ผลของ K_3PO_4 ต่อไฮโดรเทอร์มัลลิควิแฟคชันของใบอ้อยในตัวทำละลายร่วมเอทานอล-น้ำ

นายกง กวน เหงียน

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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EFFECT OF K_3PO_4 ON HYDROTHERMAL LIQUEFACTION OF SUGARCANE LEAVES IN ETHANOL-WATER CO-SOLVENT

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A Thesis Submitted in Partial Fulfillment of the Requirements
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Thesis Title	EFFECT OF K_3PO_4 ON HYDROTHERMAL LIQUEFACTION OF SUGARCANE LEAVES IN ETHANOL-WATER CO-SOLVENT
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งานวิจัยนี้ได้ทำการศึกษาการผลิตน้ำมันดิบชีวภาพด้วยไฮโดรเทอร์มัลลิควิแฟกชันจากใบอ้อย โดยใช้ตัวทำละลายร่วมเอทานอลและน้ำในเครื่องปฏิกรณ์แบบกึ่งต่อเนื่อง การทดลองนี้ใช้อุณหภูมิในการทำปฏิกิริยาระหว่าง 280 – 320 องศาเซลเซียส ในภาวะความดันที่เหมาะสมเป็นเวลา 2 ชั่วโมง ตัวแปรที่ส่งผลต่อปริมาณผลิตภัณฑ์ที่ได้ทำการศึกษา คือ อัตราการไหล อุณหภูมิ อัตราส่วนของตัวทำละลายร่วม จากการทดลองพบว่าภาวะที่สามารถผลิตน้ำมันดิบชีวภาพที่ได้มากที่สุดในกรณีใช้ตัวเร่งปฏิกิริยาโปแตสเซียมฟอสเฟต (K_3PO_4) คือ อุณหภูมิ 300 องศาเซลเซียส อัตราการไหล 0.5 มิลลิลิตรต่อนาที และใช้สารละลายโปแตสเซียมฟอสเฟตร้อยละ 1 โดยน้ำหนัก เติมลงในตัวทำละลายร่วมระหว่างเอทานอลและน้ำที่อัตราส่วน 50/50 โดยปริมาตร ซึ่งให้ร้อยละน้ำมันดิบชีวภาพ 30.63 แต่การเพิ่มขึ้นของตัวเร่งปฏิกิริยาและอัตราการไหลทำให้ผลผลิตน้ำมันดิบชีวภาพมีปริมาณน้อยลง ซึ่งผลที่ได้เหมือนกับกรณีที่ใช้น้ำเป็นตัวทำละลายเดี่ยวและมีตัวเร่งปฏิกิริยา การใช้ตัวเร่งปฏิกิริยาอัลคาไลน์สามารถลดองค์ประกอบที่เป็นกรดในน้ำมันดิบชีวภาพได้ชัดเจน ซึ่งตรวจสอบได้จากการไตเตรดคาร์ลฟิสเชอร์ และการไทเทรตกรด นอกจากนี้ในกรณีที่ไม่ใช้ตัวเร่งปฏิกิริยา การใช้น้ำเป็นสารละลายร่วมกับเอทานอลในอัตราส่วน 25/75 โดยปริมาตร อุณหภูมิ 300 องศาเซลเซียส อัตราการไหล 1 มิลลิลิตรต่อนาทีให้ผลดีที่สุดโดยให้ร้อยละผลได้น้ำมันดิบชีวภาพ 29.47 การวิเคราะห์แบบแยกธาตุแสดงให้เห็นว่าตัวเร่งปฏิกิริยาส่งผลทำให้ปริมาณออกซิเจนของน้ำมันดิบชีวภาพลดลงทำให้ค่าความร้อน (HHV) มีค่าเพิ่มขึ้น ในขณะเดียวกันโปแตสเซียมฟอสเฟตในตัวทำละลายร่วมมีผลทำให้สารประกอบเฟอร์ฟูรอลหายไป และเพิ่มอนุพันธ์ของเอสเธอร์ ซึ่งตรวจสอบได้จากผลการวิเคราะห์แก๊สโครมาโตรกราฟี – แมสสเปกโตรสโคปี (GC –MS)

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CONG QUAN NGUYEN: EFFECT OF K_3PO_4 ON HYDROTHERMAL LIQUEFACTION OF SUGARCANE LEAVES IN ETHANOL-WATER CO-SOLVENT. ADVISOR: ASST. PROF. PRAPAN KUCHONTHARA, Ph.D., 86 pp.

The purpose of this project is to study the production of biocrude derived from hydrothermal liquefaction (HTL) of sugarcane leaves using co-solvent in a semi-continuous flow reactor. Experiments were carried out at a temperature range of 280 - 320 ^{o}C with appropriate pressures for 2 hours holding time. The effects of operating parameters, including various flow rates, temperatures, proportion of co-solvent and an addition of alkaline catalyst (K_3PO_4) on the oil yield were comprehensively investigated. The maximal biocrude$_1$ (dichloromethane-soluble fraction) was roughly 30.63% at a temperature of 300 ^{o}C, a flow rate of 0.5 ml/min in mixture of ethanol and water (50/50 v/v) with 1 wt% K_3PO_4. In contrast, an increase in either catalytic concentration or a flow rate lessened the yield of biocrude$_1$. The similar observation was also recorded in case of pure water with the presence of K_3PO_4. Besides, the blend of water and ethanol (25/75 v/v) dominated entirely as the most suitable ratio of co-solvent for the HTL in this system, yielding the biocrude$_1$ of 29.47% at 300 ^{o}C, a flow rate of 1 ml/min and without the catalyst. As regards the usage of alkaline catalyst, a drastic reduction of acid compounds existed on the ingredient of biocrude$_1$ was also determined by Karl-Fischer titration and total acid number titration. Furthermore, the elemental composition analysis outcomes indicated that the catalyst played a role as the deoxygenating agent, resulting in dwindling the oxygen content and enhancing HHV of the biocrude$_1$. The dispersion of K_3PO_4 into co-solvent was attributed to both a disappearance of furfural components and an upturn in ester derivatives as apparently depicted by gas chromatography/mass spectroscopy (GC-MS) technique.

