A Selective Extraction Method for Recovery of Monofunctional Methoxyphenols from Biomass Pyrolysis Liquids

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A selective process to recover monofunctional methoxyphenols (MPs) from biomass pyrolysis liquids has been developed. The process integrates distillation and extraction. Exploiting slight differences between acid strengths of various phenolics enabled the concentration of the MPs. A bio-product containing up to 88 wt% eugenols and guaiacols was recovered.

Pyrolysis of lignocellulosic biomass produces a liquid product that contains valuable monomeric phenolic compounds such as simple phenols (e.g., phenol, cresol, xylenol, higher alkylphenols) and functionalized phenolics with hydroxyl (e.g., catechols), methoxy (e.g., guaiacols, eugenols), dimethoxy (syringol), carbonyl (e.g., acetovanillone, coniferyl aldehyde, guaiacyl acetone, vanillin), and carboxyl (e.g., homovanillic) groups. Generally, the concentration and types of these phenolics are dependent on the lignocellulosic feedstock and the conversion process. For instance, conventional pyrolysis of woody biomass produces about 4–5 wt% of guaiacolic types of phenols.[1] Under mild catalytic pyrolysis conditions, biocrudes containing up to 10 wt% eugenols and up to 6.5 wt% guaiacols can be produced.[2] Also, up to 13 wt% of phenol, guaiacol, cresol, xylenol, and syringol has been reported from pyrolysis of agricultural feedstocks such as sugarcane bagasse and empty fruit bunch.[3] For lignin pyrolysis, total monomeric phenolic yields between 6 wt% and 17 wt% have been reported;[4-10] the differences in yields are due to the source of lignin and the pyrolysis conditions.

Renewable phenolics such as eugenols and guaiacols are of industrial interest because of their potential use as chemical building blocks in the synthesis of various flavorings such as vanillin[11], and they are used in the food industry, personal care products, detergents, household cleaners, and perfumery products.[12] Their derivatives are also used for active pharmaceuticals and specifically used medicinally as an expectorant, antiseptic, and local anesthetic[13]. They can also be used to synthesize phenolic resins[14], polymers[15], polymerization initiators, flame retardants[16], pesticides, antioxidants, and biocides[17, 18]. It is worth pointing out that each of the applications requires different purity levels of the separated phenolic product. For instance, applications such as resins and other polymers may not need very pure phenolic streams. However, other applications like pharmaceuticals will require very high purity and even a single-compound product.

Over the years, several separation techniques have been explored to recover phenolic compounds from pyrolysis liquids.[1,12, 18-25] LLE or solvent extraction is a method that has been extensively used to separate pyrolysis liquids into chemical families for compositional analysis and for the recovery of chemicals. Many research groups have developed different LLE protocols/schemes.[1,3, 12, 18-20, 25-30] The traditional extraction method for the separation of phenolic species begins with basification of the feed mixture; utilizing strong alkaline aqueous solutions, such as NaOH, to react with phenols to form phenolates. The phenols are then extracted at a pH below 7 by acidification with mineral acid. [3, 25, 30] Additionally, extraction with switchable hydrophilicity solvents such as tertiary amines (N,N-dimethylcyclohexylamine) and supercritical carbon dioxide have been demonstrated as promising methods for phenolic extraction.[19, 20, 24]

Studies to date show varying degrees of success with different solvent extraction schemes. Fele Žilnik and colleagues[1] recovered a phenolic fraction from pyrolysis oil by aqueous extraction and simultaneous use of a hydrophobic-polar solvent and antisolvent. The phenolic product consisted of a mixture of phenol, cresol, catechol, guaiacols, eugenols, vanillin, acetovanillone, and sinapinaldehyde. Wang and colleagues[30] separated a mixture of phenolics including phenols, guaiacols, eugenols, syringols, vanillin, catechols, and syringaldehyde from bio-oil using the traditional alkaline solvent extraction method that used alkaline (NaOH) solutions, mineral acid (HCl), and dichloromethane (DCM).

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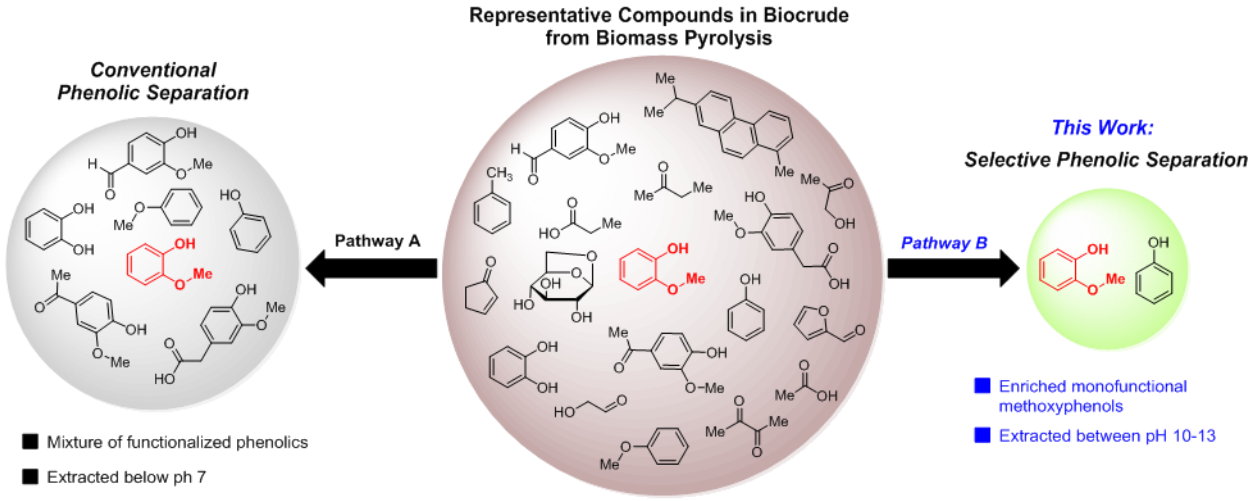


