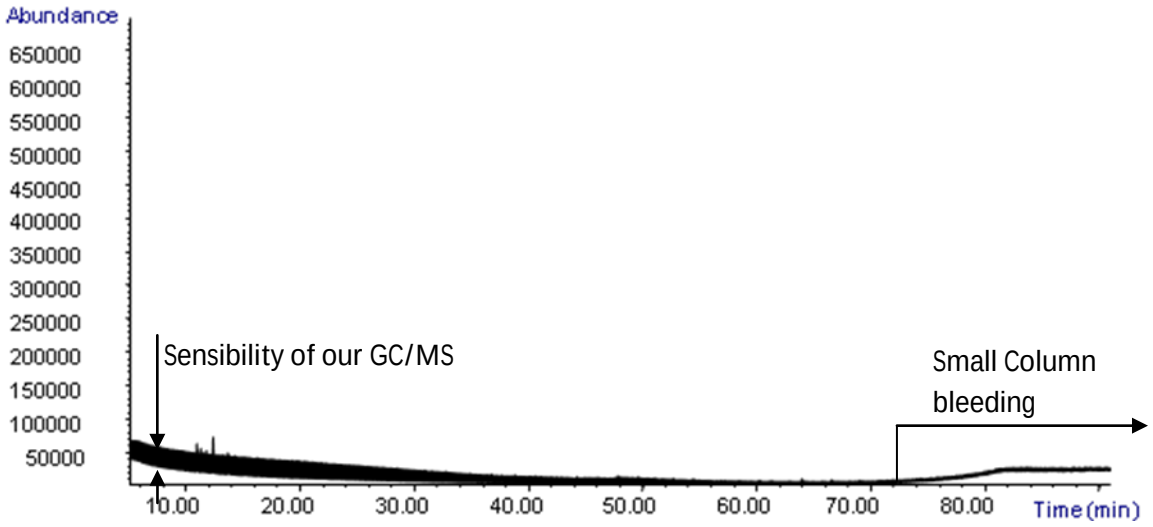

Figure A1.- Bark derived Bio-char (Pyrolysis Temperature 350 ^{o}C)

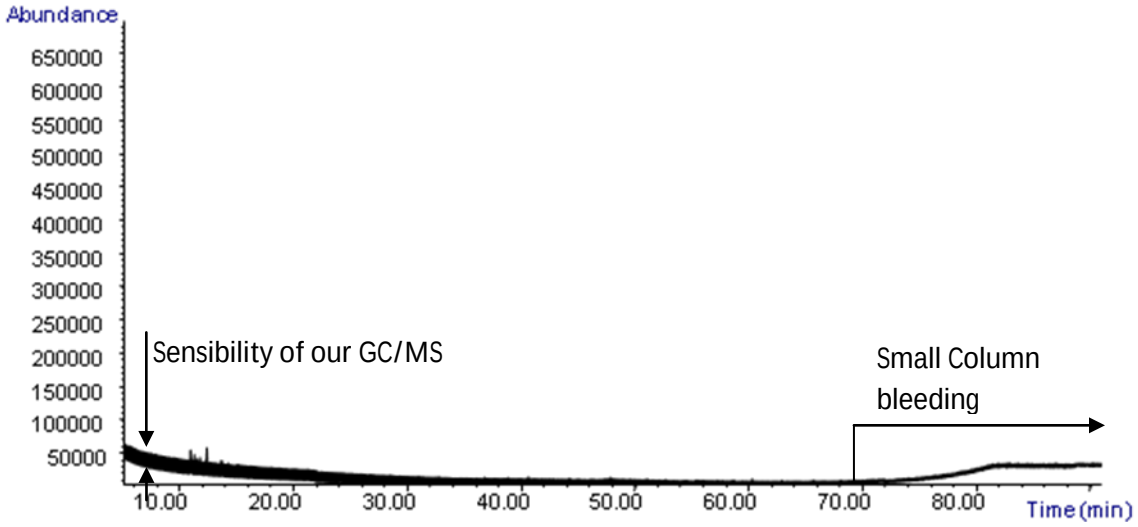

Figure A2.- Bark derived Bio-char (Pyrolysis Temperature 425 ^{o}C).