Department:	Chemical Technology	Student's Signature	....
Field of Study:	Chemical Technology	Advisor's Signature	....
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LIST OF ABBREVIATIONS

A	Ash content
CHN analysis	Elemental composition (Carbon, Hydrogen, Nitrogen) analysis
DCM	Dichloromethane
DTG	Differential thermal gravimetric
daf. basis	Dry-ash free basis
FC	Fixed carbon
GC-MS	Gas chromatography-mass spectroscopy
HTL	Hydrothermal liquefaction
HHV	High heating value
^{1}H NMR	Proton nuclear magnetic resonance
ID	Inside diameter
KF	Karl-Fischer
OD	Outside diameter
TAN	Total acid number
TGA	Thermal gravimetric analysis
VM	Volatile matter
v/v	Volume/volume
wt%	Weight percent

CHAPTER 1

INTRODUCTION

1.1. Background and motivation

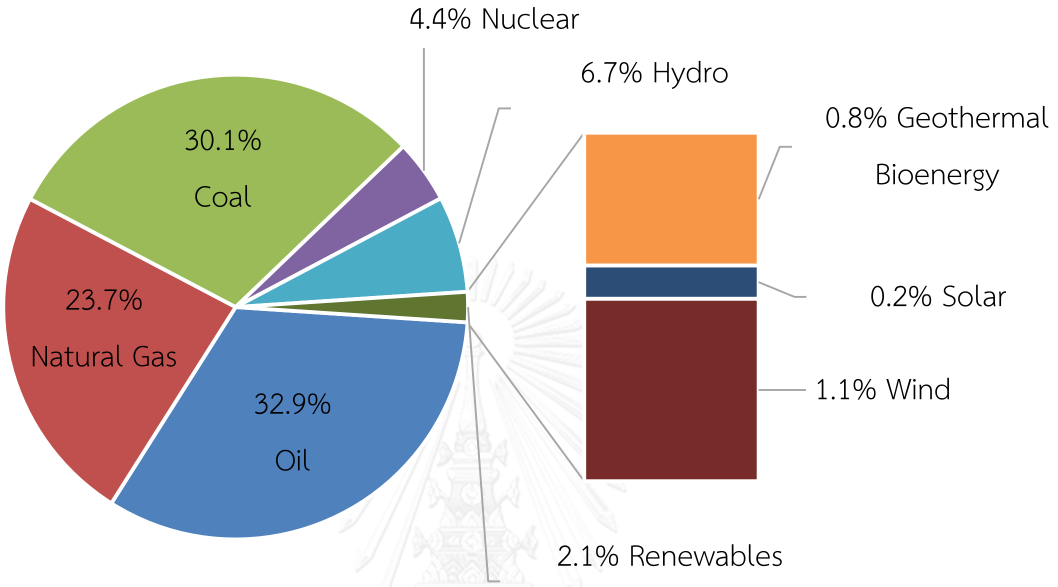

Figure 1.1. The global primary energy consumption in 2013 [1]

In a recent report from BP statistical review of world energy, global primary energy consumption grew by 2.3% in 2013. Figure 1.1 indicated that the conventional fossil fuels account for 86.7% of world primary energy consumption, with oil (32.9%), coal (30.1%) and natural gas (23.7%) as the major fuel [2]. However, the significant decrease in fossil fuel resources in coming time in conjunction with the undoubted increase in greenhouse gas emissions prompt researchers to explore safe and sustainable alternatives. Besides, the widespread availability of biomass derived from residue crops also urges scientists to figure out appropriate methods to produce biofuels and valuable chemicals.

Especially, as reported by Moodley et al. [3], sugarcane leaves, are an abundant lignocellulosic material worldwide. Annually, approximately 20 million tons of sugarcane are produced by South Africa, 65 million tons in Thailand and 590 million tons from Brazil, illustrating its importance as to the economic crops. Sugarcane leaves have constituted up to 40% of the harvested biomass [3]. In the past, there were a few of environmental troubles such as the air pollution, emitted noxious gases, unbalanced ecosystems that stemmed from directly combustion of agricultural residue. Another important thing is that the lignocellulose feedstock is very low-priced and nearly unlimited capacity as well as sidestep of competitive global food chains. As a result, it is perfectly feasible for the hydrothermal conversion processes to convert the environmental burden into valuable energy.

Hydrothermal liquefaction (HTL) or direct liquefaction terminology used in the 1970 – 1980s is a complex pyrolysis process in hot compress water or suitable solvents [4]. Ordinarily, the process is carried out at low temperatures (from 250 ^{o}C until 400 ^{o}C) and high pressures (10 - 25 MPa). Besides, it is an environment-friendly technology. Biocrude production manufactured from the HTL has typically lower oxygen which constitutes to better qualities of oil than the other techniques. Besides, applying catalysts for the HTL process is the newest resolution in order to enhance a proportion of recoverable biocrude as well as boosting characteristics of the one. Therefore, this thesis is concentrated on assessing an impact of alkali-based catalyst, herein K_3PO_4, on the HTL of sugarcane leaves in ethanol-water co-solvent.

1.2. Objectives

There are two main objectives in this research, namely:

1. To study biocrude production from hydrothermal liquefaction (HTL) of sugarcane leaves in a semi-continuous flow reactor.
2. To investigate the effect of K_3PO_4 and operating parameters on the HTL of sugarcane leaves in ethanol-water co-solvent.

1.3. Scope of the research

The experimental procedure was concretely conducted in the following steps:

1. Review the publications related to this topic.
2. Prepare all tools, equipment and chemical reagents required for the experiments.

3. Prepare raw materials, sugarcane leaves (grinding and sieving for suitable size of sample).
4. Test the properties of biomass sample by TGA, proximate and ultimate analyses.
5. Study an effect of operating parameters on the HTL of sugarcane leaves:
    - Ratios of co-solvent (ethanol/water): 100/0, 25/75, 50/50, 75/25, 0/100.
    - Flow rates of co-solvent: 0.5 ml/min, 1 ml/min.
    - Reaction temperatures: 280 ^{o}C, 300 ^{o}C, 320 ^{o}C with correspondence pressure between 6 MPa and 20 MPa.
    - Catalyst concentration (K_3PO_4): 0 wt%, 1 wt% and 3 wt%.
6. Characterize the amount of water and organic acid of the obtained biocrude by the Karl-Fischer titration, total acid number titration, respectively; its elemental composition by CHN analyzer and the composition using gas chromatography/mass spectroscopy technique (GC-MS).
7. Summarize the experimental outcomes and write dissertation.