Scheme 1. Illustration of the convention phenolic separation approach in comparison to the selective process reported in this work

Li and colleagues[25] explored alkaline extraction, followed by DCM extraction to recover phenol derivatives from bio-oil. Mantilla and colleagues[3] also compared solvent LLE with alkaline extraction and found that the solvent LLE of the bio-oil using DCM followed by a second extraction with ethyl acetate gave a higher separation yield for phenolic compounds. Fu and colleagues[20] studied the extraction of phenols from lignin-derived bio-oil using a switchable hydrophilicity solvent. Patel and colleagues[23] investigated extraction of cardanol and phenol from bio-oil using a supercritical fluid extraction method. Also, Naik and colleagues[24] employed supercritical CO_2 to fractionate furanoids, pyronoids, and benzenoids from bio-oil.

All these approaches have been identified as having additional step-out potential to isolate valuable compounds from bio-oil. However, a major drawback of the reported extraction methods is that the phenolics are isolated as one fraction; as such, the product contains various classes of phenolics with different functionalities. This limits the application of the recovered phenolic fraction and thus explains why most of the interest on the recovered phenolic fractions from extractions has been for phenol-formaldehyde resins[31].

The separation of individual classes of phenols is nontrivial because of similarities in their physical and chemical properties; such as solubility, boiling point, melting point, and acidic strength (pKa). Additionally, depending on the method, significant material losses and low separation efficiency are realized during separation. For instance, traditional alkaline extraction of pyrolysis liquids results in significant formation of amorphous residue or tarry caustic soda precipitates; also, some components in the final aqueous phase raffinate are difficult to recover[32, 33]. Furthermore, in a previous study, distillation and adsorption chromatography[34] was used to recover a phenolic bioproduct rich in guaiacols and eugenols form loblolly pine biocrude. Nonetheless, the distillation step resulted in significant material loss (22 wt%) as residue. Also, the chromatography step utilized large volumes of organic solvents to attain the reported purity levels (87-93 wt%).

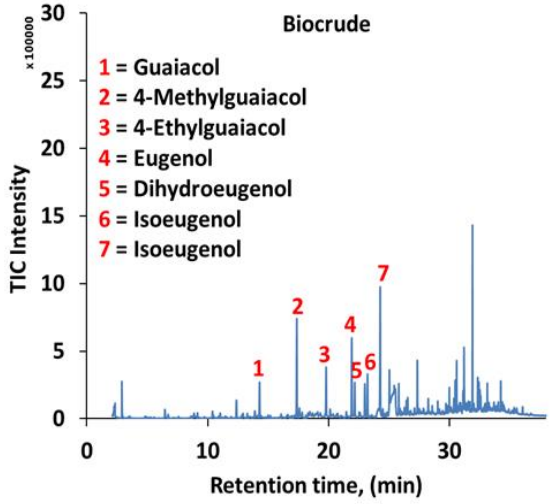


Figure 1. GC-MS chromatogram of a typical biocrude sample showing the target phenolics

Thus, there is a need to develop a separation strategy that addresses the issue of material losses in the form of residues/precipitates when distillation/alkaline extraction techniques are used for phenolic separation. Importantly, there is a need to advance the traditional alkaline extraction method to enable the separation of different types of phenolics. In the present work, we have developed a selective extraction method that demonstrates exclusive recovery of guaiacols and eugenols from pyrolysis liquids as monofunctional methoxyphenols (MPs). The method can be tailored to recover different phenolic compounds. The illustration in Scheme 1 distinguishes the separation objective pursued in the present work relative to past studies on phenolic compound recovery from biomass pyrolysis liquids. The developed process integrates solvent extraction/distillation, and a selective alkaline extraction technique. Specifically, in the first isolation step, a suitable solvent is used to extract a fraction containing primarily the MPs and other thermally stable components in the biocrude that is then fractionally distilled to obtain a crude MP-mixture

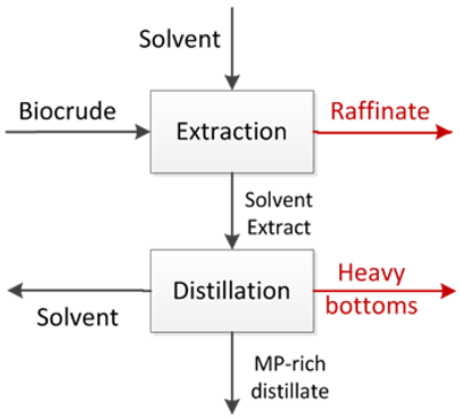
boiling between 165 °C and 315 °C. In the subsequent step, the crude MP-mixture is preferentially extracted by exploiting slight differences between the acid strength (i.e., acid dissociation constant) of the phenolics present. As a result, a bioproduct containing mainly guaiacols and eugenols is obtained. The separation process prevents material losses in the form of solid residue during distillation and eliminates the formation of caustic soda precipitates during alkaline extraction. Thus, the process enables the remaining fraction to be usable for other applications including upgrading into biofuel intermediates.

