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Review Article

Hydrogen-Assisted Thermal Cracking for Enhanced Bio-Oil Production

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ABSTRACT

This study outlines the pyrolysis and thermal cracking processes used to produce bio-oil from a variety of agricultural wastes, including used soybean frying oil, coffee grounds, sawdust. A light fraction and a heavy fraction were created from the fractions produced during the pyrolysis and/or cracking procedures. Comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry detection (GCGC/TOFMS) was used to analyse all the fractions. While the fractions obtained by pyrolysis contained significant amounts of compounds such as furanmethanol, hexanol, benzofuran, whose commercial value is high, the characteristics of the fractions obtained in the presence of hydrogen were similar to those of petroleum-based naphtha.

Keywords: Thermal Cracking, Biomass Pyrolysis, Hydrogen, Chromatography

Introduction

The usage of fossil fuels has recently been subject to environmental limitations, which has accelerated research into new alternative energy sources. Biomass is one of the many alternative technologies that have been researched to create greener fuels and has shown promise.[1-4] There has been interest in biomass as a renewable resource because of a number of factors, most notably its affordability and accessibility. Various techniques, such as reductive combustion, liquefaction, pyrolysis, gasification, can turn biomass into biofuel.[5] The use of biomass is especially intriguing when it involves waste materials that are also potential energy sources, such as used vegetable oil, fruit seeds, sugarcane bagasse, sugarcane straw, rice husks, coconut fibres, coffee grounds.[6-8]

biomass-derived biofuel Pyrolysis, also referred to as pyrolysis oil, is a dark brown to virtually black liquid with a distinct smokey odour. Its elemental makeup is similar to that of the biomass it arises from. It is a complicated mixture of molecules that are oxygenated and contain a sizable amount of water that comes from the moisture in the biomass and cracking reactions. Small coal particles and dissolved alkali metals from the ash may also be present in bio-oil.

The raw material utilised and the production conditions have an impact on its composition. An aqueous microemulsion known as pyrolysis oil is produced when cellulose, hemicellulose, lignin are fragmented.[9,10]

Pyrolysis is a biomass thermal degradation process that has received a lot of attention.[11-13] The literature describes a wide range of different reactors and conditions for this process. The potential uses for bio-oil are severely hampered by the presence of oxygen. In the case of oxygen, for instance, these effects include a reduction in the heating value, the development of immiscibility with petroleum fuels, the development of corrosiveness and instability during long-term storage and transit.[14] An economically viable method for creating chemicals and/or fuels is biomass pyrolysis.[15,16]More than 300 organic molecules make up the bio-oil produced by the pyrolysis process.[17] but its processing, separation, characterisation present technological obstacles.

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The volatile chemicals produced during pyrolysis also offer a strong potential for energy generation in the thermal cracking process.[18] Additionally, catalytic cracking, hydrogenation, steam reforming are typically required during the upgrading process, which reduces oxygenates and is required to enhance the quality of bio-oil.[19-22]

An important method for raising the calibre of bio-oil made from biomass pyrolysis is hydropyrolysis. Because hydrogen is a reducing gas, cracking biomass in its presence can lower the oxygen concentration of the resulting bio-oil.[23] The characterization of bio-oil produced by the pyrolysis of a variety of waste materials, including used soybean frying oil, used coffee grounds, sawdust, is covered in this work. Lower molecular weight fractions and a significantly lower concentration of oxygenated and nitrogenated species were produced as a result of the thermal cracking procedure that was carried out in the presence of hydrogen in order to upgrade the bio-oil.

Experimental Materials

The bio-oil was produced through the pyrolysis of a mixture (1: 1: 1, in mass) of waste materials, including used coffee grounds, eucalyptus sawdust, used soybean frying oil. The solids were combined with the frying oil after being ground to a particle size of 0.21 mm. Calcium oxide (20 mass%) and enough water were added to this combination to create a pliable mass that could be formed into cylindrical samples (50 mm 180 mm). The samples were left to dry for a week at room temperature.

Biomass pyrolysis and thermal cracking of the bio-oil

Another reactor (stainless steel, 20 mm in diameter and 600 mm in length) was used to treat the volatiles created throughout the process using isothermal hydrocracking. The water phase was separated by decantation after the final effluent was cooled to 100 C.

The effluent was condensed at 5 °C following phase separation, the aqueous phase separation process was then repeated while the gaseous phase was discarded.

