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Hemicelluloses obtaining from rapeseed cake residue generated in the biodiesel production process

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Abstract

The processing of rapeseed oil seeds for biodiesel production generates huge amounts of lignocellulosic cake residue mainly composed by cellulose, hemicelluloses and lignin. In this work, the valorisation of these components, especifically the majoritary fraction, hemicelluloses, was studied. Hemicelluloses were extracted, purified and characterized by different techniques (FTIR, ^{1}H-NMR, ^{13}C-NMR, GPC). Autohydrolysis and acid hydrolysis processes were applied to obtain sugar monomers and oligomers. Glucose and xylose were the main simple sugars in the obtained hydrolysates, representing 22.7% and 40.2% of total sugars content in the autohydrolysis hydrolysates and 27.7% and 36.6% in the acid hydrolysates respectively. Arabinose, galactose and mannose were present in relatively minor quantities.

Keywords: Biodiesel, Waste rapeseed, Hemicelluloses, Hydrolysis

1. Introduction

An increasing energy demand all over the world, the instability of crude oil market and environmental concerns included in the Kyoto protocol have pushed up the transition of the global energy system to renewable fuels [1]. In this context, biodiesel production from vegetable oils remains a strong growth market in the United States and Canada as well as in the European Union [2]. However, in spite of the favourable impact, biodiesel production presents some drawbacks related with the economics of the process, deeply dependent on feedstock costs [3]. Refined and edible-grade vegetable oils present good characteristics that have converted them in the most commonly used raw materials for biodiesel production with the objection of their high prices [4]. Specifically, EU-25 biodiesel is mainly obtained from rapeseed oil (*Brassica napus Linnaeus*), whose production ascended to 16 million tons in 2006 of which more than 4.0 million tons were used for biodiesel production [5].

In the processing of rapeseed oil seeds for biodiesel production, 65% of the feedstock is converted in a lignocellulosic cake that is, sometimes, post-treated by hexane extraction in order to increase the oil yield. After the extraction process, the remaining solid part is called rapeseed meal residue [5, 6]. Cake composition, mainly cellulose, hemicelluloses and lignin, depends on the type of rapeseed plant, which also determines its possible applications, as cattle feed (canola variety) or energy production [7]. Nevertheless, the expansion of biodiesel production makes necessary to find other applications for the

residues. The upgrading of this by-product through the use of its components, especifically the majoritary fraction, hemicelluloses, could entail economical and environmental improvements for the process.

Hemicelluloses are components of the polysaccharide fraction of the cell wall in plants. Hemicelluloses are associated with cellulose and pectic substances and comprise several non-starch, noncellulosic polysaccharides, including xylans (arabinoxylans and 4-0-methyl-glucuronoxylans), galactomannans, glucomannans, ß-D-glucans (3- and 4-linked), ß-D-glucan-callose (3-linked), and xyloglucans (4-linked ß-D-glucans with attached side chains) [8]. Xylans, xyloglucans and galacto-arabino-glucorono-xylan are the main hemicellulose pentosans present in annual plants and can be converted to xylose by hydrolysis process [9]. The carbohydrate component of rapeseed (canola) meal represents about 30-40% of the total dry matter content and is composed of sucrose, oligosaccharides, starch and non-strach polysaccharides. The carbohydrates with low molecular weights are similar to those of soybean meal although the latter contains higher levels of oligosaccharides [10].

Hemicelluloses obtaining and isolation is an essential step for their biological conversion to ethanol or to produce a whole range of fuels and chemicals [11, 12]. A variety of effective methods to hydrolyze and fractionate hemicellulosic components have been studied, including hot water extraction (autohydrolysis) [13], dilute acid pre-treatment [14], steam explosion-based extraction [15], dilute-acid steam explosion [16] and alkaline extraction [17].