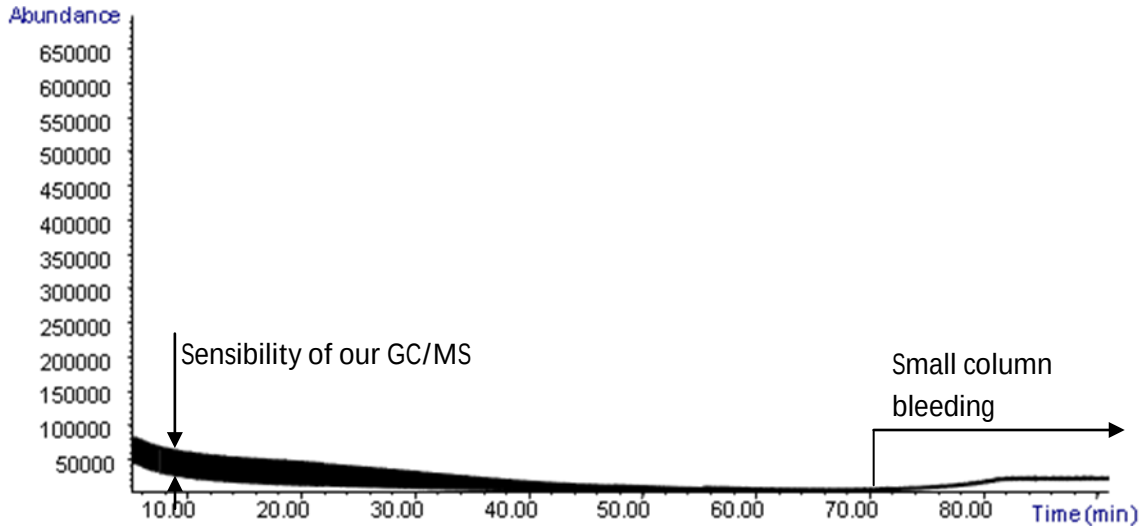

Figure A3.- Bark derived Bio-char (Pyrolysis Temperature 500 ^{o}C).

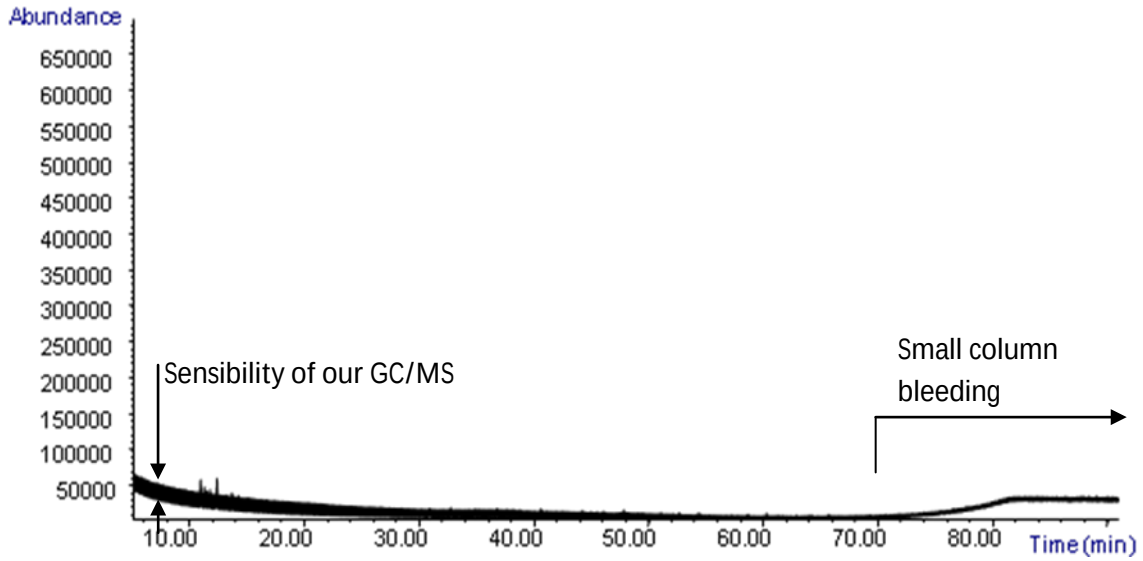

Figure A4.- Bark derived Bio-char (Pyrolysis temperature 600 ^{o}C).