Isolation of Crude MP Fraction

The biocrude samples used are produced from loblolly pine at an average temperature of 477 °C in RTI's 1 ton per day (1 TPD) catalytic biomass pyrolysis unit. A commercially available spray-dried, nonzeolite, alumina-based catalyst with a BET surface area of 114.6 m^2/g and a mean particle size of approximately 70 µm is used. Details of the operation of the catalytic pyrolysis in the 1 TPD unit can be found in previously published work.[2,25] The moisture content of the biocrude measured by Karl Fischer titration (V20, Mettler Toledo) is about 7.25 wt%. The organic elemental composition (CHONS) is determined by an elemental analyzer (FLASH2000, Thermo Scientific), and the oxygen content (by difference) of the biocrude is 24.2 wt% on a dry basis. An example of the chromatogram of the biocrude sample is shown in **Figure 1.** The mass concentration of the monofunctional MPs guaiacols and eugenols in the biocrude samples are between 9.5 and 11 wt%. The mass concnetration of MPs in the starting biocrude and the product stream from each separation step is determined by gas chromatography–mass spectrometry (GC-MS) by using calibration curves developed with pure forms of eugenol, isoeugenol (Z and E), guaiacol, 4-methylguaiacol, 4-ethylguaiacol, and 4-propylguaiacol. The GC-MS analysis is performed with an Agilent 6890 GC and 5975C MS. An HP-5MS column (30 m × 0.25 mm, 0.25 µm film thickness with 5% phenyl-methyl-polysiloxane as the stationary phase) is used for the separation of the components.

Prior to developing the new separation protocol, the amount of residue formed by directly distilling the biocrude is determined for reference. A fully automated bench-scale PILODIST laboratory distillation unit (PETRODIST 300 CC) with one theoretical stage column is used. The unit consists of a glass distillation apparatus, a 500-mL round-bottom flask, a flask heater/stirrer, vacuum pump, cooling system, and a control console. The experiment is performed sequentially in two steps to obtain an MP-rich distillate with a boiling range of 205–280 ºC under vacuum (20 kPa). The initial mass concentration of the targeted MPs in the biocrude sample used is 11wt%. The distillation process resulted in a distillation step efficiency of 86.9% and the mass concentration of the targeted MPs in the MP-rich distillate is 49.3 wt%. The amount of solid residue formed by the biocrude during the distillation is 23 wt%. Of note, residue formation is typical in the distillation of pyrolysis bio-oils due to the presence of thermally unstable oxygenates. Past studies show that the amount of residue formed could be up to 50 wt% depending on the quality and oxygen content of the pyrolysis liquid.[21, 22, 35-37] For instance, residue formation in yields between 30-50 wt% has been observed by observed Elkasabi et al. [36]

The alternative strategy reported herein to prevent material losses in the form of solid residue during distillation requires solvent extraction prior to distillation to recover the crude MP-rich distillate as illustrated in **Scheme 2.** The objective of the solvent extraction is to prevent solid residue formation during isolation of the crude MP-rich distillate.



Scheme 2. Isolation of crude-enriched fraction from biocrude.

First, a solvent capable of selectively extracting the MPs and other thermally stable components in the biocrude is identified. The process entail screening of four solvents (methyl tert-butyl ether [MTBE], methyl isobutyl ketone [MIBK], toluene, and isopropanol). Eventually, toluene is found to have relatively poor solubility for residue-forming components such as complex phenolics, pyrolytic lignin, and water-soluble oxygenates such as anhydrosugars and carboxylic acids present in the biocrude. Importantly, toluene doesn't form emulsion with the biocrude even at low solvent-to-oil volume ratios (e.g., 0.25:1). Further, the residence time for phase separation is shorter for toluene. For a typical experiment, two extractions with toluene are performed; about 500 mL of biocrude is mixed with 350 mL of toluene for the first extraction. The raffinate from the first extraction is then mixed with 150 mL of toluene for a second extraction. The toluene soluble fractions (TSFs) from both washes are then combined and distilled to recover the toluene solvent and an MP-rich fraction boiling between 165 and 315 °C. A summary of the results from five sets of experiments is provided in **Table 1**. The +/- sign attached to the average yields correspond to a single standard deviation. The breakdown of the yields for the solvent extraction and the distillation steps are on initial biocrude mass basis and toluene-free basis. The reported separation step efficiency is for both the solvent extraction and distillation steps. The result show that about 47.5 wt% of the biocrude used is toluene extractable, and about 52.5 wt% is toluene insoluble (raffinate). On a solvent-free basis, distillation of the toluene extract resulted in an

average yield of 19.3 wt% MP-rich fraction and 28.9 wt% bottoms with respect to the initial mass of the biocrude. The process increased the concentration of the targeted MPs from about 9.5 wt% in the biocrude to 41.7 wt% in the MP distillate.

Table 1. Summary results for isolation of crude MP fraction from biocrude.

Isolation parameters	Average Yield*
Solvent extraction	
TSF, wt%	47.5 ± 3.2
Raffinate, wt%	52.5 ± 3.2
Distillation of TSF	
MP-rich distillate, wt%	19.3 ± 1.9
Bottoms, wt%	28.9 ± 2.3
Solid Residue, wt%	0.0
Step efficiency (solvent extraction and distillation) **, wt%	
Guaiacol	87.1 ± 4.2
4-methylguaiacol	84.8 ± 2.8
4-ethylguaiacol	87.8 ± 3.6
Eugenol	99.5 ± 1.3
4-Propylguaiacol (dihydroeugenol)	92.3 ± 6.5
Isoeugenol (cis and trans)	78.2 ± 4.4

*On initial biocrude mass and toluene-free basis. **Separation efficiency for both toluene extraction and distillation steps.