1.4. Expected benefit

To obtain the suitable condition for the hydrothermal liquefaction of sugarcane leaves in the presence of ethanol-water co-solvent.

CHAPTER II
THEORY AND LITERATURE REVIEWS

Prior to the main work, this is a comprehensive picture of the fundamental knowledge of the hydrothermal liquefaction (HTL) technique as well as some recent researches. It provides a good understanding of what the liquefaction is and the reasons why it will becomes expected technology in coming time.

2.1. Biomass

Biomass is the biological materials assembled from diverse resources, such as forestry, agricultural wastes, industrial processing residues, etc. Comparing to the fossil fuels, biomass has much lower heating values, though it has been considered to be renewable sources because of CO_2 neutral. The CO_2 would be produced during some conversion processes and then, it is conceivable to be retaken by photosynthesis during a period growth of biomass [5]. Regarding some literature reviews, we are likely to divide into four fundamental groups, namely:

I. Agricultural and forestry residues: silviculture crops.
II. Herbaceous crops: weeds, napier grass.
III. Aquatic and marine biomass: algae, water hyacinth, aquatic weeds, plants, sea grass beds, kelp and coral reel.
IV. Wastes: municipal solid waste, sewage sludge, animal and industrial waste, etc. [6].

Otherwise, there are some researches standing up for differences in the compositions and structures of biomass in order to separate into categories in Figure 2.1 comprising of lignocellulosic biomass, microalgae and organic waste. In there, lignocellulose is the most utilizable feedstock to produce biocrude through liquefaction due to an auxiliary yield of the agriculture, many source provisions.

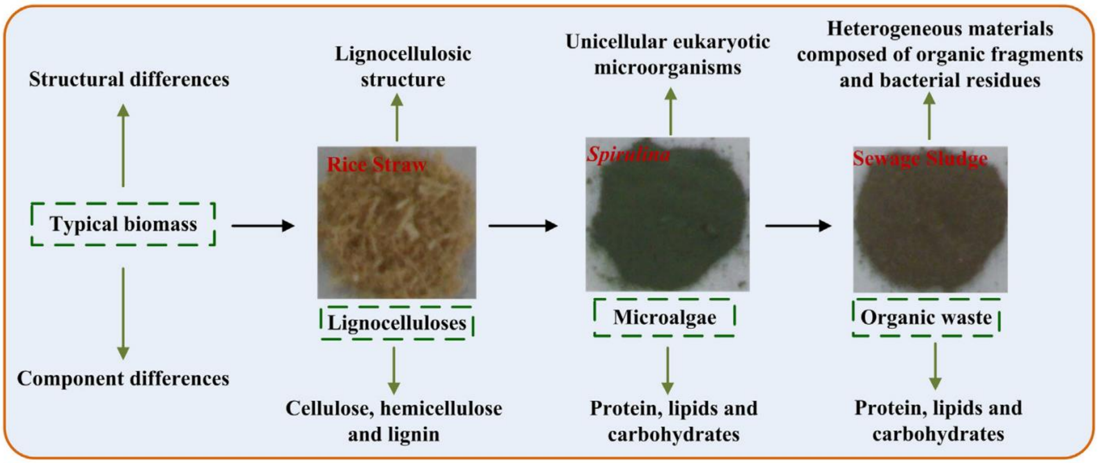

Figure 2.1. The classification of typical biomass [7]

2.2. Liquid biofuels

Nowadays, the world is facing up to exhaustedly conventional energy in conjunction with the global warming and higher level of environmental pollution. Liquid biofuels produced from several renewable sources and even waste organic substrates are emerging as one of the most expectably alternative energy sources in the future. The comparison of advantages between biofuels and fossil fuel were definitely depicted in Table 2.1.

Table 2.1. Profits of using biofuels over fossil fuels [8]

Fuel type	Biofuel	Fossil fuel
Emissions	Biofuels are carbon neutral since most of the carbon involved in the ones has been already absorbed from the atmosphere.	Fossil fuels discard the greenhouse gases (CO_2, CO, NOx, etc.), which trap the Sun's ray inside the Earth's atmosphere and cause global warming.
Renewability	Raw materials used to manufacture biofuels can be produced continuously.	The fossil fuels will be entirely exhausted in the next few decades
Safety	Producing biofuels through farming is highly safe.	Exploiting the fossil fuels under the Earth is a risky process.

	Spills of biofuels can be harmlessly dismantled and absorbed naturally.	Oil spills induce a serious effect on environment as long as they are not biodegradable.
Economic enhancement	The development of biofuel declines imports, create more jobs and keep the economy out of the energy crisis.	Depending on the fossil fuels imports affects adversely the economy growth and national security.

Another beneficial outcome is that it is desirable depletion of the greenhouse gas emission in transportation (i.e. from 90% and 70% compared to gasoline) with only humble modification of vehicle technology and an existing fuel distribution infrastructure [9]. So far, biofuels have been over three generations, namely:

- First-generation biofuels bioalcohols (bioethanol) were realized by yeast (Saccharomyces cerevisiae) fermentation of plant sugars and starches gained from harvest, including sugarcane (Saccharum sp.) sugar beet, and corn (Zeamays) [10, 11]. Nonetheless, this generation revealed several adverse effects on the greenhouse gas, biodiversity, land use, water usage because of an upward demand of utilized fertilizer to grow crop. As a result, the higher nitrogen and phosphorus content were apparently detected on the ground and surface water [12].
- Second-generation liquid biofuels were referred to biological or thermochemical processing from lignocellulose as a more sustainable fashion. This is because of a fact that the one is truly carbon neutral or even carbon negative under its influence on CO_2 concentration. Otherwise, the lignocellulose materials are either non-edible residues of crop production with lower cost or whole plant biomass (e.g. grasses or trees) being a sidestep of main food-chain [13].
- Marine biomass would belong to “Third-generation of biofuel”, including microalgae, macroalgae and cyanobacteria. An important thing is that there

is no change characteristic of the biofuels in those generations. However, the material sources are changed in each one [8, 14]. Interesting aspects of algal biofuel production were comprehensively included high productivity, nonfood feedstock, unnecessarily cultivable land, motivation of carbon dioxide captured.