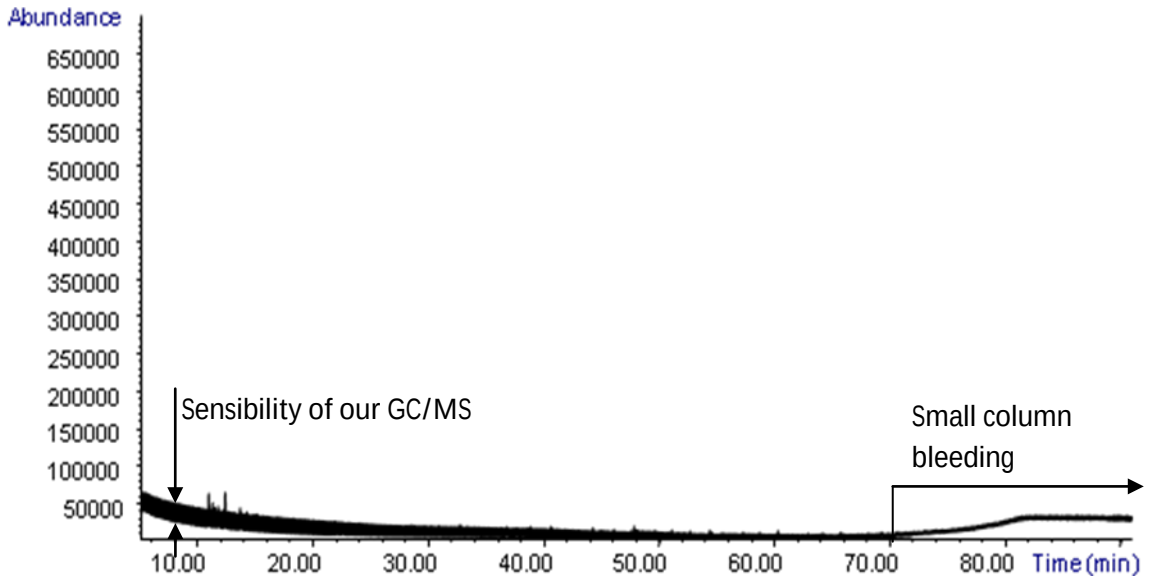

Figure A5.- Fiber derived Bio-char (Pyrolysis Temperature 350 ^{o}C).

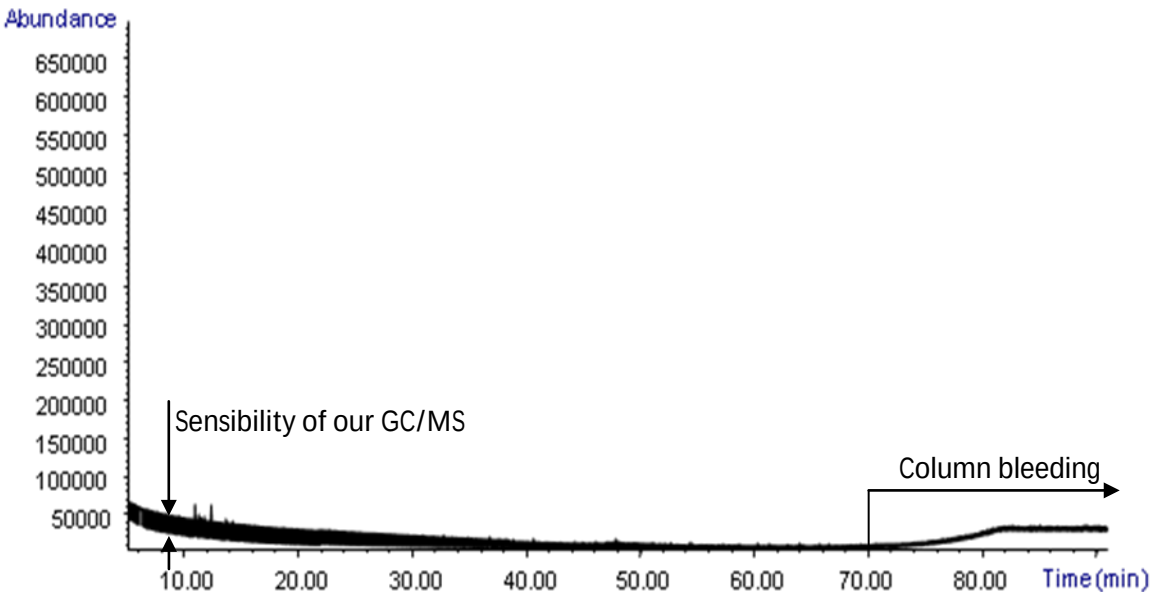

Figure A6.- Fiber derived Bio-char (Pyrolysis Temperature 425 ^{o}C).