Dilute-acid and hot water treatments have been demonstrated to be effective in recovering hemicelluloses from hardwoods and herbaceous materials. Dilute-acid hydrolysis (sulphuric acid; solid-liquid ratio 1:20 w/v) at 130°C for 30 min was reported to yield 89.1% of the hemicelluloses content [14]. Hot water hydrolysis (solid/liquid ratio 1:5 w/v; 150–170ºC; 15–30 min) was applied to recover hemicelluloses from sugarcane bagasse obtaining 89% of the original amount of xylose [18].

In the autohydrolysis process, much of the hemicelluloses are transformed into soluble sugars by the cleavage of the acetyl groups in the hemicelluloses forming acetic acid, by a process with lower equipment corrosion and low degradation of hemicelluloses. In the acid hydrolysis, under more severe conditions, it is expected that a higher percentage of the hemicelluloses are dissolved but they may be transformed into degradation products, as furfural or hydroxymethyl furfural, by secondary reactions [19].

In this work we have foccused on the obtaining of polymeric hemicelluloses from rapeseed (*B. napus*) cake residue generated in biodiesel production. The first proposed task was to isolate and characterize the hemicelluloses contained in the rapeseed cake residue. For this purposal, different techniques were used (FTIR, HPLC, GPC, ^{1}H-NMR, ^{13}C-NMR). Furthermore, dilute-acid and hot water hydrolysis treatments were applied to obtain monomeric (mainly glucose and xylose) and oligomeric sugars which were also characterized and compared.

2. Material and methods

2.1 Material

Rapeseed cake pellets were supplied by Öko-Line Ltd., Hungary. Its chemical composition was analyzed following standard methods and procedures found in the literature: ash (TAPPI T211 om-93); lignin (TAPPI T222 om-98); holocellulose [20], α-cellulose and hemicelluloses content [21].

2.2 Elemental analysis

Rapeseed cake pellets elemental analysis for carbon, hydrogen and nitrogen was carried out (Euro EA3000 series Elemental Analyzer from EuroVector SpA, Milano, Italy). Total oxidation of the sample (10 mg) was conducted at 1020º C. Combustion products were separated in a chromatographic column (PTFA column for CHNS, 2m; carrier gas: He, 70 KPa; purge flow: 80 ml/min; Poxygen: 35 kPa)

2.3 Isolation of hemicelluloses

Rapeseed cake pellets hemicelluloses were isolated following a multiple step treatment used to obtain hemicelluloses from different sources [22]. Rapeseed cake pellets were dewaxed by ethanol-toluene extraction (1:2, v/v, 6 h) and treated with hot water (1:20, w/v, 80 ºC, 2 h). Water-soluble polysaccharides were precipitated from the obtained filtrate by adding ethanol. Obtained precipitate was washed with ethanol-water (70:30 v/v), dried and stored for further characterization. On the other hand, the water-soluble free solid was

treated with sodium chlorite in acidic solution (pH 4.0, adjusted by 10% acetic acid, 75ºC, 2 h) in order to remove lignin and filtrated to obtain the holocellulose fraction. Hemicelluloses were extracted from holocellulose by alkaline treatment (10% NaOH, 1:15 w/v, 10 h, 20 ºC). The filtrate was neutralized with 6 M HCl to pH 5.5 and hemicelluloses were precipitated in ethanol (1:25; w/v) and washed with ethanol-water (70:30; v/v), dried and stored for further characterization.

2.4 Rapeseed lignocellulosic wastes hydrolysis

Rapeseed cake pellets were submitted to different hydrolysis treatments. Autohydrolysis (water/solid 20:1; w/v) and acid hydrolysis (96% w/w H_2SO_4; acid/solid 20:1; w/v, pH 3) were carried out in a 1 L batch cylindrical reactor (Parr 5100) with temperature-pressure control at the following operating conditions: temperature 180 ºC, extraction time: 15 min preheating and 30 min at reaction temperature.

2.5 Characterization of hemicelluloses

Different techniques were used to define the chemical structure and properties of obtained hemicelluloses and sugars resulting from the hydrolysis processes.