The pyrolysis was carried out once more without thermal cracking for comparison's sake. Thus, two types of bio-oil were produced: one at 100 °C and the other at 5 °C, both with and without thermal cracking. These samples are referred to as OCH (Oil after Cracking obtained at 100 C-High temperature) and OCL (Oil after Cracking obtained at 5 C-Low temperature) for those obtained after thermal cracking. OPH (Oil from Pyrolysis obtained at 100 C-High temperature) and OPL (Oil from Pyrolysis obtained at 5 C-Low temperature) refer to samples obtained solely by pyrolysis. The four fractions produced—OPH and OPL by pyrolysis, OCH and OCL by pyrolysis followed by thermal cracking—are shown in Figure 1's production scheme.Characterization of the Products, Section 2.2

The four fractions were examined using an LECO Pegasus IV (LECO, St Joseph, MI, USA) equipment for GCGC/TOFMS analysis. At 320 °C (1 °L) with a split ratio of 1: 30, experiments were conducted in a typical split/splitless injector (Agilent Technologies). As the carrier gas, 1 mL min-1 of helium (99.999%, Linde Gases, Porto Alegre, RS, Brazil) was employed. The oven's temperature ranged from 40°C to 300°C at a rate of 3°C per minute. The modulation period (cryogenic quadjet modulator, chilled with liquid nitrogen) was 8 s, the difference in temperature between ovens 1D and 2D was 15 C. The electron impact ionisation source and transfer line ran at 300°C and 250°C, respectively. The detector's acquisition frequency was 100 Hz, with a mass range of 45 to 400 Daltons.

At 70 eV, electron ionisation took place. The Pegasus 4D platform of the ChromaTOF software was used to process the data. Using a cryogenic modulator, a DB-5 column was employed as the first dimension and a DB-17 column as the second-dimension column.

Retention times, spatial structuring zones, mass spectral match factor (NIST library), spectrum deconvolution were used to identify the chemicals. Since the elution area in two-dimensional (2D) space and other factors provide a higher degree of reliability in the identification of analytes, several compounds with similarity below 700 were considered to be identified given the spatial structure supplied by GC–GC. In order to create dispersion images and better understand the distribution of compounds in 2D space, the data generated in the peak table were imported into the Microsoft ExcelTM programme.

Results and Discussion

Product yields from pyrolysis and thermal cracking

The distribution of the pyrolysis products is influenced by the initial biomass as well as reaction parameters like temperature, heating rate, reactant particle size.

The oil fractions obtained in this study were produced using different production techniques, but they were made from the same raw ingredients and under the same conditions. While the OPH sample was only acquired by pyrolysis, the OCH sample was obtained through pyrolysis and thermal cracking. At a temperature of 5 C, the condensed fraction significantly increased after the addition of thermal cracking following pyrolysis. 30% oil fractions, 50% aqueous fractions, 20% gas phase (uncondensed, acquired via difference) make up the average yield of the pyrolysis process. Ninety percent or so of the oil fraction in the pyrolysis process is the oil fraction that condenses at a temperature of 100 C. A distribution of around 40% of the fraction condensed at a temperature of 5 C (OCL) and 60% of the oil fraction condensed at a temperature of 100 C (OCH) is the result of the pyrolysis process followed by thermal cracking.