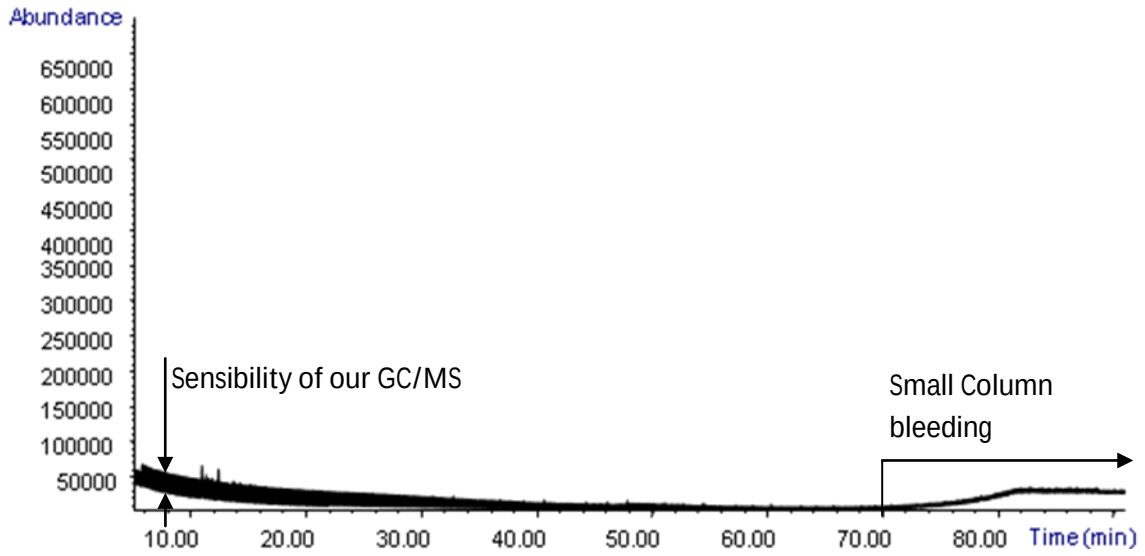

Figure A7.- Fiber derived Bio-char (Pyrolysis Temperature 500 ^{o}C).

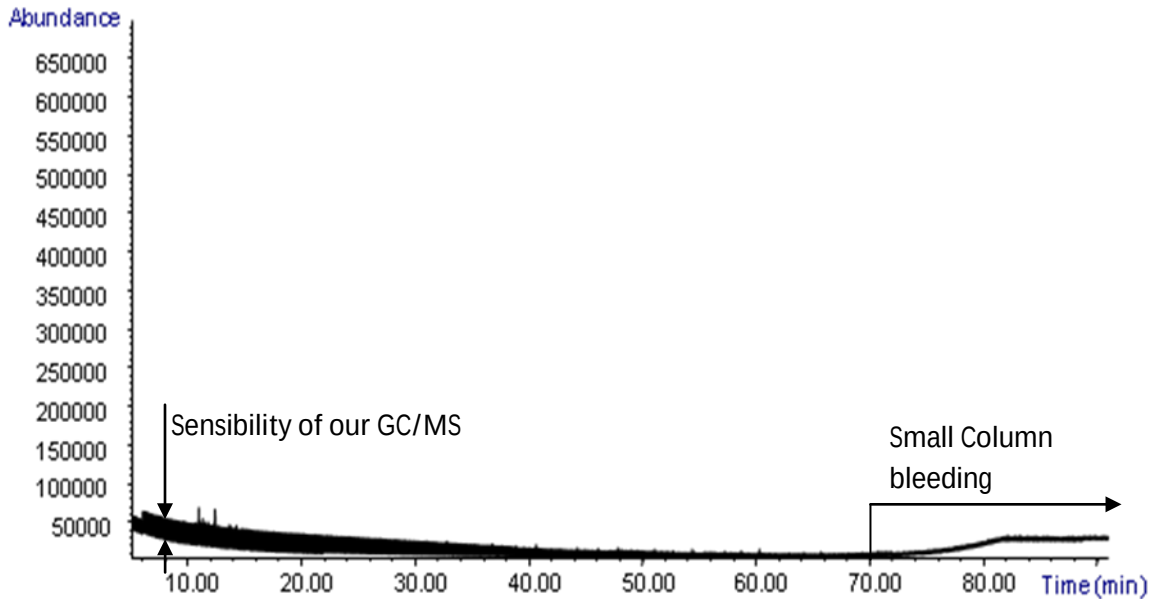

Figure A8.- Fiber derived Bio-char (Pyrolysis Temperature 600 ^{o}C)