In summary, it is simple to distinguish apparently between the second-generation and the third-generation feedstock in Table 2.2.

Table 2.2. Basic differences between lignocellulose and algal biomass [10]

Lignocellulose	**Algal Biomass**
Major ingredient of cellulose, hemicellulose and lignin.	Mainly composed of proteins, lipids, carbohydrates, nucleic acids, and lack the structural component lignin.
Contain predominantly cellulose I_β (monoclinic crystalline form).	Algal cells enclose cellulose I_α (triclinic crystalline form).
Rely on fresh water.	Grow in saline, brackish, and wastewater.
Multicellular, specialized cells for specific functions.	Single-cell microorganisms.

2.3. Lignocellulosic biomass

As mentioned in the beginning, the main components of lignocellulose are cellulose, hemicellulose and lignin. Concretely, cellulose is constructed from more than 10,000 glucose units by means of β-1,4 glycosidic bonds [15]. The D-glucose is linked each other in a long-chain homogeneous polysaccharide as drawn in Figure 2.2. These structures are stabilized by hydrogen linkages between adjacent the D-glucose units in same strand.

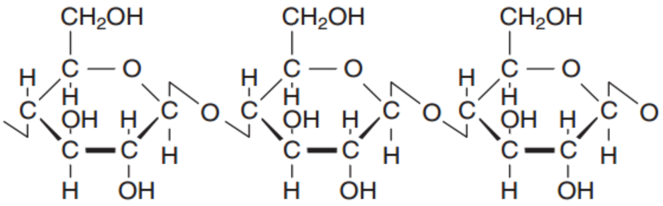

Figure 2.2. The chemical structure of cellulose

Hemicelluloses are built up from different hexoses (C6-sugars) and pentoses (C5-sugars), occasionally attached uronic acids by polysaccharides. It has backbones of 1, 4- β-linked sugar units which were morphologically correlated with cellulose and lignin in plant cell. Thus, these polysaccharides are generally heterogeneous [16].

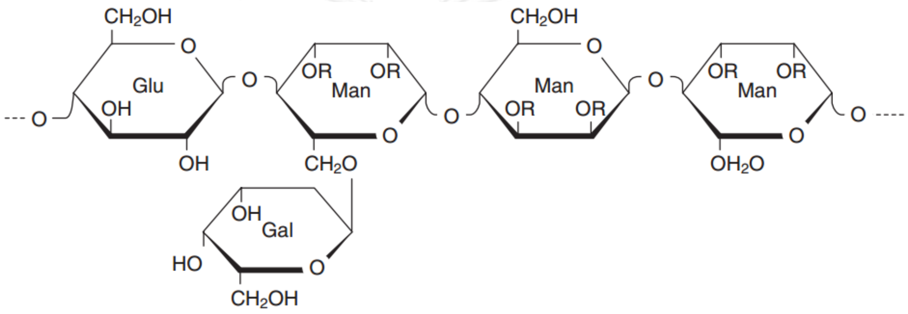

Figure 2.3. The chemical structure of hemicellulose

The chemical structure of lignin is more complex than the others. It is randomly assembled by a network of aromatic compounds.

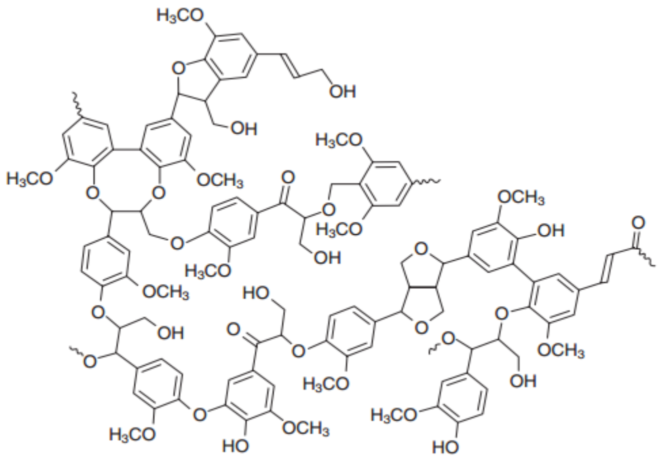

Figure 2.4. An example of chemical structure of lignin

In the ingredient of lignocellulose, cellulose is generally the largest fraction, continued to hemicellulose, lignin, ash, etc. [17].

There are several advantages of those materials enumerated in following characteristics:

- Renewability: whenever the solar radiation is still survival, the photosynthesis of green plants will keep working on. It is a meaning that lignocellulose will never exhausted.
- Richness: the widespread resources on earth were estimated around 2×10^{11} tons per year.
- Alternative: Obviously, it is likely to substitute fossil fuels via thermochemical conversion processes into liquid and gaseous fuels or other chemicals. As a result, it could suppress dependence on traditional energy.
- Cleaning performance: Environmental quality will be considerably improved owing to less emissions of SO_2, CO_2, and other pollutants than the others. Moreover, almost previous researches symbolized that they have not caught up SO_2 released during lignocellulose bio-refining yet. The CO_2 eliminated will be equal to the dose of CO_2 consumed by photosynthesis process, hence CO_2 emitted from the application of conversion processes might be zero.
- Degradation: It is probably to degrade lignocellulose by microbes, so there are no solid waste and environmental pollution [18].

2.4. Sugarcane leaves

Sugarcane (scientifically named saccharum officinarum) is an important part of agricultural economy of many countries including Thailand. Globally, as some statistical reports, sugarcane production is around 2×10^9 tons per year, therein Thailand occupies 1×10^8 tons per year (approximately 10.7 thousand million square-meters) corresponding to 5% of the world production [19].

Accordingly, a ratio of production and sugarcane residue (including leaves and tops) was 0.302 [20]. As a consequence, the leftover part has been eliminated 6.6×10^8 tons per year. Unit now, the resolution ways of sugarcane leaves has become a remarkable headache as to manufacturers and researches. On the other hand, prior to harvesting of sugarcane in Thailand, the removal of the leaves by formerly combusting causes serious air pollution and lower price of sugarcane stalk because it had been absolutely useless to industrial process [21]. Those urged scientists on developing the thermochemical conversion methods to handle it and that is also a reason why the hydrothermal liquefaction was taken out.

Biologically, there are two main segments in sugarcane leaves, including sheath and blade as described in Figure 2.5. It is substantially differed by a blade joint. The sheath wraps completely an internode of the stalk.