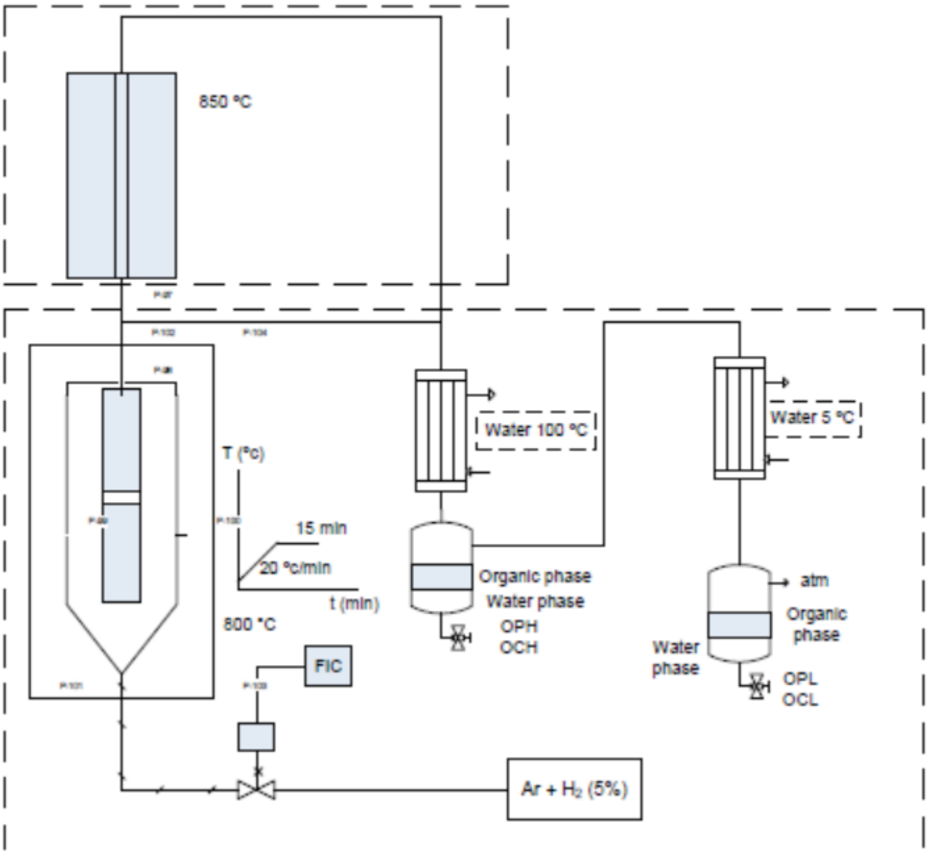

Figure 1.Production Scheme of the fraction produced: OPH and OPL bye the Pyrolysis process followed by thermal cracking

Composition of Bio-Oil Fractions

A GC/GC/TOFMS was employed to identify the four bio-oil fractions since they are extremely complex mixtures of various chemical species created by the depolymerization and fragmentation of the major components of the biomass, which consist of a wide range of molecular weights. According to the sorts of chemical compounds they include, the four bio-oil fractions depicted in Figure 2 are composed of acids, aldehydes, ketones, alcohols, phenols, aromatics, cyclic and aliphatic hydrocarbons, ethers, nitrogen compounds. When there was a greater than 750 percent match between the spectrum of a sample and the library, the compounds were considered to be known. 214 chemicals were tentatively identified in OCH, 324 in OCL, 84 in OPH, 312 in OPL

Some findings hold true for both the light fraction of pyrolysis and the bio-oils produced by thermal degradation (OPL-Figure 2). Consider the fact that there is a significant amount of hydrocarbon compounds, with aromatic and aliphatic compounds accounting for the majority (57–79 wt%) of the products. The OPH sample, on the other hand, which was produced by pyrolysis and condensed at 100 °C (the fraction containing heavy chemicals), is primarily made up of ketones and nitrogens, with smaller amounts of alcohols, ethers, phenols.

Hydrocarbons are absent from this percentage. Nitrogenous chemicals are produced by the thermal breakdown of caffeine derivatives found in coffee grounds and are found in bio-oil.

The fractions produced by pyrolysis and thermal cracking (OCH and OCL), as shown in Figure 2, are mostly composed of aliphatic, aromatic, cyclic hydrocarbons. The majority of the OPH fraction is made up of hydrocarbons that contain nitrogen (46% of the area) and oxygen (47% of the area) molecules. Most of the more than 300 molecules contain oxygen, pyrolysis bio-oils typically have an oxygen content between 45 and 50 w/w%.[10,24,25]The type of biomass and the process conditions have the biggest impact on how these chemicals are distributed.Bio-oil's calorific value is decreased and it becomes chemically unstable due to the presence of oxygenated compounds,[9] which restricts its usage as fuel or in formulations for direct use in diesel cycle engines.[9,26,27] They do, however, have significant increased commercial value when separated.[28]

Table 1 displays the major chemicals that have been identified together with the percentage of each compound in the bio-oil and fractions (OPH, OPL, OCH, OCL). The Appendix contains a list of the other substances found in the study's fractions.