2.5.1 Fourier transform infrared spectroscopy (FTIR)

Measurements were performed in a Perkin-Elmer 16PC instrument by direct transmittance using KBr pellet technique. Each spectrum was recorded over 20 scans, in the range from 4000 cm^{-1} to 500 cm^{-1} with a resolution of 4 cm^{-1}. KBr was previously oven-dried to avoid interferences due to the presence of water,

and background spectra were collected before every sampling.

2.5.2 ^{1}H NMR spectroscopy

Standard proton spectra were recorded at 25 ºC on a Bruker Avance 500 MHz spectrometer equipped with a z-gradient BBI probe. Samples were dissolved in deuterated water (D_2O). Experimental conditions included a spectral width of 4500 Hz, 30º flip angle (pulse width of 6.1 µs for 90º), a repetition time of 7.6 s (2.6 s for acquisition time and 5 s for the interpulse delay), and 16 scans.

2.5.3 ^{13}C NMR spectroscopy

Standard carbon spectra were obtained at 25 ºC on a Bruker Avance 500 MHz spectrometer equipped with a z-gradient BBI probe using a spectral width of 4500 Hz, 30º flip angle (pulse width of 12.5 µs for 90º) with decoupling. Samples were dissolved in deuterated water (D_2O). The repetition time was 5.5 s (0.5 s for the acquisition time and a 5 s interpulse delay).

2.5.4 Gel permeation chromatography (GPC)

GPC was used to determine the molecular weight (MW) and molecular weight distribution (MWD) of isolated hemicelluloses which were previously acetylated to enhance solubility in THF. Samples were dissolved in filtered (Phenex Filter Membranes 0.45 µm 47 mm nylon) GPC grade THF (Tetrahydrofuran, Multisolvent® GPC grade ACS, without stabilizer, Scharlau) and then filtered again (Phenomenex, Phenex-RC 4mm Syringe Filters 0.45 µm) before being injected into the column. The used Perkin Elmer instrument was equipped with an interface (PE Series 900), three Waters Styragel columns (HR 1, HR 2 and

HR 3) ranging from 100 to 5×10^5 and a refractive index detector (Series 200), with a flow rate of 1 mL/min. Calibration was made using polystyrene standards.

2.5.5 High performance liquid cromatography (HPLC)

After hydrolysis treatment, elemental sugars composition of hemicelluloses present in obtained hydrolysates were quantitatively determined in a Perkin Elmer instrument (LC Oven 101, 250 Biocompatible binary pump) equipped with an interface (PE Nelson 900 Series) and a refractive index detector (Perkin Elmer LC-30). A Phenomenex Rezex ROA HPLC column (300 x 7.8 mm) with precolumn (Phenomenex Security Guard holder with carbo-H^+ cartridges) was used for the experiments. Ffiltered (Phenex Filter Membranes 0.45 µm, 47 mm, nylon) 0.005N H_2SO_4 prepared with 100% deionized and degassed water (Water, gradient HPLC grade, Scharlau) was used as mobile phase (0.3 mL/min flow, ambient temperature and injection volume 20µL). High purity xylose, glucose, galactose, mannose and arabinose purchased from Sigma-Aldrich were used for calibration. Standards were prepared at different sugar concentrations (0.1%, 0.5%, 1% and 2%, w/w). A linear calibration (R^2>0.999) was obtained for all sugars.

3. Results

3.1 Rapeseed pellets chemical composition

Raw material presented the following chemical composition: (% on an oven-dry weight basis): ash content: 5. 0 ± 0.1%; lignin: 16 ± 5.2; holocellulose: 62 ± 3.2, α-cellulose: 22 ± 1.2 and hemicelluloses: 40 ± 0.5. The high hemicelluloses percentage found suggested the suitability of this material for sugars obtaining.

3.2 Rapeseed pellets elemental analysis

Table 1 shows obtained values for the elemental analysis of rapeseed cake residues. High carbon and oxygen percentages, 44.87% and 43.78% respectively were found in rapeseed cake residues composition. Oxygen percentage can be calculated as the remaining component after nitrogen, carbon and hydrogen percentages have been calculated if the sample does not present considerable sulphur quantity, as it was rapeseed cake residues case.