Figure 2 shows the distribution of the concentration of the individual MPs in the biocrude, the TSF, and the MP distillate. High separation step efficiencies for the extra are also achieved after the toluene extraction and the distillation steps; on average, 87.1% guaiacol, 84.8% methylguaiacol, 87.8% ethylguaiacol, 99.5% eugenol, and 92.3% 4-Propylguaiacol were isolated from the biocrude. The separation of isoeugenol was relatively less efficient with an average efficiency of 78.2%. Overall, the isolation approach reported herein eliminates residue formation during distillation; instead, a heavy fraction that flows freely at 40 °C is obtained. In contrast, a direct distillation of the biocrude without the solvent extraction step results in significant residue formation as reported herein and other work.[26]

Alkaline Extraction of the Crude MP Distillate

Alkaline solvent extraction is used as the next separation step to further concentrate the MPs. In a conventional alkaline extraction method, phenolics are recovered at a pH below 7 as illustrated in **Scheme 3**. This approach is however nonselective and limits separation of different phenolics with different functionalities. The conventional methodology entails increasing the pH of the sample to 14 using a strong basic aqueous solution (NaOH solution). This enables extraction of neutral compounds such as ketones and aromatics with an organic solvent. The phenolic compounds in the form of phenolates (salts) and other polar compounds remain in the aqueous phase raffinate. To recover the phenolics, the raffinate is neutralized to a pH lower than 7 using aqueous mineral acid (HCl), and the phenolics are extracted with organic solvent. Further acidification on the remaining aqueous solution to a pH of about 1.5 is done to recover the remaining compounds. The limitation of using the conventional method in concentrating the MP-rich distillate fraction is demonstrated first. Using the traditional protocol, basification of the MP-rich distillate to a pH of 14 with aqueous NaOH is performed to extract the neutral components with MTBE. In the subsequent steps, the remaining fraction is acidified/neutralized to a pH of 6 to recover the phenolic product using MTBE. The remaining compounds in the aqueous raffinate is recovered at a pH of 2. Analysis of the recovered phenolic product showed a marginal increase (25%) in the concentration of the MPs; the phenolic product had a mass concentration of 58 wt% for the MPs. The low purity level realized is because the extracted product still had

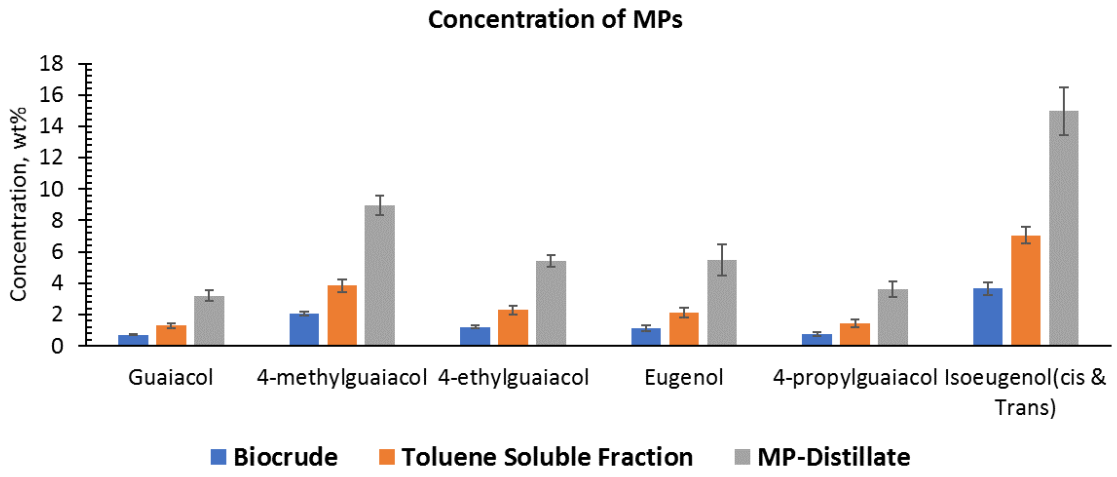
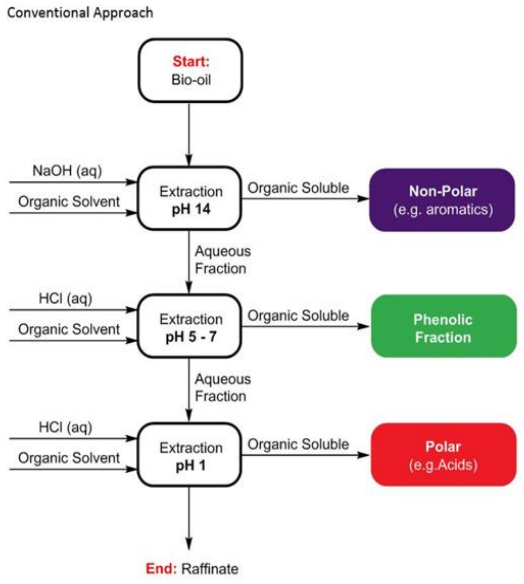


Figure 2. Average concentration of the individual MPs in the biocrude, TSF, and the MP distillate.