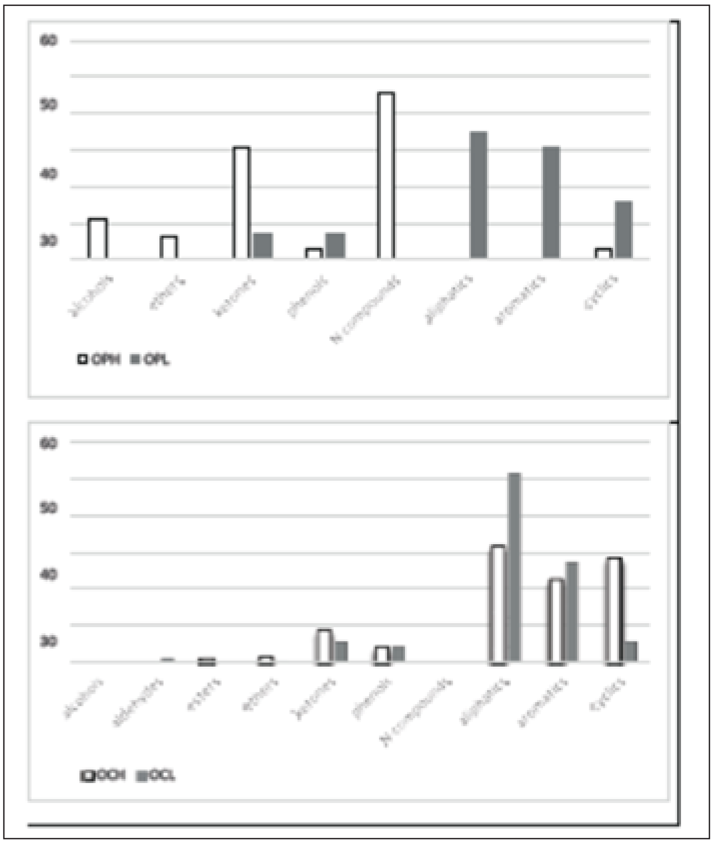

Figure 2.Percentage of peak area by chemical class for the OPH, OPL, OCH and OCL fraction

Furanmethanol (8% in area) and hexanol (2% in area) are two examples of the oxygenated molecules found in the OPH fraction alcohols, as shown in Table 1. These two alcohols are crucial building blocks for creating a variety of pharmaceuticals and industrial goods with significant commercial and industrial value.[29] The OPH fraction also contains benzofuran and dioxyethane ethers in percentage amounts of 2.0 and 4.0, respectively. A significant group of heterocyclic chemicals known as benzofurans are found in many bioactive natural items, medicines, polymers. Due of its wide variety of microorganisms, benzofuran is one of the most significant heterocyclic rings. Because of its clinical significance, medicinal chemistry is heavily involved in the synthesis of the benzofuran ring. In addition to being an enzyme activator and inhibitor, benzofuran also functions as an antioxidant, antibacterial, anti-inflammatory, anti-cancer, antiviral, anti-tuberculosis agent.[30]

The four research fractions—roughly 7% OPL, 4% OCH and OCL, 3% OPH—contained phenolic chemicals. These substances are frequently used to make phenolic resins.[31] When added to diesel fuel formulations and/or biodiesel for use in engines (usage of biomass-derived chemicals), they also have antioxidant and antibacterial properties that hinder the proliferation of microorganisms, corrosion, deposits.[32,33] Additionally, the majority of chemical compounds that contain oxygen are made from fossil fuels by introducing oxygen-containing functional groups to olefins by oxidation or hydration. Fortunately, bio-oil already contains these functional groups. Therefore, a feasible strategy for the effective utilisation of biomass energy is to produce value-added compounds from bio-oil.

In terms of the N-compounds found only in the OPH fraction, pyrazines accounted for 25% of the total area. In the synthesis of quinoxaline, also known as benzopyrazine, which is scarce in nature but is simple to make, pyrazine is a crucial component that works with benzene. Due to its capacity to prevent metal corrosion[34] during the production of porphyrins,[35] quinoxaline and its derivatives have significant economic significance. They may be of interest to the pharmaceutical business due to the wide range of biological features they possess.[36-38]

In the OPH fraction, there were essentially no aromatic hydrocarbons. On the other hand, the alkylbenzenes in the OPL, OCH, OCL fractions, which could be separated and used, together with the pyrazines of the OPH fraction, as a starting point for the synthesis of quinoxaline and its derivatives, each contained around 16% of the total area.

A stronger breakdown of the heavier organic compounds into lighter organic compounds, as well as the elimination of nitrogen from the nitrogenated compounds, were the results of the OCL and OCH fractions obtained by thermal cracking in the presence of a mixture of argon and 5% hydrogen.[39] Oxygen was also eliminated (deoxygenation) with the formation of water. The supplemental material and Figure 2 both provide illustrations of this. As a result of thermal cracking, different C-C fragments may go through oligomerization to create olefins, which may then go through aromatization, followed by alkylation and isomerization, to create aromatics. These hydrocarbons were represented by percentage areas of 82 and 84 in the OCH and OCL fractions, respectively. With 81% of its area made up of hydrocarbons, the OPL fraction produced by pyrolysis had a profile comparable to that of the OCH and OCL fractions with respect to oxygenated chemicals.