3.3 Yield of isolated hemicelluloses

Material balances of the hemicelluloses isolation steps were established. Ethanol-toluene extractives represented the 6% of the dry raw material whereas the pre-treatment with hot water gave as a result a yield of 5.5% corresponding to water soluble polysaccharides fraction. After sodium chlorite delignification, 59.5% of the dry raw material remained as holocellulose fraction. Obtained yield of isolated hemicelluloses from dry rapeseed cake pellets after alkaline extraction was 41%.

3.4 Physico-chemical characterization of hemicelluloses

3.4.1 Fourier transform infrared spectroscopy (FTIR)

Absorption spectra of isolated hemicelluloses recorded in the region of 1000–4000 cm^{-1} are shown in Fig. 1. Hemicelluloses indicative bands were found. The glycosidic bond vibrations of the arabinoxylans gave an intense signal at 1072 cm^{-1} and hydroxyl groups in hemicelluloses, associated with the broad band at 3430 cm^{-1}, resisted the alkali conditions of the treatment [23]. The bands at 1434 cm^{-1} and 1370 cm^{-1} were associated with O-H and C–H bendings [24]. The band at 2920 cm^{-1} was due to C-H stretching of methyl groups while the band at 1652 cm^{-1} was related to the absorbed water. The absence of bands at 1520 and 1330 cm^{-1}, typical of aromatic skeletal vibrations in lignin and the syringyl ring breathing with CO stretching, respectively, indicated the effectiveness of sodium chlorite treatment to remove lignin [25].

3.4.2 ^{1}H NMR spectroscopy.

Fig. 2 shows ^{1}H-NMR spectrum of isolated hemicelluloses. Solvent (D_2O) peak appeared at 4.71 ppm. The methyl protons of few amounts of 4-*O*-methyl-α-*D*-glucuronic acid exhibited weak peaks at 1.05 ppm. The chemical shifts of 3.5–4.3 ppm arised from the equatorial proton and other protons of anhydroxylose units of hemicelluloses gave a shoulder at 5.2 ppm [26]. Non-reducing terminal 4-*O*-methyl-α-*D*-Glucoronic acid groups gave signal at 5.24 ppm [17].

3.4.3 ^{13}C NMR spectroscopy.

^{13}C NMR spectroscopy of isolated hemicelluloses gave the spectrum presented in Fig. 3. Signals at 104.6ppm, 80.98 ppm, 79.99 ppm, 75.92ppm and 68.73 ppm were associated with C-1, C-4, C-3, C-2 and C-5 positions of (1-4)-linked β-D-XylP units [9, 22]. The signals at 108.1 ppm, 88.1 ppm, 83.6 ppm, 73.1 ppm and 63.2 ppm corresponded to C-1, C-4, C-2, C-3, and C-5 of α-L-arabinofuranosyl residues linked to β-D-xylans, respectively. Two signals at 70.9 and 70.1 ppm were originated from C-4 and C- 2 of galactose residue in the xylan. Signals at 59.7 ppm and 57.6 were characteristic of the 4-O-methyl group of glucuronic acid residue in the xylan. ^{13}C NMR spectrum of hemicelluloses indicated that the major component in the isolated fraction was xylan.

3.5 Hemicelluloses molecular weight

Weight-average (M_w) and number-average (M_n) molecular weights, and the polydispersity (M_w/M_n) of obtained water-soluble polysaccharides and isolated hemicelluloses are presented in Table 2.

Isolated hemicelluloses presented moderate MW values in comparison with reported data of hemicelluloses MW extracted from other raw materials as sugarcane bagasse with NaOH (55,700 g/mol) [22] or barley straw with alkaline peroxide (from 38,470 to 41,050 g/mol) [23], indicating a moderate degradation of the molecular structure of hemicelluloses which is also reflected in the obtained polydispersity. Steam exploded treatment has been reported to

conduce to heavily degraded polymers resulting in the obtaining of lower MW hemicelluloses (from 12,120 to 18,210 g/mol) [27].