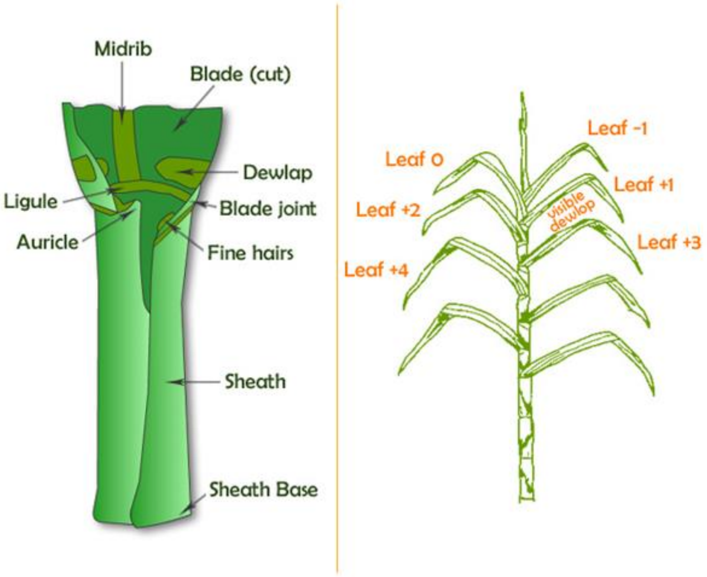

Figure 2.5. The structure of sugarcane leaves

In common, surface area of a leaf was approximately estimated 0.5 square meter. Each one has ten green leaves on the stalk, depending on growing condition and environment. The calculation method of how many leaves was mentioned by Kuijper's system, and it was quoted by Casagrande (1991) later. Concretely, the first leaf with clearly visible dewlap at top of the stalk is attributed as +1. Until bottom, the numbers will be +2, and +3, respectively.

There were roughly 36% of the cellulose, hemicellulose (21%) and lignin (16%) in dried sugarcane leaves residue according to harvesting season and different countries [22]. It is the worthy witness to classify sugarcane leaves into the lignocellulose group.

2.5. Hydrothermal liquefaction

To the best of knowledge, there are four main types of thermochemical conversion process, including torrefaction, pyrolysis, gasification and liquefaction [23]. Notwithstanding, this thesis is only concentrated on the hydrothermal liquefaction (HTL) of sugarcane leaves in a semi-continuous reactor. Ordinarily, the process is executed at low temperatures (from 250 ^{o}C until 350 ^{o}C) and high pressures (between 10 and 25 MPa) [4, 24]. The region for liquefaction process is roughly covered by the two red dash lines in Figure 2.6.

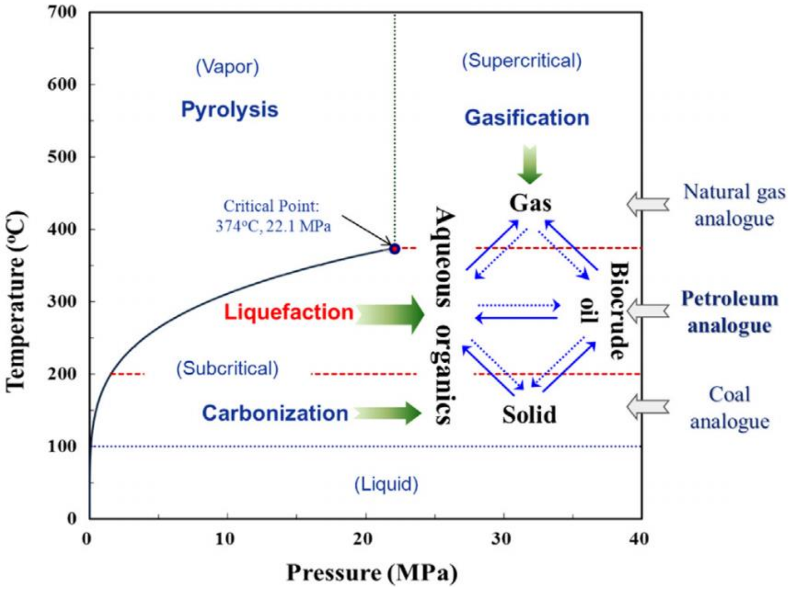

Figure 2.6. The hydrothermal processes diagram [25].

During the HTL, biomass is converted into fundamental products being gas, liquid, including aqueous phase and oil phase, which is often called biocrude, and solid residue or char. As a rule, scientists hypothesized the key reaction pathways for the liquefaction of biomass as unveiled in Figure 2.7.

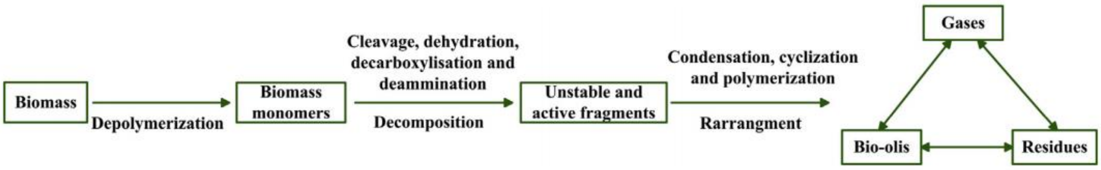

Figure 2.7. The basic reaction pathways for the liquefaction of biomass [7]

The scheme illuminates that there are three particular steps for the sake of converting biomass into the beneficial products. It is uncomplicated for us to interpret reaction mechanisms, namely:

I. Depolymerization of the biomass into monomers.

II. Disintegration of biomass monomers by cleavage, dehydration, decarboxylization and deamination forms light fragments which are unstable and active.

III. Rearrangement of light fragments through condensation, cyclization and polymerization progresses to new compounds [7, 26].

After fully delving into thermochemical conversion routes, it is feasible to conclude that the HTL possesses more auspicious than others. At first, both gasification and pyrolysis require dried biomass as feedstock, and those occur in an extreme environment with temperatures from 500 ^{o}C to 1400 ^{o}C [27]. The HTL is perceived as direct liquefaction of biomass in presence of water and perhaps some catalyst to convert materials into the valuable yield at temperatures of less than 400 ^{o}C [16]. Secondly, it is an environmental-friendly technology. Thirdly, the liquid product or so-called biocrude manufactured from that process has typically lower oxygen and thus the qualities will be better than that of the other techniques [28, 29].