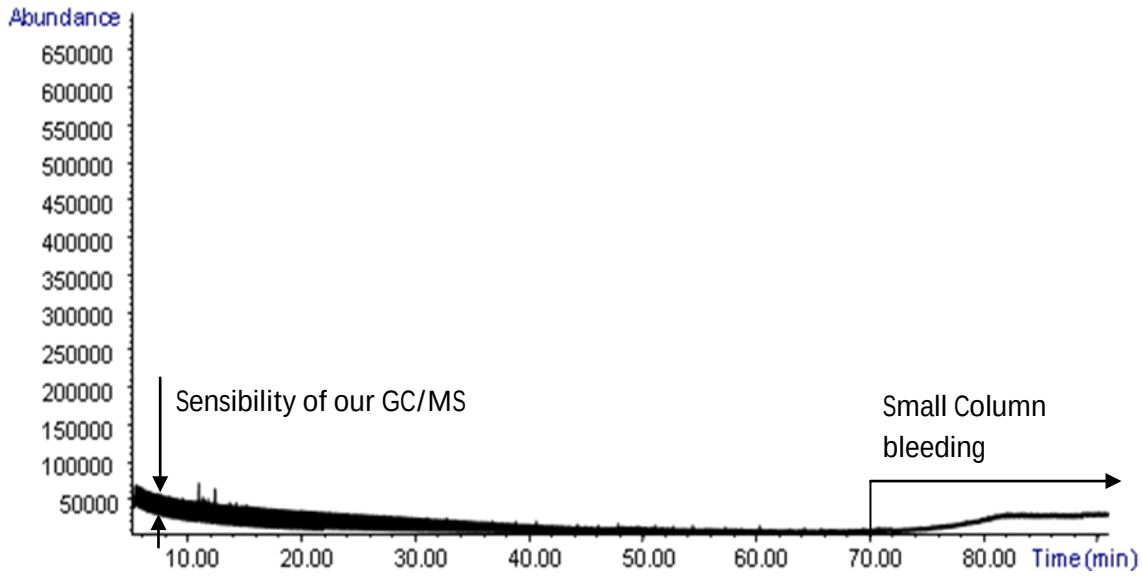

Figure A9.- Grass derived Bio-char (Pyrolysis Temperature 350 ^{o}C)

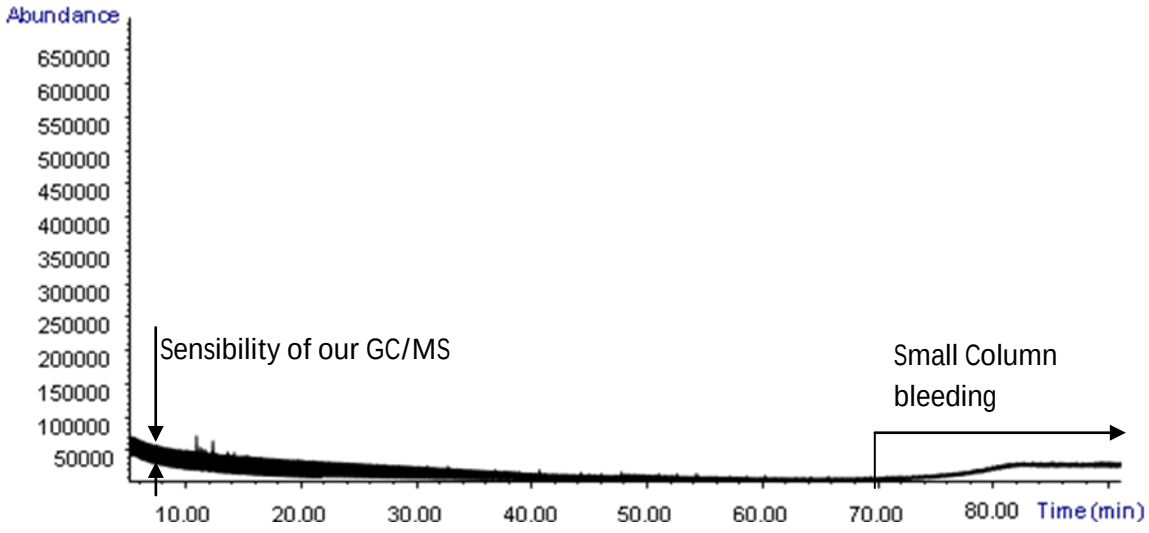

Figure A10.- Grass derived Bio-char (Pyrolysis Temperature 425 ^{o}C)