Hemicellulosic polymers with MW values similar to those found in hemicelluloses extracted from rapeseed cake residue have been reported to be successfully modified through esterification reactions to afford conventional thermoplastics [28].

3.6 Neutral sugar composition

Autohydrolysis process gave a yield of 70% of hemicelluloses to dissolved sugars and acid hydrolysis was found to yield 81.1% of hemicelluloses content to monomers. Monosaccharide concentrations measured in the hydrolysates obtained in the autohydrolysis and acid hydrolysis processes are presented in Table 3. Sugar composition in the water extracts of rapeseed cake residues autohydrolysis and acid hydrolysis showed that glucose and xylose were the main components in the obtained hydrolysates, representing 22.7% and 40.2% of total sugars content in the autohydrolysis hydrolysates and 27.7% and 36.6% in the acid hydrolysates respectively. Noticeable amounts of arabinose were found while galactose and mannose were present in relatively minor quantities. The concentration of xylose and arabinose in the extracted hemicellulosic fractions indicated that the hemicelluloses in rapeseed cake residues were mainly composed of xylan and arabinoxylan-type polysaccharides.

These results are in concordance with reported values for other annual crops and agricultural wastes [29, 30]. In fact, arabinoxylans from different annual

plants present a similar general chemical structure with differences in the substituent's type and position in the backbone. Xylose to arabinose ratio was found to be 2.3 and 2.1 for autohydrolysis and acid hydrolysis obtained hydrolysates respectively. This parameter is indicative of the degree of branching of hemicelluloses; the higher the xylose to arabinose ratio, the higher the hemicelluloses polymerisation degree [31]. Obtained results, moderate ratios, indicated medium-chain polymer with monosaccharide substituents which meant that considerable proportion of arabinose was present in comparison with xylose proportioning higher degree of branching of the xylan chains and less water solubility. Higher values of xylose to arabinose ratio (from 4 to 12) have been reported for other agricultural residues [29].

Regarding the comparison between autohydrolysis and acid hydrolysis processes, the latter gave as a result higher sugars content, particularly glucose content, which was more than double. This fact could indicate that the acid treatment partially converted the cellulose into glucose. Thus, acid hydrolysis would be a proper treatment to maximize polysaccharides conversion to glucose for subsequent fermentation of the latter to obtain ethanol, as glucose conversion to ethanol by fermentation presents high yields, about 30% higher than xylose [31]. Rapeseed cake residues hexose monomers obtained by acid hydrolysis (glucose, xylose, mannose, galactose and arabinose) were found in high concentrations in obtained hydrolysates. The low lignin percentage in the raw material composition (16%), specially compared with the high holocellulose content (62%), would ensure the sugars accessibility to enzymes [32].

Other applications of isolated hemicelluloses from rapeseed could be precursor chemicals for the synthesis of a large number of substances via established chemical methods (furfural, 5-hydroxymethylfurfural, levulinic acid) [33] or via biotechnological methods (lactic acid and succinic acid production) [34]. Finally, these materials have been reported to be precursors to a wide variety of macromolecular materials [35].

4. Conclusions

Physico-chemical characterisation of rapeseed cake residues revealed high hemicelluloses content, mainly xylan and arabinoxylan-type polysaccharides, and a low lignin percentage, optimal conditions to apply hydrolysis (enzymatic or chemical) to obtain raw material sugars content. Both autohydrolysis and acid hydrolysis processes presented high yields of conversion of hemicelluloses to monomers (70% and 81.1% of hemicelluloses to monomeric sugars respectively). High glucose concentrations were found in the acid hydrolysates that could be processed by fermentation to produce ethanol with high yields.

Valuable products have been successfully extracted from rapeseed cake residues by a simple treatment that could improve the economic and environmental aspects of the biodiesel obtaining process from rapeseed plant.

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Table captions.

Table 1. Rapeseed cake residues elemental analysis. Results are given in percentage. RSD: relative standard deviation.

Table 2. Weight-average (M_w) and number-average (M_n) molecular weights and polydispersity (M_w/M_n) of obtained water soluble polysaccharides and isolated hemicelluloses.