Conclusions

In the pyrolyzed fractions, 84 chemicals in the heavy fraction and 312 in the light fraction were tentatively identified. In order to improve the bio-oil, the vapours were thermally cracked in the presence of 5% hydrogen, 214 chemicals in the heavy fraction and 324 in the light fraction were found. Most of the hydrocarbons created by the thermal cracking method were aliphatic, aromatic, cyclic, giving around 80% of the weight of these compounds, which had properties akin to those of naphtha produced by atmospheric distillation of petroleum and may be used as fuels. Hydrocarbons with nitrogen (46% of the area) and oxygen (47% of the area)-containing compounds made up the majority of the fractions that could only be produced through pyrolysis. The oxygenated substances included benzofuran, dioxyethane ethers, furanmethanol, hexanol alcohols. Phenolic chemicals were present in every fraction that was examined. These compounds are a fantastic source of raw materials for the manufacture of pharmaceuticals and industrial goods with great commercial and industrial value when they are isolated.

References

1. Arbogast S, Bellman D, Paynter JD, Wykowski J (2012) Advanced bio-fuels from pyrolysis oil: The impact of economies of scale and use of existing logistic and processing capabilities. Fuel Processing Technol 104: 121-127.
2. Arbogast S, Bellman D, Paynter JD, Wykowski J (2013) Advanced biofuels from pyrolysis oil... Opportunities for cost reduction. Fuel Processing Technol 106: 518-525.
3. Khan AA, Jong W, Jansens PJ, Spliethoff H (2009) Biomass combustion in fluidized bed boilers: Potential problems and remedies. Fuel Processing Technology 90: 21-50.
4. Cataluña R, Kuamoto PM, Petzhold CL, Caramão EB, Machado ME, et al. (2013) Using Bio-oil Produced by Biomass Pyrolysis as Diesel Fuel. Energy Fuels 27: 6831-6838.
5. Laksmono N, Paraschiv M, Loubar K, Tazerout M (2013) Biodiesel production from biomass gasification tar via thermal/catalytic cracking. Fuel Processing Technology 106: 776-783.
6. Dukua MH, Gu S, Hagan EB (2011) A comprehensive review of biomass resources and biofuels potential in Ghana. Renewable and Sustainable Energy Reviews 15: 404-415.
7. http://www.unep.org/ietc/Portals/136/Publications/Waste%20Management/ WasteAgriculturalBiomassEST_Compendium.pdf Virmond E, Rocha JD, Moreira RFPM, José HJ (2013) Valorization of agroindustrial solid residues and residues from biofuel production chains by thermochemical conversion: a review, citing Brazil as a case study. Braz J Chem Eng 30: 197-229. Bridgwater AV (2004) Biomass fast pyrolysis. Thermal science 8: 21-49.
8. http://www.ieabioenergy.com/
9. Mohan D, Pittman Jr CU, Steele PH (2006) Pyrolysis of wood/biomass for biooil: a critical review. Energy Fuel 20: 848-889.Li S, Xu S, Liu S, Yang C, Lu Q (2004) Fast pyrolysis of biomass in free-fall reactor for hydrogen-rich gas. Fuel Processing Technol 85: 1201-1211.