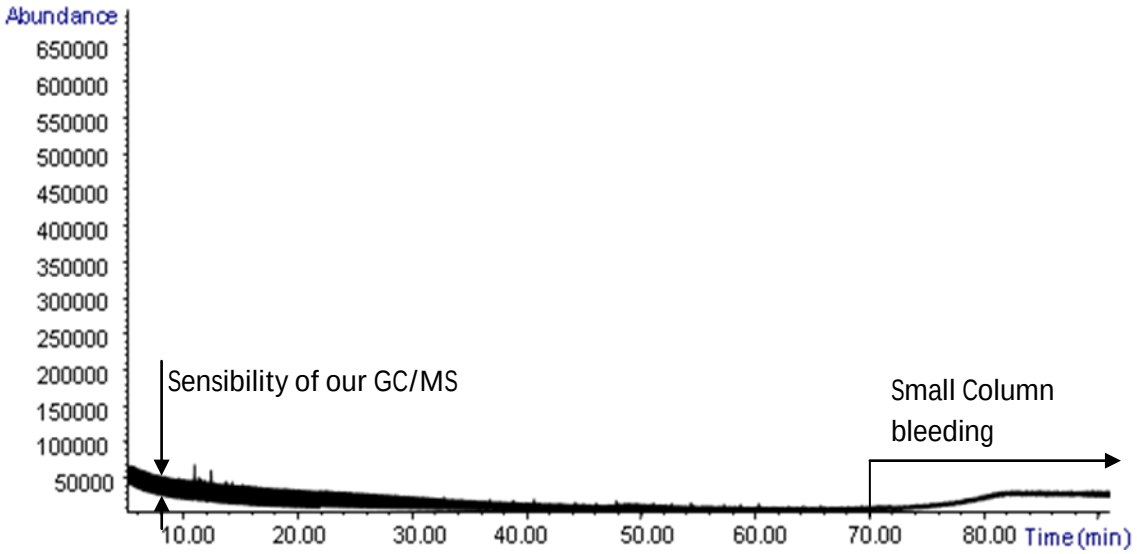

Figure A11.- Grass derived Bio-char (Pyrolysis temperature 500 ^{o}C)

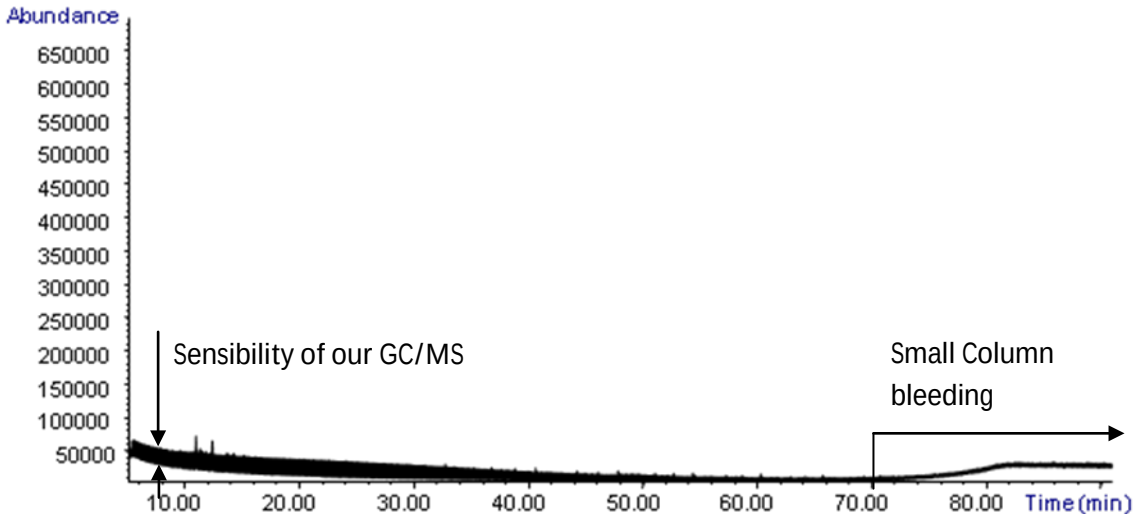

Figure A12.- Grass derived Bio-char (Pyrolysis temperature 600 ^{o}C)