2.6. Effect of operating parameters

First of all, we are not able to let essential role of water pass unnoticed with respect to the HTL process. It is impossible for water to react with organic molecules at 20 ^{o}C and 1 atm in common. Nevertheless, most of its properties are going to change entirely when water is at sub/supercritical conditions. Almost all of water properties are substantially changed such as lower density, fewer and less stable hydrogen bond, downturn solvent polarity. For instance, at supercritical conditions (e.g. 550 ^{o}C and 20 MPa), water behaves as a nonpolar organic solvent like pentane with good solubility for organic components, gases and restricted solubility for salts [30] that were perfectly highlighted in Figure 2.8.

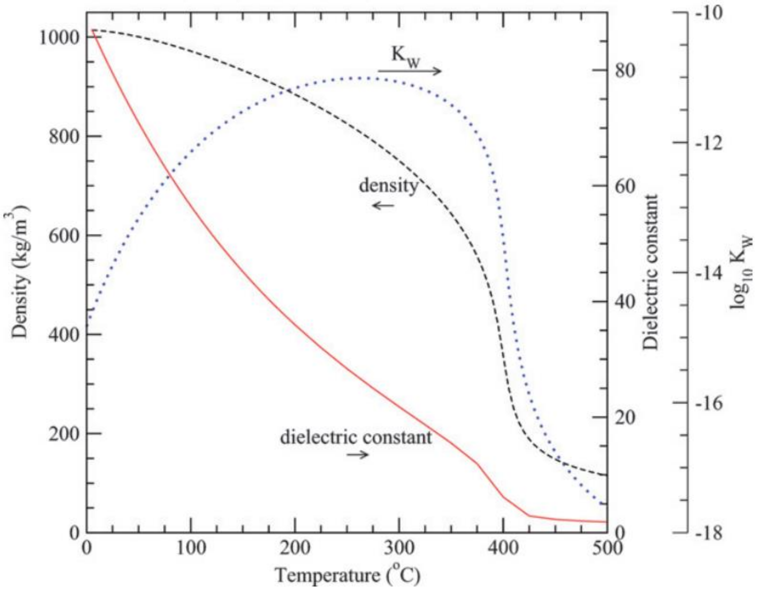

Figure 2.8. Density, static dielectric constant, and ionic product of water at 30 MPa as a function of temperature [31].

Water could be divided into H^+ or H^* radical and OH^- in the conditions of upward temperature [32]. That is a reason why organic compounds in biomass are effortlessly disconnected and rebuilt by intersecting H^+ or H^* radical with carbon linkages. Unstable inter-molecules are generated and revamped into hydrocarbons later.

A plenty of parameters directly impact on the HTL process in conjunction with product distribution. Biomass feedstock type is an important factor that plays a role in the disintegration mechanism since each component such as the lignin, hemicellulose and cellulose has a distinct behavior during the HTL. In general, the greater liquid yield is produced from biomass with the higher cellulose and hemicellulose content due to amorphous structure [10]. It is too difficult to disconnect lignin matrix mostly existed on residue fraction. We are able to determine a relationship between the topmost heavy oil as well as the minimal solid residue and lignin content in raw material in following equations [33].

$$\text{Maximum heavy oil yield} = 40.525 - 0.583 \times \text{lignin (wt\%)}$$

$$\text{Minimum a volume of solid residue} = \text{lignin (wt\%)} - 5.477$$

The feedstock type influences on physical characteristics of biocrude, for example oxygen, moisture content and viscosity, etc. Concurrently, it also affects chemical ingredient of oil product. This is a catalogue of popular compounds existing on liquid yield through the hydrothermal decomposition of hollocellulose: cellohexaose, cellopentaose, cellotriose, fructose, glucose, erythrose, glycolaldehyde, glyceraldehydes, pyruvaldehyde and furfurals [34].

Supplementary to that, another key parameter is temperature. It does not only controls the competition among hydrolysis, fragmentation and repolymerization reaction during this process, but also provides the activation energy for bond dissociation. From some researches, the biomass liquefaction would be constrained by further rising temperature. Therefore, too high temperature is not actually reasonable for both cost and efficiency of process. In common, there are two reasons to explain for these attitudes. Firstly, the formation of gases will dominate at upper temperature due to active of the secondary liquefaction step and Bourdard gases reaction. Secondly, the recombination reactions among free radicals to generate the char/tar will be in favor at that conditions owing to densely unsaturated substance [34]. Moreover, pressure seems to be the other aspect in order to maintain liquid state of solvent during the HTL and boost repolymerization reaction.

Although water is commonly employed as a solvent in the one, mixtures of alcohol-water have also been frequently utilized in many recent researches because of relatively mild reaction conditions and better quantity and quality of biocrude. Co-solvents showed profound effect on extraction and depolymerization process by means of specific interplay between solvent and solutes though hydrogen bonds and **π-π** interaction [7]. In there, the most attractive organic solvent is ethanol, and the process is also designed solvolysis [35]. There are many advantages of ethanol as solvent in the liquefaction process, namely:

- It is desirable to react with acidic compounds to generate diesel or esters by esterification reaction.
- One of the most important purpose is that coke formation will be remarkably inhibited as long as ethanol has the ability to dissolve high molecular weight liquid products.
- It also contributes to the stabilization of free radicals to drop the recombination reaction owing to its hydrogen donor capability.

- Otherwise, the HTL process with co-solvent (water/ethanol) will be conducted under milder reaction conditions since the critical temperature and pressure of ethanol are quite lower than others [36].
- Besides, the presence of organic solvents (e.g. ethanol, propanol, butanol, methyl ethyl ketone) also behaved positive impact on lower viscosity of heavy oil produced by the HTL of lignocellulose [37].

Additionally, the catalytic liquefaction process is the newest resolution for the sake of enhancing the proportion of recoverable liquid product as well as boosting the product quality. A lot of homogeneous catalysts have been employed in recent literatures such as base catalysts (e.g. Na_2CO_3, K_2CO_3, KOH and $Ca(OH)_2$), acid catalysts (e.g. H_2SO_4, CH_3COOH and HCOOH), and salt compounds (e.g. $FeSO_4$, $ZnCl_2$). Besides, heterogeneous catalysts were ZrO_2, anatase, ZSM5, Ce/HZSM5 and Ru/H-beta support. Most of those catalysts have not contributed expectably influence on quantity and quality of biocrude yet. Even descending in weight of biocrude appeared occasionally. A few of those catalysts showed specific effect on the conversion. None of previous works assures us which the actually applicable one for the HTL is.