Table 3. Monosaccharide concentrations (g/L hydrolysate) obtained in the autohydrolysis and acid hydrolysis of rapeseed cake residues.

Table 1.

	Nitrogen	Carbon	Hydrogen
Percentage (%)	4.93	44.87	6.42
RSD	2	0.3	0.5

Table 2.

Polysaccharide fraction	M_w	M_n	M_w/M_n
Water soluble polysaccharides	7850	4745	1.82
Isolated hemicelluloses	24185	7219	3.35

Table 3.

	Glucose	Xylose	Mannose	Galactose	Arabinose	Total
Autohydrolysis	0.171	0.351	0.062	0.129	0.201	0.914
Acid hydrolysis	0.408	0.671	0.125	0.209	0.320	1.833

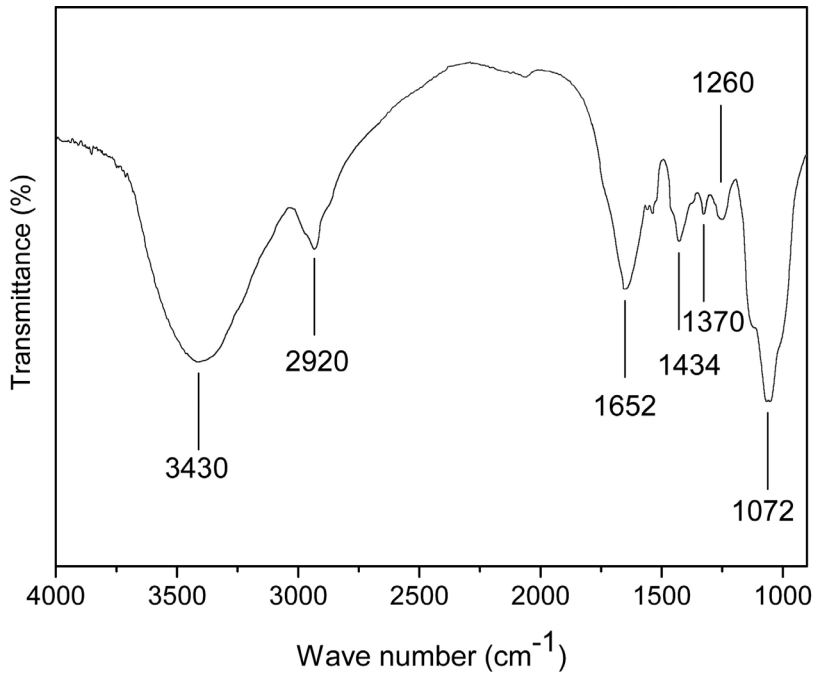
Figure captions.

Figure 1. FTIR spectra of isolated hemicelluloses from rapeseed cake pellets.

Figure 2. ^{1}H NMR spectra of isolated hemicelluloses from rapeseed cake pellets.

Figure 3. ^{13}C NMR spectra of isolated hemicelluloses from rapeseed cake pellets.

Figure 1.