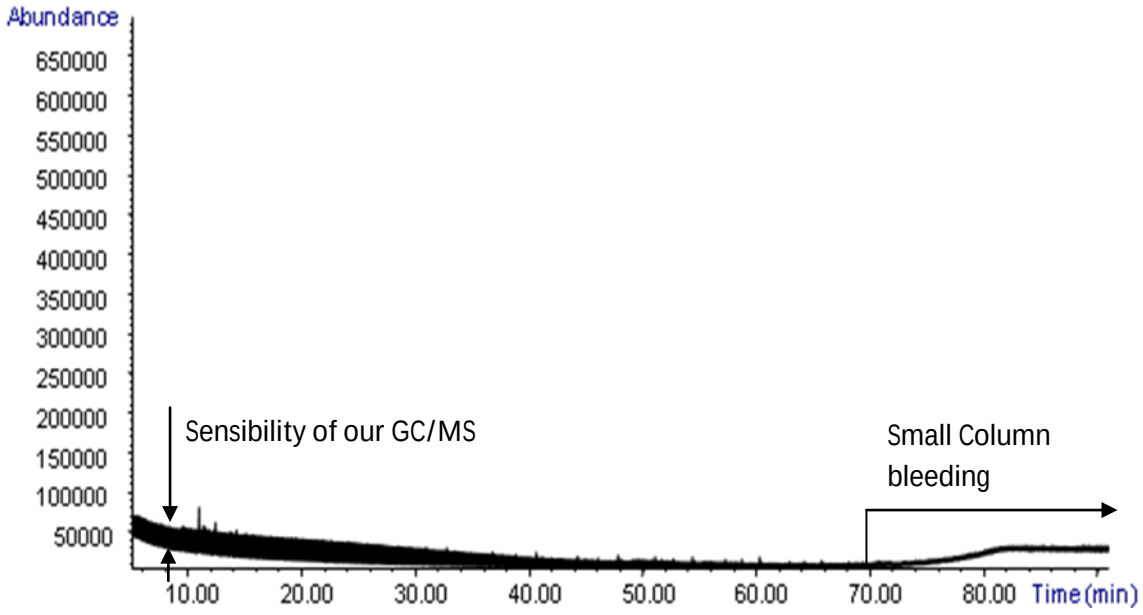

Figure A13.- Pine Pellet derived Bio-char (Pyrolysis Temperature 350 ^{o}C)

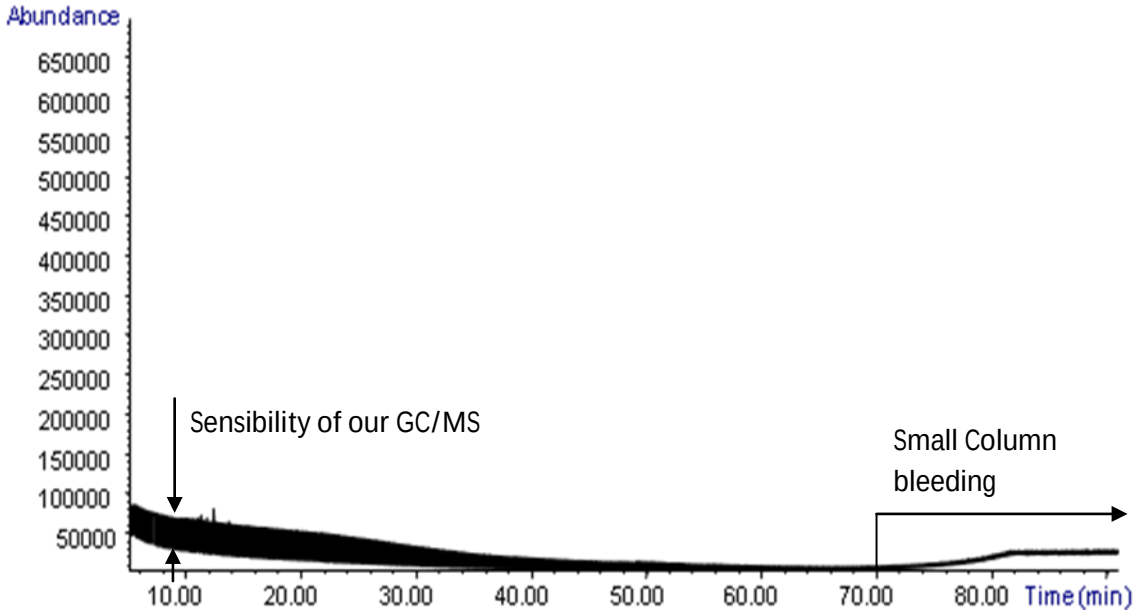

Figure A14.- Pine Pellet derived Bio-char (Pyrolysis Temperature 425 ^{o}C)