Scheme 3. Conventional alkaline extraction method for separation of phenolics.

significant concentration of other phenolics (alkylphenols, catechols, anisoles, and other phenolics with ketone, aldehyde, and carboxylic acid functionalities).

Effect of pH on MP separation during alkaline extraction

To enable selective separation of the MPs during alkaline solvent extraction, we exploited minor differences between the acid strength of the phenolics that are present in the crude MP distillate. As shown in **Figure 3**, the pKa values for the major phenolics in the distillate vary between 4 and 11[38]. Specifically, the targeted MPs have pKa values between 9.88 and 10.3[38]. The pKa for most of the higher alkylphenols is above 10.3. Besides, several of the functionalized phenolics have pKa less than 9.88, such as pyrocatechol (9.6), acetovanillone (8.17), coniferyl aldehyde (9.52), vanillin (7.4), and homovanillic acid (4.36). Based on these pKa values, we hypothesized that the various phenolics could be extracted at different pH levels instead of the traditional pH level of 6–7. The major challenge of the hypothesis is that the simple phenols (phenol, methylphenol,
ethylphenol, and propylphenol) have pKa values in the same range of the targeted MPs. Therefore, those simple phenols, if present, are bound to co-extract out with the MPs.

The development of the selective alkaline extraction started with screening studies to identify the pH range where most of the MPs could be selectively extracted into the organic solvent (MTBE) phase after basification. The experiment entailed sequential extraction of the basified MP-rich distillate at the following pH levels: 12.5, 10.1, 9.0, 8.1, 7.0, 6.0, 5.0, 3.5, and 1.5. The procedure is such that in the first step, the pH of the MP distillate is increased to 12.5 with 50 wt% aqueous hydroxide solution, and then solvent extraction is performed with MTBE. After that extraction, the pH of the aqueous raffinate is reduced to 10.1 with 6N HCl, and solvent extraction with MTBE is performed. The extraction is continued with subsequent pH reduction of the aqueous raffinate and solvent extraction with MTBE untilled the last pH level of 1.5. Of note, all the extracts recovered at pH above 7 are neutralized further with 6N HCl to free any phenolates prior to solvent recovery and product analysis. The MTBE solvents are then recovered to obtain the products at pH levels screened. Also, It is worth pointing out that MTBE was selected for the initial screening due to its low boiling point, poor aqueous solubility, and high MP solubility (a comparison of extraction solvents can be found in the next section). The extraction product yield distribution in **Figure 4** shows that most (about 69 wt%) of the mass of the MP distillate were recovered above a pH of 7. Importantly, the compositional analysis of the extracts showed that most of the MPs were extracted above pH 8. Table 2 shows the breakdown of the cumulative separation step efficiencies at pH 12.5, 10.08, and 9.03. The MPs (4-propylguaiacol, eugenol, 4-ethylguaiacol, and 4-methylguaiacol) with pKa values > 10 had higher extraction efficiencies at pH 12.5 than guaiacol and isoeugenol with pKa values < 10. In contrast, the MPs with lower pKa had higher recoveries at pH 10 than those MPs with higher pKa. In general, the targeted MPs are selectively separated from other phenolics with lower pKa values such as benzenediols, guaiacyl acetone, pyrocatechol, coniferyl aldehyde, vanillin, acetovanillone, and homovanillic acid.

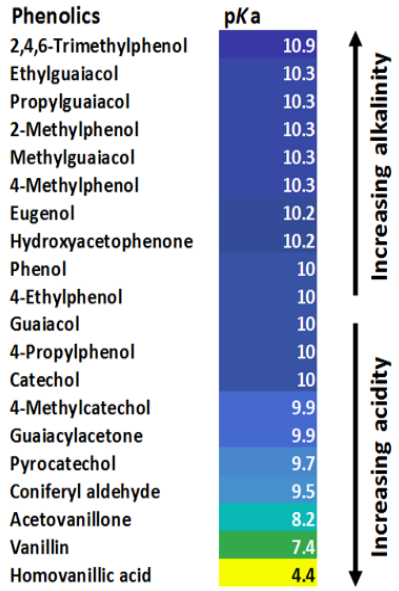


Figure 3. pKa values of major phenolics in the MP distillate.

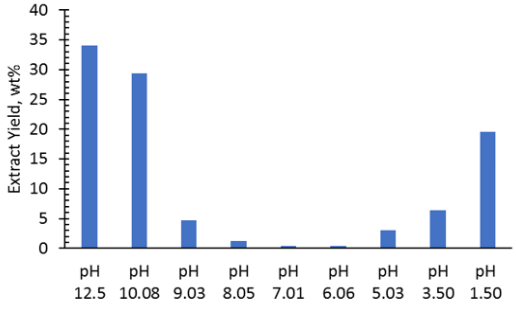


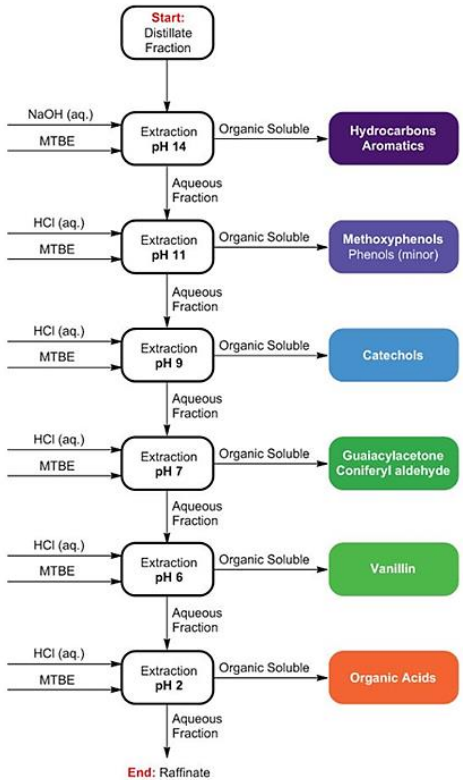
Figure 4. Extraction product yield distribution by pH