10. Özbay N, Uzun BB, Varol EA, Pütün AE (2006) Comparative analysis of pyrolysis oils and its subfractions under different atmospheric conditions. Fuel Processing Technol 87: 1013-1019.
11. Girisuta B, Kalogiannis KG , Dussan K, Leahy JJ, Hayes MHB, et al. (2012) An integrated process for the production of platform chemicals and diesel miscible fuels by acid-catalyzed hydrolysis and downstream upgrading of the acid hydrolysis residues with thermal and catalytic pyrolysis. Bioresource Technology 126: 92-100.
12. Vispute TP, Zhang H, Sanna A, Xiao R, Huber GW (2010) Renewable chemical commodity feedstocks from integrated catalytic processing of oils. Science 330: 1222-1227.
13. Wright MM, Daugaard DE, Satrio JA, Brown RC (2010) Techno-economic analysis of biomass fast pyrolysis to transportation fuels. Fuel 89: 52-510.
14. Mythili R, Venkatachalam P, Subramanain P, Uma D (2013) Characterization of bioresidues for bioil production through pyrolysis. Bioresour Technol 138: 71- 78.
15. Mortensen PM, Grunwaldt JD, Jensen PA, Knudsen KG, Jensen AD (2011) A review of catalytic upgrading of bio-oil to engine fuels. Applied Catalysis A: General 407: 1-19.
16. Zhu XF, Zheng JL, Guo QX, Zhu QS (2005) Upgrading and utilization of bio-oil from biomass. Engineering Science 7: 83-88.
17. Zhang Q, Chang QJ, Wang TJ, Xu Y (2006) Progress on research of properties and upgrading of bio-oil. Petrochemical Technology 35: 493-498.
18. Guo XY, Yan YJ, Li TC (2004) Influence of catalyst type and regeneration on upgrading of crude bio-oil through catalytical thermal cracking. The Chinese Journal of Process Engineering 4: 53-58.
19. Kanaujia PK, Sharma YK, Garg MO, Tripathi D, Singh R (2014) Review of analytical strategies in the production and upgrading of bio-oils derived from lignocellulosic biomass. J Analyt Appl Pyrolys 105: 55-74.
20. Thangalazhy-Gopakumar S, Adhikari S, Gupta RB, Tu M, Taylor S (2011) Production of hydrocarbon fuels from biomass using catalytic pyrolysis under helium and hydrogen environments. Bioresour Technol 102: 6742-6749.
21. Meier D, Oasmaa A, Peacocke GVC (1997) Proper ties of Fast Pyrolysis Liquids: Status of Test Methods. Characterization of Fast Pyrolysis Liquids, in: Develop ments in Thermochemical Bio mass Conversion. Blackie Academic & Professional (Eds.), London.
22. Huber GW, Corma A (2007) Synergies between bio- and oil refineries for the production of fuels from biomass. Angew Chem Int Ed Engl 46: 7184-201.
23. Wang SR, Wang YR, Cai QJ, Wang XY, Jin H, et al. (2014) Multi-step separation f monophenols and pyrolytic lignins from the water-insoluble phase of bio-oil. Sep Purif Technol 122: 248-255.
24. Zhang Q, Chang J, Wang TJ, Xu Y (2007) Review of biomass pyrolysis oil properties and upgrading research. Energy Conversion and Management 48: 87- 92.
25. Bridgwater VA, Meier D, Radlein D (1999) An overview of past pyrolysis of biomass. Org Geochem 30: 1479-1493.
26. Liu W, Wang X, Hu C, Tong D, Zhu L, et al. (2014) Catalytic pyrolysis of distillers dried grain white solubles: An attempt towards obtaining value-added products. International Journal of Hydrogen Energy 39: 6371-6383.
27. Nevagi RJ, Dighe SN, Dighe SN (2015) Biological and medicinal significance of benzofuran. Eur J Med Chem 97: 561-581.
28. Migliorini MV, Moraes MSA, Machado ME, Caramão EB (2013) Caracterização de fenóis no bio-óleo da pirólise de caroço de pêssego por GC/MS e GCxGC/ TOFMS. Scientia Chromatographica 5: 47-65.
29. Almeida LR, Hidalgo AA, Veja ML, Rios MAS (2011) Utilização de compostosderivados da biomassa para solução problemas industriais do setor de biocombustíveis. Estudos Tecnológicos 7: 163-176.
30. Yang H, Zhao W, Norinaga K, Fang J, Wang Y, et al. (2015) Separation of phenols and Ketones from bio-oil produced from ethanolysis of wheat stalk. Sep Purif Technol 152: 238-245.
31. Zarrouk A, Zarrok H, Salghi R, Hammouti B, Al-Deyab SS, et al. (2012) A Theoretical Investigation on the Corrosion Inhibition of Copper by Quinoxaline Derivatives in Nitric Acid Solution. Int J Electrochem Sci 7: 6353-6364.
32. Kim J, Jaung JY (2008) The synthesis and optical properties of meso- substituted porphyrins bearing quinoxaline derivatives. Dyes and Pigments 77: 474-477.
33. Pereira JA, Pessoa AM, Cordeiro MN, Fernandes R, Prudêncio C, et al. (2015) Quinoxaline, its derivates and applications: A State of the Art rewiew. Eur J Med Chem 97: 664-672.