Compositional analysis of bio-oils from hydrothermal liquefaction of tobacco residues using two-dimensional gas chromatography and time-of-flight mass spectrometry

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Abstract
Sustainable energy from biomass is one of the most promising alternative energy sources and is expected to partially replace fossil fuels. Tobacco industries have normally rid their processing residues by landfilling or incineration, affecting the environment negatively. These residues can be used to either extract high-value chemicals or generate bio-energy via hydrothermal liquefaction. The main liquid product or bio-oil consists of highly complicated chemicals. In this work, the bio-oil from hydrothermal liquefaction of tobacco processing residues was generated in a batch reactor at biomass-to-deionized water ratio of 1:3, temperature of 310°C, and 15 min residence time, yielding the maximum liquid products for more than 50% w/w. The liquid products were analyzed, using two-dimensional gas chromatography and time-of-flight mass spectrometry (GC × GC/TOF MS). This technique allowed for a highly efficient detection of numerous compounds. From the results, it was found that hydrothermal liquefaction can cleave biopolymers (cellulose, hemicellulose, and lignin) in tobacco residues successfully. The hydrothermal liquefaction liquid products can be separated into heavy organic, light organic, and aqueous phase fractions. By GC × GC/TOF MS, the biopolymers disintegrated into low molecular weight compounds and classified by their chemical derivatives and functional groups could be detected. The major chemical
derivative/functional groups found were cyclic ketones and phenols for heavy organic and light organic, and carboxylic acids and N-containing compounds for the aqueous phase. Additionally, by the major compounds found in this work, simple pathway reactions occurring in the hydrothermal liquefaction reaction were proposed, leading to a better understanding of the hydrothermal liquefaction process for tobacco residues.

Keywords
Biomass conversion, bioenergy, hydrothermolysis, wet pyrolysis, fuel technology, chemical engineering, agricultural residues

Introduction
The anxiety of depleting fossil fuels has been manifested, and it results in a growing desire for energy sustainability. Biofuels from conversions of lignocellulosic biomass are expected to be used alongside conventional fuels.\(^1,2\) Lignocellulosic biomass is considered a universal carbon resource on the Earth, in which it can be recycled from sunlight to chemical energy via CO\(_2\) and water in the presence of plant photosynthetic systems.\(^3,4\)

In the past decades, sustainable development, based on biorefining of biomass to produce value-added biochemicals, such as alcohols, furfurals, and organic acids, and to substitute fossil fuels (in views of hydrogen, methane, ethanol, and butanol productions), has increasingly been of considerable interest.\(^5\) However, these technologies have to be continually improved and as efficient as possible to generate valuable products.

Agricultural biomass is one of the most promising alternative energy resources, as it is abundant and renewable naturally. Apart from upgrading processes such as ionic liquid pretreatment\(^6\) and torrefaction\(^7\)–\(^9\) where some unwanted properties of biomass are addressed, it can be converted to biofuels and biochemicals using modern thermochemical platforms such as gasification,\(^10\) pyrolyses,\(^11,12\) and hydrothermal processing.\(^13\) In Thailand and many countries, tobacco is a secondary-income-generating crop traditionally used for manufacturing cigarettes. Resulting tobacco residues, a very high moisture content type of biomass, are usually rid by landfilling or incineration, causing noxious emissions and affecting environmental wellbeing. Tobacco residues consist mainly of cellulose, hemicellulose, and lignin, and therefore, they could be also converted to biofuels or valuable biochemicals in similar fashions to others.\(^14\)–\(^16\) Among those mentioned thermochemical processes, hydrothermal liquefaction (HTL) is an interesting technology for the conversion of tobacco residues to biofuels and/or chemicals. HTL is generally undertaken in the presence of water at high temperatures and pressures, for example, 250–350°C and 5–20 MPa.\(^17\) This process imitates the geological formation of fossil fuels underground for many years, but the HTL reaction occurs within minutes or hours to produce liquid bio-oils from biomass. It is also environmentally friendly and not limited to dried biomass materials.\(^18\) The HTL mechanism is relevant to the changes in the water structure to hydrophobic compounds, a high polar property, leading to effectively dissolving components in lignocellulosic biomass. The H\(^+\) and OH\(^-\), which are generated at a subcritical condition, can promote the hydrolysis reaction and catalyze the biomass decomposition, generating new chemical compounds. These new products are considered as high-value bioenergy and biochemicals, and further application.\(^19\)
To investigate chemical components of bio-oils, in general, a one-dimensional gas chromatography-mass spectrometry (GC-MS) technique is usually applied. Wang et al. investigated HTL of waste Tetra Pak and found that the bio-oils were composed mainly of ketones, phenolics, esters, and alcohols. Qian et al. reported that HTL of sludge provided long-chain aliphatic hydrocarbon moieties and aliphatic acids. Many complex reactions take place during the HTL of biomass to generate bio-oil products. Durak and Genel who studied HTL of *Xanthium strumarium*, also applied GC-MS to analyze the resulting liquid products. They found that the liquid products could be identified for over 70 chemical compounds. This illustrates that a complicated process of biomass degradation occurs during the HTL. Biomass is a mixture of cellulose, lignin, hemicellulose, carbohydrates, lipids, and proteins. Therefore, the complex reactions during the HTL process can be from simultaneous decompositions of those components inside the biomass, making the discovery of all chemicals in the bio-oil analyzed by GC-MS difficult. In other words, the one-dimensional GC-MS may only provide limited information. It may not be able to identify molecules with high boiling points. To receive better resolution and detectability, a higher-dimensional GC-MS technique could be used. In this point of view, two-dimensional, GC×GC/time-of-flight (TOF) MS has been demonstrated to give highly effective detection and identification of chemical compounds in organic liquids more than conventional GC-MS. To the authors’ knowledge, deploying GC×GC/TOF-MS for HTL liquids from tobacco residues remains rare.