MP compound	*Extraction step efficiency, wt%		
	pH 12.5	pH 10.1	pH 9.03
Guaiacol	27.6	62.0	7.9
4-Methylguaiacol	47.7	44.7	4.8
4-Ethylguaiacol	53.6	39.9	3.7
Eugenol	50.1	43.3	4.4
4-Propylguaiacol	58.0	35.2	3.2
Isoeugenol (cis and trans)	34. 8	57.1	5.7

Table 2. Alkaline extraction step efficiency for each MP at different pH levels

*One (1) extraction experiment performed sequentially at the various pH levels. The alkaline separation step efficiencies are cumulative.

The screening extraction at the various pH values indicates that the MPs can be recovered at a pH greater than 10. Therefore, further sets of experiments were performed to independently evaluate the extraction of the MPs at pH levels of 12.5, 12.0, and 11.5. Three separate experiments were performed non-sequential manner. In each experiment, the MP distillate was basified to a pH of 14.5 with 50 wt% NaOH solution, and MTBE extraction was performed to remove the neutral compounds. After extracting the neutral components, 6N HCl solution was used to lower the pH of the aqueous raffinate to the targeted levels (12.5, 12.0, or 11.5) for extraction of the MPs with MTBE in the respective experiments. Finally, the pH of the aqueous raffinate in each experiment was decreased to 10 with 6N HCl solution, and extraction with MTBE was performed to evaluate the alkaline separation efficiencies. In summary, the sequences of extractions were Exp 1: pH levels of 14.5, 12.5, 10; Exp 2: pH levels of 14.5, 12.0, 10; and Exp 3: pH levels of 14.5, 11.5, 10. Also, in these experiments, MTBE solvent extraction was done three times at each pH level to enhance the separation. The extracts were neutralized before solvent recovery and product analysis. **Table 3** shows the extraction efficiencies for the targeted MPs at each pH level (12.5, 12.0, and 11.5) after removing neutral components at pH levels of 14.5. The results indicate that except for guaiacol, all the MPs of interest can be recovered at pH 11.5 with more than 90 wt% efficiency.



Scheme 4. Illustration of selective alkaline extraction for separating different phenolics

Table 3. Alkaline extraction step efficiency for each MP at different pH levels.

MP compound	*Extraction step efficiency, wt%		
	pH 12.5	pH 12.0	pH 11.5
Guaiacol	55.8	64.8	78.4
4-Methylguaiacol	81.2	87.8	97.8
4-Ethylguaiacol	82.6	87.8	95.7
Eugenol	91.1	92.4	94.4
4-Propylguaiacol	93.3	94.4	96.1
Isoeugenol (cis and trans)	83.4	88.9	97.1

*Three (3) extraction experiments performed independently at each pH level. The alkaline extraction step efficiency at each pH level experiment are independent.

The extraction for guaiacol was the lowest (56 wt%) at the 12.5 pH level and highest (about 78 wt%) at pH 11.5. As shown in Figure 5 and Figure S1, almost complete extraction of the eugenols is achievable at pH 11.5. Of note, simple phenols co-extract with the MPs as anticipated. Nonetheless, the extracts at pH 10 contained predominantly catechols and other multifunctional phenolics like 4-hydroxy-3-methoxy-benzeneacetic acid, 1,2-dimethoxy-4-n-propylbenzene, 1-(4-hydroxy-3-ethoxyphenyl)-ethanone, 4-(2-hydroxyethyl)-2-methoxyphenol, and 4-hydroxy-3-methoxybenzaldehyde. After extraction of the MPs, the various phenolics could also be extracted separately, as illustrated in Scheme 4. The approach reported herein is much more selective compared with the conventional alkaline extraction (**Scheme 3**) that allows all the phenolics to be recovered a singular pH level. For instance, if desired, catechols and other functionalized phenolics could be selectively extracted after recovering the MPs.

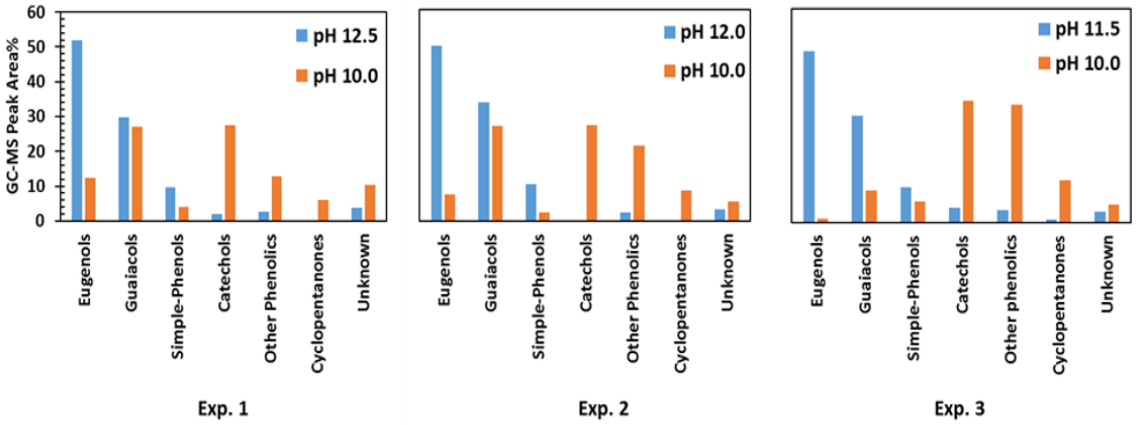


Figure 5. GC-MS peak area distribution of different phenolics at different pH levels in three different experiments.