In conclusion, the HTL is a great way to convert abundant biomass and waste sources into energy. Nevertheless, the process still comes up with some urgent problems and this is research’s responsibility nowadays.

2.7. Literature reviews

Firstly, Singh et al. [38] delved into the effect of alkaline catalyst on hydrothermal upgrading of wheat husk. The experiments were realized in a batch reactor at a specific condition (280 °C and 15 min) in presence of KOH and K_2CO_3 solution. Their results portrayed both KOH and K_2CO_3 exhibited remarkably positive influence on the HTL of wheat husk. Especially, the highest percentage of biocrude extracted by diethyl ether was 22% in case of K_2CO_3 catalyst. As stated in KOH catalyst, the yield of biocrude was massively lower, with only 14%, than the other. However, it was still much greater than without making use of catalyst (8% of conversion). Besides, other portions of oil gleaned from acetone and defined as heavy hydrocarbon were 16% and 9% corresponding to KOH and K_2CO_3, respectively. In non-catalyst condition, this oil fraction was obtained 20% and it was higher than that of others. As reported by authors, alkaline solutions were in charge of catalyst and hydrolytic reagent in the macromolecular degeneration.

Secondly, Xu et al. [39] investigated how the solid acid (HZSM5) and bi-functional (Ce/HZSM5) catalyst impact on the HTL of chlorella pyrenoidosa. Their results indicated that the utilization of HZSM5 catalyst gave 34.02% of biocrude and more than 40% of gas + loss, which closely resembled non-catalyst run. On the contrary, Ce/HZSM5 was better catalyst for the HTL of microalgae than the other. This is because it had a larger surface area and more catalytic sites after modification of Ce on HZSM5. It did not only elevate quantity of bio-oil, reaching 49.87% but also boost quality of the produced oil. The content of C and H accelerated while the N content would be tremendous recession. In conclusion, bi-functional catalyst offered some evidential benefits as to the liquefaction process.

It is the first time that a continuous tubular reactor was entirely explored the liquefaction of wheat straw by Patil and his colleagues [40]. The authors expected to seek the different affection among water, alcohol and co-solvent (e.g. ethanol and isopropanol). Furthermore, the influence of some parameters, including temperature, pressure, water-alcohol ratio and Ru (5%) on H-Beta supports also belonged to their scope. As reported by researchers, water-ethanol mixture (50/50 v/v) was the most effective at 300 ^{o}C and 100 bar and attained higher conversion than that of pure water, ethanol and the similar quota of water-propanol mixture. In case of utilizing 5 wt% Ru/H-Beta catalyst, there was a humble recession of oil conversion compared to the test with non-catalyst. In brief, it is worth recognizing that both bi-functional catalyst (Ru/H-Beta) and mixed water-propanol highlighted apparently adverse impact on the HTL of lignocellulosic biomass.

In order to enlarge practical application, the effect of solvent on the liquefaction of macro algae ulva fasciata was favored by Singh’s group [41]. Their outcome illustrated that alcoholic liquefaction prompted to much higher total oil product than the aqua one. For instance, biocrude was recovered 42% and 39% in existence of CH_3OH and C_2H_5OH, respectively. Nevertheless, there was only 3% of oil conversion when using water. It was claimed that alcohols were in charge of both solvent and hydrogen-donors generated during the HTL. In contrast, the solid residue was ramped up undesirably to 32% and 41% with CH_3OH and C_2H_5OH respectively in comparison of pure water (24%). It was terminated that methanol and ethanol played more powerful role in the HTL of macro algae than the pure water.

The other aspects of the HTL considered conscientiously by Hafez et al. [42] were the influence of resident time as well as reasonable sort of homogenous catalysts on rapid liquefaction of giant miscanthus in ethanol-water systems. The research found that the maximum oil yield was gained approximately 50% when the temperature and water/ethanol ratio were 280 ^{o}C and 50/50 v/v, respectively, along with the reaction time of 30 min. In addition, the solid residue would be denser as the downward reaction time from 20 min to 5 min. Concretely, it rose up to around 20% at short time (5 min) and plunged down beneath 10% at longer time between 15 min and 30 min owing to a lack of liquefaction time for producing a high bio-oil. Another main purpose was also investigated that the impact of four distinct catalysts such as formic acid, $ZnCl_2$ solution, trifluoroacetic acid (TFA), and Na_2CO_3 on the process. Unfortunately, all of such catalysts were not found to reinforce the conversion and heating value of bio-oil. On the contrary, the lower oil yield and the higher residue yield were come from the addition of TFA and Na_2CO_3.

Like the mentioned researches, Tekin et al. [43] sought remarkably the effect of water tolerant Lewis acids (e.g. $In(OTf)_3$, $Yb(OTf)_3$ and $InCl_3$) on the liquefaction of poplar wood at fixed temperature of 300 ^{o}C and 10 min resident time. Regarding their consequence, it was monitored that there was unfavorable influence on biocrude yields when water tolerant Lewis acids were employed as catalysts. Definitely, percentage of the biocrude without catalyst was 17.5% and it declined obviously to 12.4%, 14.27% and 12.06% in the addition of 0.5 wt% $In(OTf)_3$, $Yb(OTf)_3$ and $InCl_3$, respectively. Another deplorable thing is that the higher concentration adapted the lower the quantity bio-oil, namely the oil yield plummeted from 12.4% to 4.6% bio-oil with 0.5 wt% $In(OTf)_3$ and 10 wt% $In(OTf)_{3,}$ respectively. This was attributed to the strong detachment of liquid product in presence of water tolerant Lewis acids.