Therefore, in this work, chemical components of liquids obtained from HTL of tobacco residues were investigated, using an advanced GC×GC/TOF MS technique. With scrupulously consideration, all the components found were differentiated, based on their derivative/functional groups. A possible pathway for the HTL reactions during the decomposition of tobacco residues was also proposed.

**Materials and methods**

**Materials**

Tobacco processing residues were kindly supplied by the Tobacco Authority of Thailand’s Denchai redrying plant in Phrae, Thailand. Deionized (DI) water was used as the solvent for the HTL reactions. Dichloromethane (DCM), acetone, and methanol with over 99% purity were used in product extractions and chemical composition analysis processes.

**HTL procedure and bio-oil extraction**

Initially, tobacco residues were sieved and collected only those in the range of 3–5 mm in diameter. Any dirt and impurities were manually removed. The sample was then dried in an oven at 105°C for 24 h. About 20 ± 1 g of the dried sample mixed with ∼60 ± 1 g DI water was loaded into an autoclave reactor with an internal volume of 200 mL (∼60 mm diameter). The HTL of tobacco residues was carried out at a temperature of 310°C, 15 min residence time, and an initial pressure of 1 atm (the reaction pressure was...
expected to be $\sim 10$ MPa close to the saturated state of water). Solid-, liquid-, and gas-phase products were separated and obtained after the process. The gas product was relieved to the atmosphere at room temperature. The solid and liquid products were separated by filtration. The solid was washed with acetone, then the crude acetone was evaporated at 60°C to obtain a heavy organic (HO) liquid fraction. The liquid product was extracted at least three times with an equal quantity of DCM. The DCM solution was evaporated at 38°C to obtain a light organic (LO) liquid fraction. The other was evaporated at 65°C for 12 h for removing DI water to obtain an aqueous phase (AP) fraction. The solid yield was about 17.1% w/w, while the HO, LO, and AP yields were 29.6, 9.8, and 12.7% w/w, respectively. For more details on a carbon balance, please see our previous work.\textsuperscript{27}

**GC×GC/TOF MS analysis**

Chemical compositions of all three-liquid products were analyzed by GC×GC/TOF MS, which consisted of a Gerstel autosampler, an Agilent GC model 7890B, a Leco MS model Pegasus 4D-C. The HO and LO were dissolved with acetone, while the AP was done with methanol. Each dissolved sample of about 1 μL was injected into the column at the split ratio of 10:1. The transfer line and injector were maintained at 280°C, while the ion source was kept at 250°C. A first-dimensional nonpolar column was Rxi-5 MS (Restek Corp., 30 m, 0.25 mm ID, 0.25 μm df) and a second-dimensional polar column was Rxi-17MS (Restek Corp., 1 m, 0.15 mm ID, 0.15 μm df). For the HO product, the first oven was started at 60°C (hold 1 min), increased to 220°C at the rate of 10°C/min, and heated up to 280°C (hold 10 min) at the rate of 5°C/min. The modulation period was 3 s. For the LO product, the first oven was started at 60°C (hold 1 min), increased to 265°C at the rate of 5°C/min, and heated up to 280°C (hold 2 min) at the rate of 40°C/min. The modulation period was 4 s. For the AP product, the first oven was started at 60°C (hold 1 min), increased to 100°C (hold 2 min) at the rate of 5°C/min, heated up to 115°C (hold 2 min) at the rate of 5°C/min, increased to 125°C (hold 5 min) at the rate of 5°C/min, and heated up to 300°C (hold 5 min) at the rate of 10°C/min. The modulation period was 4 s. For all the products, the second oven was maintained at $+5°C$ above the temperature of the first oven. The modulator temperature was $+20°C$ relative to the second oven. The helium carrier gas in the columns was used at 1 mL/min. GC×GC-TOF MS data were processed with software version 4.70.7.0 optimized for Pegasus. The components were identified by comparing their fragmentation pattern to a standard NIST mass spectral library.