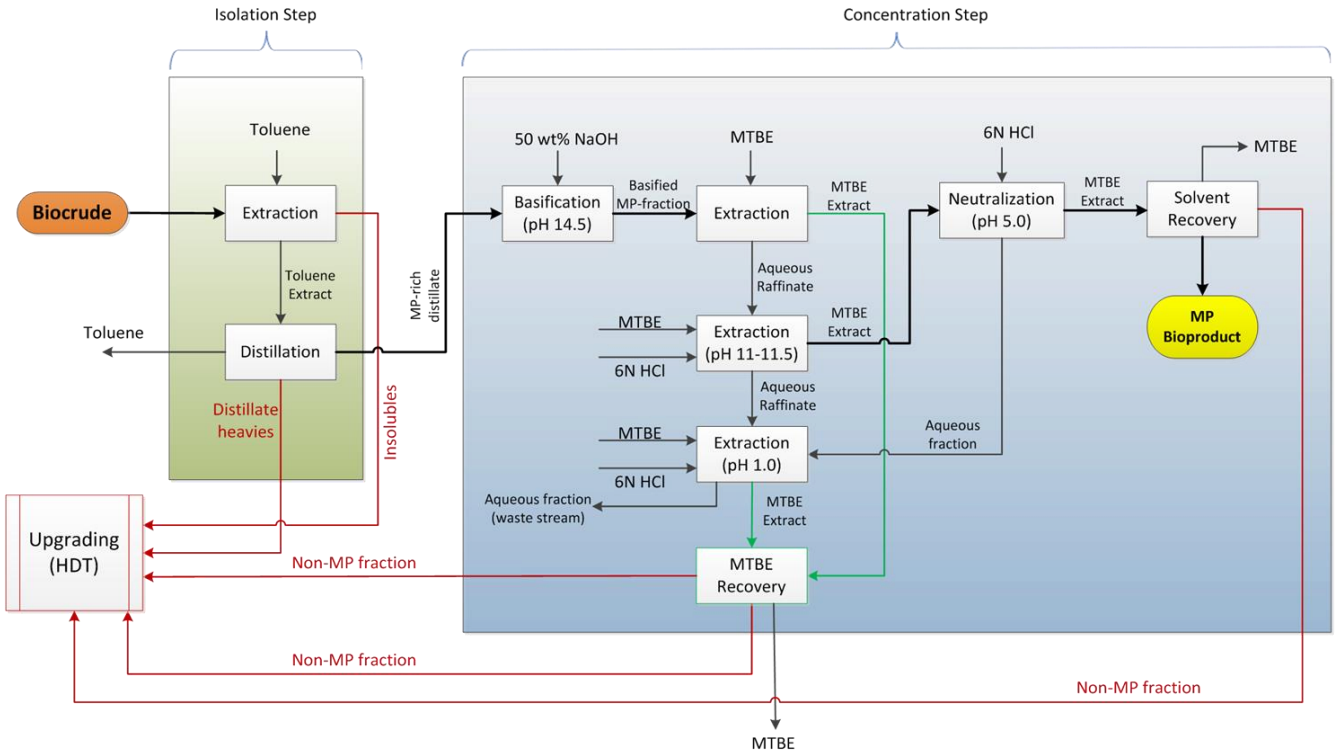
Effect of solvent

To obtain the highest extraction efficiency and MP concentration, various solvents were screened for the alkaline extraction. At the extraction pH of 10 or greater, the majority of the phenolics are expected to be in their deprotonated form, thus limiting their extraction by organic solvents. Most likely, complete protonation of the phenolates is not achieved at the extraction conditions used; rather, it appears that adding the solvent to the aqueous phase establishes an equilibrium between the phenolates and the free phenolics, and as a result, the free phenolics can be extracted as observed using MTBE. We examined three additional organic solvents, DCM, MIBK, and hexane, to explore the effect of solvent polarity on MP miscibility. The solvents rank from hexane as the least polar to MTBE, DCM, and MIBK as the most polar. Extraction of the MPs was performed at pH of 11.5 following the previously discussed approach; 50 wt% NaOH solution and 6N HCl were used. Extraction with hexane had the lowest efficiency (67 wt%). Unexpectedly, the extraction with MIBK resulted in a relatively moderate efficiency (81.4 wt%). The DCM solvent provided high extraction efficiencies (98.7 wt%) for the MPs, comparable performance to MTBE (>90 wt%). Although MIBK had the highest polarity, the MPs likely were less soluble in the solvent compared to MTBE and DCM. Extracting with DCM required longer residence times for phase separation and necessitated more safety precautions for halogenated solvents. Above all, the chemical saftety, environemtal impact, and sustainability of the solvents are all important selection factors. Therefore MTBE was considered the preferred choice of solvent for the extraction of the MPs.