Transmittance (%)
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1370
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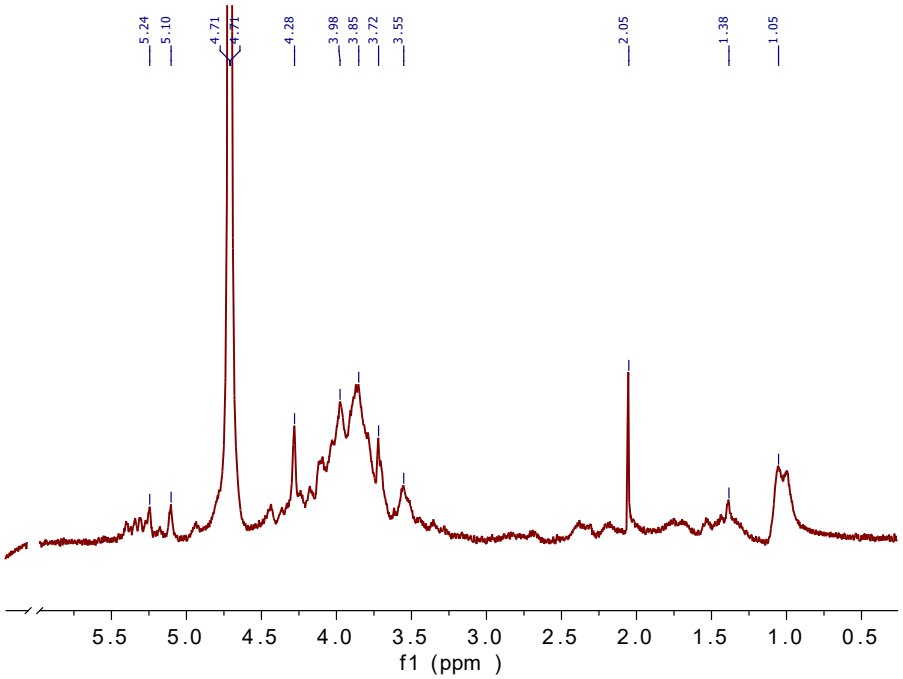
1652
3430
1072
4000
3500
3000
2500
2000
1500
1000
Wave number (cm-1)

Figure 2.


5.24
5.10
4.71
4.71
4.28
3.98
3.85
3.72
3.55
2.05
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5.0
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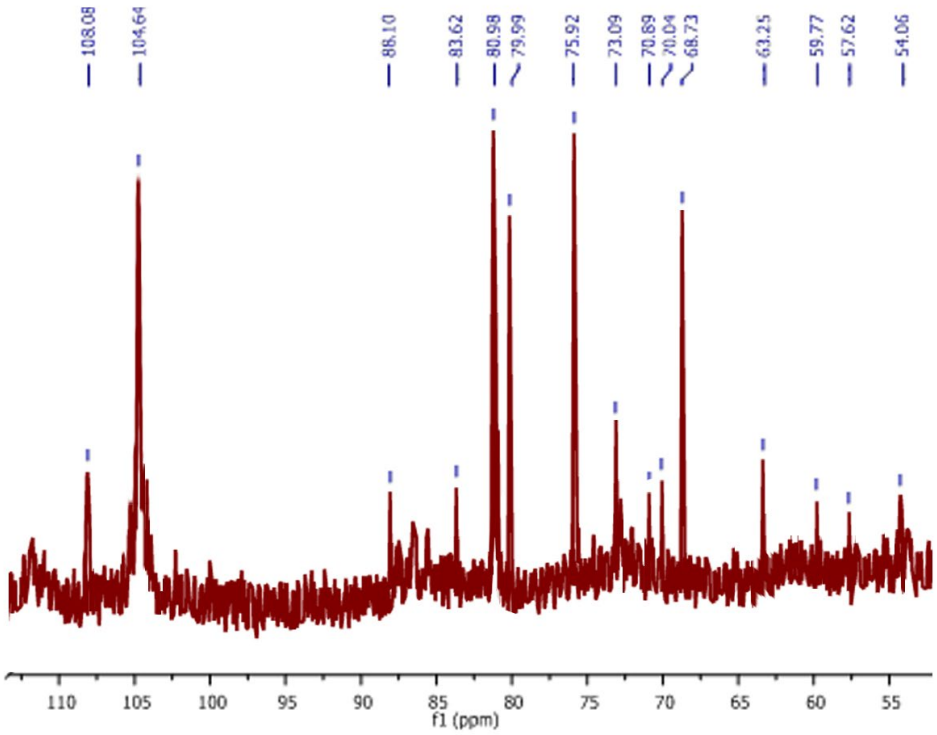
2.0
1.5
1.0
0.5
f1 (ppm)

Figure 3.


108.08
104.64
88.10
83.62
80.98
79.99
75.92
73.09
70.89
70.04
68.73
63.25
59.77
57.62
54.06
110
105
100
95
90
85
80
75
70
65
60
55
f1 (ppm)