**Results and discussion**

**Physical appearance**

Figure 1 shows the physical appearance of the liquid products from HTL of tobacco residues, in which the liquid products can be divided into three fractions: HO, LO, and AP. The HO was obtained from acetone washing of HTL solid residues. It was condensate-like, highly viscous, and in darkish black color. The LO was extracted by DCM. It was less viscous than the HO, and its color was darkish brown. The AP was more
fluid and in light yellowish color. These liquid products were from the disintegration of lignocellulose (cellulose, hemicellulose, and lignin) and other biomass fractions, depolymerized into smaller fragments.28

Chemical components of the liquid products

Chemical components of all the liquid products were reported, based on the relative percentage of the peak areas. They were classified by their functional groups and chemical derivatives (i.e. cyclic ketones, phenol derivatives, and furfural derivatives),29 as shown in Figure 2. For the HO and LO products, the phenol derivatives were the most abundant compound groups, followed by cyclic ketones and N-containing compounds. For the AP product, the main functional groups were carboxylic acids, N-containing compounds, and phenol derivatives. This indicated that the HO and LO products were clearly different from the AP for both physical appearance and chemical components. More interestingly, the HO contained aliphatic hydrocarbons, which were from cyclic and long chains, differing from the LO significantly.

The liquid products obtained were one of the evidence for the deconstruction of lignocellulosic biomass into low molecular weight compounds. It can be claimed that the liquid products were compounds that occurred during the pathway of generating new chemicals of both solid- and gas-phase products. Figure 3 depicts the carbon number distribution of the HO, LO, and AP, which may be used to imply how lignocellulose deconstruction occurred. The HO and LO were found to mainly contain low carbon compounds, compared to the AP. Furthermore, they can be also categorized by their groups of carbon number: gasoline (C7–C11), kerosene (C12–C15), and diesel (C16–C21),30 which can be used to recognize the way for utilizing or upgrading of these organic liquid products.

Figure 1. Liquid products from HTL of tobacco residues: (a) heavy organic (HO), (b) light organic (LO), and (c) aqueous phase (AP).
Possible pathway for HTL of tobacco residues

Figure 4 presents the possible pathways for HTL of tobacco residues. Note that chemicals shown in Figure 4 were only examples of the molecules detected and identified for the classification of the liquid products based on functional groups and chemical derivatives.

Figure 2. Classification of the liquid products based on functional groups and chemical derivatives.

Figure 3. The proportion of carbon number of liquid products.
presence of similar components that occurred via the same reaction pathway. Our simple pathways were proposed to improve understanding in a reaction network during the HTL, as it was rather difficult to describe all the multi-fold reactions.

Generally, the HTL process is gradually increased with temperature and pressure, leading to an increase of ionic product of water ($K_w$) in a neutral condition at sub-critical water. The initial increase of $K_w$ proliferates $H^+$ and $OH^-$, as known acid/base catalyzes resulting in hydrolyzation of lignocellulosic biomass. Cellulose, hemicellulose, and lignin, three main biopolymers in biomass are deconstructed to oligomers and monomers, respectively. Each monomer unit further reacts in many reaction pathways, potentially generating gas-phase products, for example, CO$_2$, CO, CH$_4$, and H$_2$. Along with gases, liquefied small organics are formed as this can be summarized in terms of lignin-, carbohydrate-, protein-, and nicotine-derived compounds.

Lignin is large and complex polymer in plants. It can be destroyed into oligomers and then hydrolyzed to their monomers. Lignin monomers, such as guaiacol, creosol, catechol, and phenol, were found in organic liquids. It is worth noting that the phenolic derivatives are more likely present in the organic HO and LO phases, extracted by

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**Figure 4.** Possible simple pathway of generating organic liquids from tobacco residues.
organic solvents, rather than in the AP. This was observed from relative percent peak areas of phenol derivatives (see also in Figure 2).

The carbohydrate represents both cellulose and hemicelluloses. There are a lot of monosaccharide types when being depolymerized and hydrolyzed. However, they were not indicated and identified in the organic liquids. Monosaccharides were forward reactions, possible in many pathways to deference compound groups. They would be rearranged and dehydrated to produce cyclic esters, furfural/furan derivatives, cyclic ketones, and organic acids. The cyclic esters were the elementary compounds from our pathways, which can further react and become furfural/furans. Some of them would be intermediates that have further reactions with other chemicals to generate furfural/furan derivatives. The main chemical derivatives detected were benzene and phenol, which may probably react with lignin monomer and unsaturated intermediates. Moreover, the furfural/furan intermediates might then continue to be one of the most compound detection of the cyclic ketone. The organic acids were the main relative chemical compounds detected in the AP that can undergo unsaturated intermediates pathway.