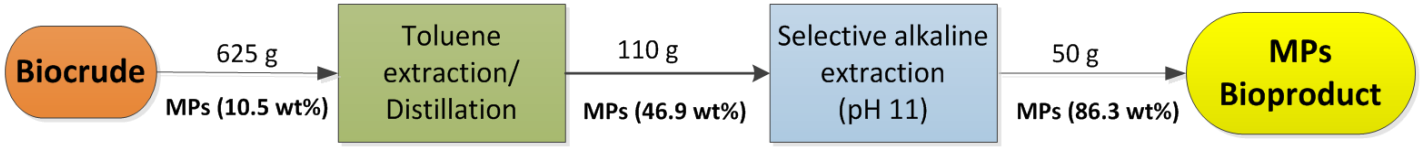
Summary of the Overall Separation Process

Scheme 5 illustrates the overall strategy developed to extract primarily monofunctional MPs from biocrude. The process is composed of two major steps: first, isolation of a crude mixture of MPs by solvent extraction/distillation and second, concentration of the MPs by alkaline extraction. In the primary isolation step, toluene is mixed with the biocrude to extract mainly a less-reactive and stable fraction containing the MPs that is fractionally distilled to recover the toluene solvent and obtain a crude MP distillate boiling between 165 °C and 315°C. After this step, a selective alkaline extraction is used to concentrate the MPs based on their acidic strength. The methodology involves increasing the pH of the MP distillate fraction with a strong alkaline aqueous solution to a pH of about 14 where neutral compounds such as ketones, aromatics, and possibly some simple phenols with higher pKa value >10.35 can
be extracted with MTBE. The pH of the raffinate is then reduced to a pH level of 11–11.5, where the targeted MPs (9.8 ≤ pKa ≤ 10.3) can be extracted with MTBE, as a mixture composed of neutral and basic MPs. The pH of the aqueous raffinate is then lowered to a level where the remaining components with lower pKa values < 9.8 such as multifunctional phenolics and organic acids are recovered with the organic solvent. The enriched MP extract is then neutralized to free any phenolates. MTBE solvents are then recovered to obtained individual step products and final bioproduct of MPs. In this work, the titrant reagents are not recovered. Nonetheless, in an actual operation, it would be economically and environmentally important to recover both NaOH and HCl if possible. The application of a circular concept would minimize waste generation in the overall process. One option could be to perform electrolysis on the aqueous solution after the last alkaline extraction step to regenerate the base and the mineral acid used.

Scheme 6 summarizes the outcome of three experiments illustrating the overall process developed to isolate and concentrate exclusively monofunctional MPs from pyrolysis liquids. The overall separation efficiency of the process depends on the individual separation step efficiencies. From the three experiments, the average separation efficiency at the isolation step was 78.6 wt%, and the average separation efficiency of the concentration step was 83.6 wt%. Thus, the overall average separation efficiency was 65.8 wt% and the average recovered bio-product purity was at 86.3 wt%. Clearly, the overall separation efficiency is significantly affected by the efficiencies at each separation step and more importantly at the initial isolation step. Hypothetically, 90% separation step efficiency at both the isolation and the concentration steps will guarantee an overall efficiency over 75 wt%. Also, the purity of the bio-product needs improvement. The challenge for further purification of the concentrated bio-product is the removal of alkylphenols. Potentially, a downstream operation such as a simulated moving bed (SMB) technology could be integrated to the developed separation method for further purification to



Scheme 5. Block flow diagram of the entire developed separation process.



Scheme 6. Block flow diagram showing average mass of material and their respective mass concentration of MPs in and out of each separation step

achieve an MP bioproduct with higher purity levels as required for certain applications.

Conclusions

Past studies have focused on separating phenolic compounds from pyrolysis liquids into one fraction, and in many cases, the isolated phenolic fraction contains various kinds of phenols. Specifically, alkaline extraction for the isolation of phenolic compounds has not focused on exclusive extraction of MPs. In this work, we have demonstrated that slight differences between the acid strength (i.e., acid dissociation constant) of the phenolics in pyrolysis liquids could be used to some extent to selectively separate out different functional classes of phenolics. The integration of solvent extraction, distillation, and a selective alkaline extraction enabled the isolation and concentration of guaiacols and eugenols from biocrude without rendering the remaining fraction unusable for downstream processing into biofuels and other bio-product intermediates. Overall separation efficiencies up to 70 wt% and concentration of MPs up to 88 wt% can be achieved.

Conflicts of interest

There are no conflicts to declare.

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A Selective Extraction Method for Recovery of Monofunctional Methoxyphenols from Biomass Pyrolysis Liquids

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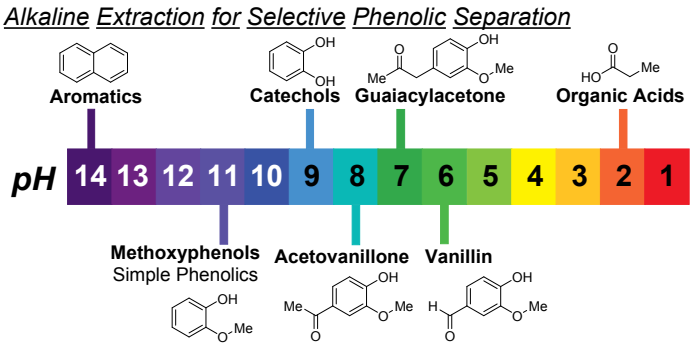

Text: Selective method for separation of phenolic compounds from biomass pyrolysis liquids.