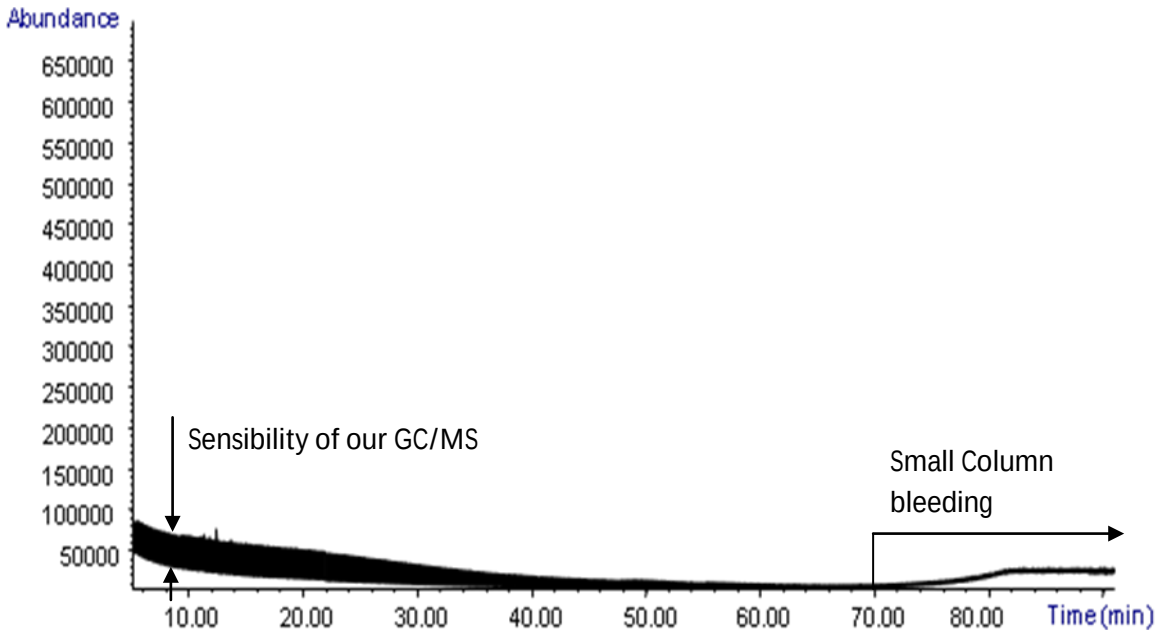

Figure A15.- Pine Pellet derived Bio-char (Pyrolysis Temperature 500 ^{o}C)

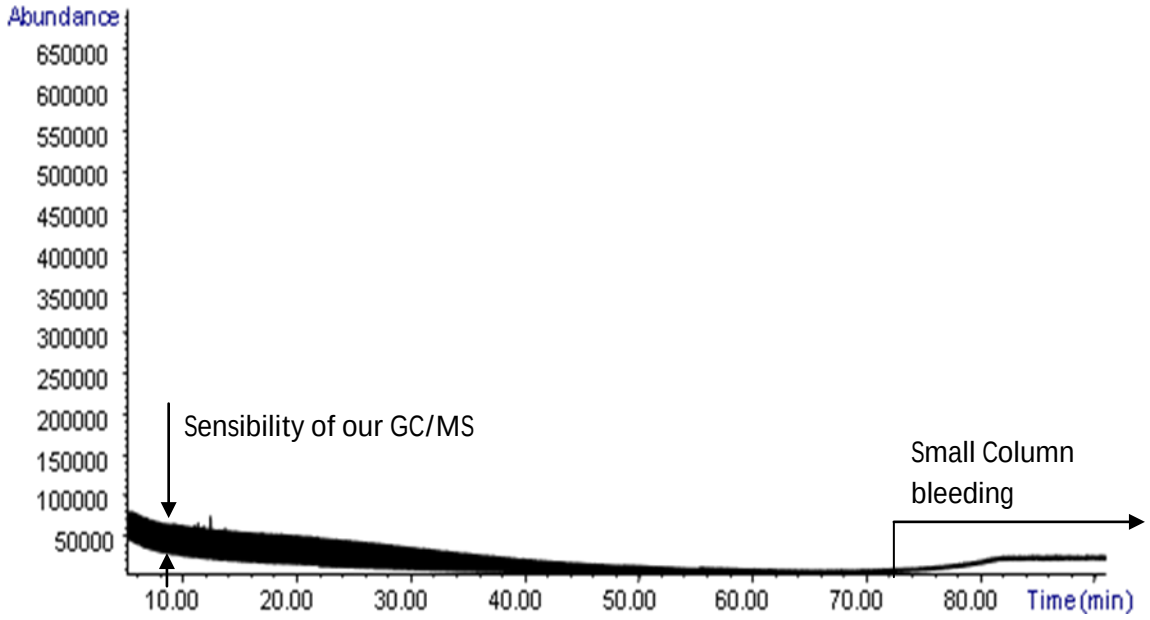

Figure A16.- Pine Pellet derived Bio-char (Pyrolysis Temperature 600 ^{o}C)