The portions of nicotine were N-containing compounds, which can only be from the feedstock. Nitrogen was a slightly small content in the feedstock, but it can contribute a lot of reactions. Maillard reaction typically came from the degradation of sugars and amino acids. The production of Maillard reaction was N-containing heterocycles, such as indole, pyrrole, pyridine, pyrazine, or pyrrolidinedione (or derivatives from them), revealed in an analysis of organic liquids in previous studies. The organic acids were not only produced from monosugers, but also obtained from the amino acids via deamination. Amides were also detected, in which they would be produced from the decarboxylation of amino acids. Some nitrogen heterocyclic compounds had a structure similar to nicotine, which can be decomposed to pyridine or rearranged and cyclized to derived nitrogen heterocyclic compounds.

In addition, HTL could encourage free-radical reaction because of decreasing water density. It could degrade and create unfamiliar compounds, not following general reaction pathways. The long-chain, cyclic, and aromatic hydrocarbons or complex chemicals would be derived from the free-radical pathway. This pathway was difficult to be examined from experimentation, but more convenient for computer simulation.

The relatively large percentage peak area compounds are listed in Table 1. The chemicals were reported following possible precursors to point out how lignocellulosic biomass was cleaved. Although cyclic ketone was the main chemical derivative from carbohydrates in both the HO and LO, acetic acid and 4-hydroxybutyric acid from carboxylic acid showed a large peak. This pointed out that cyclic ketone was plenty. Lignin-derived compounds were their monomer units. It can be referred that chemicals bigger than monomer units were not in organic liquids or present at below analysis detection. These chemical compounds were commonly found from HTL of biomass, in agreement with Capraris et al. More interestingly, the AP can recover specific chemical configurations, such as (2S,3S)-(+)2,3-butanediol and (S)-(+)2',3'-dideoxyribonolactone, which were high-value chemicals.
Table 1. The large relative percentage peak areas of each precursor-derived compound in organic liquids.

| Carbohydrate-derived compounds | Lignin-derived compounds | Protein and nicotine-derived compounds |
|---------------------------------|---------------------------|----------------------------------------|
| HO                              | Area (%)                  | Compound Area (%)                      | Compound Area (%)                  |
| Acetic acid                     | 14.9                      | 2-Methoxyphenol 9.4                    | 3-Pyridinol 1.2                     |
| 2-Methyl-2-cyclopentenone       | 1.7                       | 2-Methoxy-4-methylphenol 4.5           | N-Methylpropionamide 1.1           |
| 2,3-Dimethyl-2-cyclopentenone   | 2.8                       | 1,2-Dihydroxybenzene 2.5               | 12,3-Trimethyl-1H-indole 1.1       |
| LO                              |                           |                                        |                                       |
| 3-Methyl-2-cyclopentenone       | 9.6                       | 2-Methoxyphenol 8.7                    | N-Methylsuccinimide 1.6            |
| 4-Hydroxybutyric acid           | 5.4                       | 1,2-Dihydroxy-3-methoxybenzene 7.4     | N-Methylacetamide 1.5              |
| 2,3-Dimethyl-2-cyclopentenone   | 4.9                       | Phenol 7.1                             | N-Methylpyrrolidone 0.5            |
| AP                              |                           |                                        |                                       |
| Acetic acid                     | 59.3                      | Hydroquinone 1.4                       | 3-Pyridinol 4.1                    |
| 4,5-Dihydro-5-methyl-2(3H)-furanone | 1.6                 | 1,2-Dihydroxy-3-methoxybenzene 0.4     | 3-Hydroxy-2-methylpyridine 0.5     |
| (2S,3S)-( +)-2,3-Butanediol     | 1.2                       | 1,2-Dihydroxybenzene 0.4               | 2-Pyrrolidone 0.4                  |

HO: heavy organic; LO: light organic; AP: aqueous phase.
Conclusion

HTL was successfully applied to convert tobacco residues to organic liquids. The organic liquids including HO, LO, and AP products of about 50% w/w dry basis of biomass were acquired at a condition of 310°C, 15 min residence time, and 1:3 biomass-to-water ratio. The HO, LO, and AP fractions were 57, 19, and 24%, respectively. By GC×GC/TOF MS, the composition of the organic liquids was analyzed. The main components of the HO and LO were found to be cyclic ketones and phenol derivatives, while those of the AP were carboxylic acids and N-containing compounds. Simple pathways of producing bio-oils from HTL of tobacco residues were proposed and discussed which may improve understanding of this process.

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