Yang et al. [44] considered employing acid catalysts (e.g. sulfuric acid and acetic acid) for direct hydrothermal liquefaction of undried macroalgae enteromorpha prolifera. The experiments were set up in autoclave at different ratios of biomass to water and reaction times. After that, the optimal point would be choose for finding out the impact of sulfuric acid and acetic acid on the HTL from 250 ^{o}C until 310 ^{o}C. The results suggested apparently that the volume of biocrude stemmed from whole catalytic experiments slumped to roughly 15 wt% in different temperatures, prolonged by accelerating extensively the solid residue from 1.61 wt% to 3.24 wt% when adding acid catalysts. According to the author's attitudes, most of those carbohydrate compounds were entirely broken to polar water soluble organics, or acid catalysts promoted the formation of solid residue from the unsaturated components by polymerization reactions. Nevertheless, both sulfuric and acetic acid did not light up comprehensively pessimistic catalysts on that process. The apparent witness was the better properties of biocrude when exercising acid catalysts than that of others. Especially, the viscosity of biocrude was sharply fallen down 600 cp when confronting with 1400 cp in non-catalyst situations.

Narari et al. [45] is the pioneer researcher in exploring the effect of combination between homogeneous and heterogeneous catalysts on the liquefaction of woody biomass in hot-compressed water and characteristics of biocrude. Those reactions were resulted in stirred reactor at 300 ^{o}C for 30 min so as to compare the activity of KOH, $FeSO_4.7H_2O$, K_2CO_3, MgO, synthetic hydrotalcite (HT), mixture of HT/KOH and ground colemanite (calcium borate mineral) as catalysts. Their outcomes demonstrated that whole catalysts executed the positive influence on percentage of the biocrude (30 – 40 wt%) compared to 19 wt% in case of blank test. It was noticeable that a peak of biocrude yield attained 39.5 wt% and 38.5 wt% by applying KOH and K_2CO_3 in liquefied experiments, respectively. It also suppress the solid residue from around 33 wt% to 12 wt%. The most restrictive ability of catalysts for biocrude conversion in this work are $FeSO_4.7H_2O$ and MgO in a following arrangement:

$$KOH > K_2CO_3 > Colemanite > HT/KOH > HT > FeSO_4 > MgO$$

As what I have just recommended, the HTL products are comprised of three mainly parts being gas, liquid including aqueous portion and oil phase and solid residue. Until now, many aspects were fully exploited, for example the effect of operating parameters, using catalysts or diversified feedstock resources on percentage of gas, biocrude and residue. Nonetheless, there have been few researches detailing how to deal with the aqueous phase, which is assigned to industrial contaminant. Therefore, the impact of temperature and aqueous fraction recirculation on the liquefaction of barley straw were firstly considered by Zhu et al. [46]. This work was carried out a wide range of temperatures from 280 °C to 400 °C and 10 wt% K_2CO_3 out of the feedstock as a catalyst in batch mode. After initial reaction accomplished, aqueous phase would be collected and filtrated for the purpose of substituting fresh water in further experiments. It was observed that the biocrude ascended strongly from 34.9 wt% to 38.4 wt% after three recirculation runs. This is due to the fact that the presence of organic matters in aqueous phase advocated thermal cracking rate of barley straw. Moreover, they might be associated with other radicals to form liquid products. Another interesting thing is that the extent of solid residue escalated significantly into 17.3 wt% after three cycles from only 9.2 wt% of the first run since repolymerization reactions might be accelerated by reactive substances remained in that fraction.

Finally, the positive effect of alkaline catalyst on the HTL of barley straw was affirmed twice by Zhu et al. [2]. There was a dramatic increase in percentage of the biocrude up to 34.85% with adding K_2CO_3 catalyst compared to only 17.88% without catalyst. Moreover, the solid residue was apparently reduced from 30% to 10% of the total product exercising the catalyst. Regarding author's explanation, this is obviously favorable because K_2CO_3 could react with water to generate its hydroxide and bicarbonate species, which were intermediate and assumed to be secondary promoter in the liquefaction process as attached by the equations below.

$$K_2CO_3 + H_2O \longrightarrow KHCO_3 + KOH$$

$$2KHCO_3 \longrightarrow H_2O + K_2CO_3 + CO_2$$

Moreover, the quality of biocrude was also enhanced. The high heating value (27.29 MJ/kg) and lower O/C molar ratio (0.26) was acquired when utilizing K_2CO_3 catalyst compared with the values of 24.87 MJ/kg and 0.34 in non-catalyst case. Thus, alkaline catalysts involving to improve in both quantity and quality of the biocrude would be the most suitable choice for the HTL of lignocellulosic biomass.

CHAPTER III

EXPERIMENTAL METHODOLOGY

3.1. Materials

Sugarcane leaves were directly collected from agricultural residue in Thailand. Subsequently, the raw materials would be used for the catalytic liquefaction process. All chemicals were used as received for whole experiments in Table 3.1.

Table 3.1. List of experimental reagents

Reagent	Function	Supplier
Tripotassium phosphate	Catalyst	Sigma-Aldrich, USA
Ethanol (99.9% purity)	HTL Solvent	QREC New Zealand
Dichloromethane (DCM)	Extraction solvent	ZEN POINT, Thailand
Acetone	Washing	ZEN POINT, Thailand
2-Propanol	GC-MS solvent	Merck, Germany
Diethyl ether	TAN solvent	QREC New Zealand
Hydranal methanol dry	KF solvent	Sigma-Aldrich, USA
Potassium hydroxide	TAN	Merck, Germany
Potassium hydrogen phthalate	TAN	Merck, Germany

3.2. Hydrothermal liquefaction of sugarcane leaves

3.2.1. Experimental setup

Firstly, sugarcane leaves as would be manually milled in a grinder and put it through a sieve in order to select suitable sizes (between 500 – 850 μm) for experiments. Secondly, the liquefaction reactions were carried out in a semi-continuous flow reactor as shown in Figure 3.1.

Concretely, sugarcane leaves (5 g) and inert material (quartz) were firstly added into stainless steel tube reactor (SUS316, OD: 0.5 inch, 29.5 inch of length and 0.083 inch of thickness). Thereafter, a variety of alkaline concentrations (K_3PO_4) in either water or ethanol/water co-solvent would be continuously passed through the reactor at a flow rate of 0.5 - 1 ml/min by the HPLC pump (PU-2080, JASCO Ltd) during 2 hours operating time. Pressure was adjusted using a back-pressure regulator (BP-66, GO regulator). The tube furnace (CTF12/65/550, Carbolite Ltd.) was used for controlling temperature. The liquefaction reactions were carried out between 280 °C and 320 °C corresponding to the pressures 10 - 20 MPa.

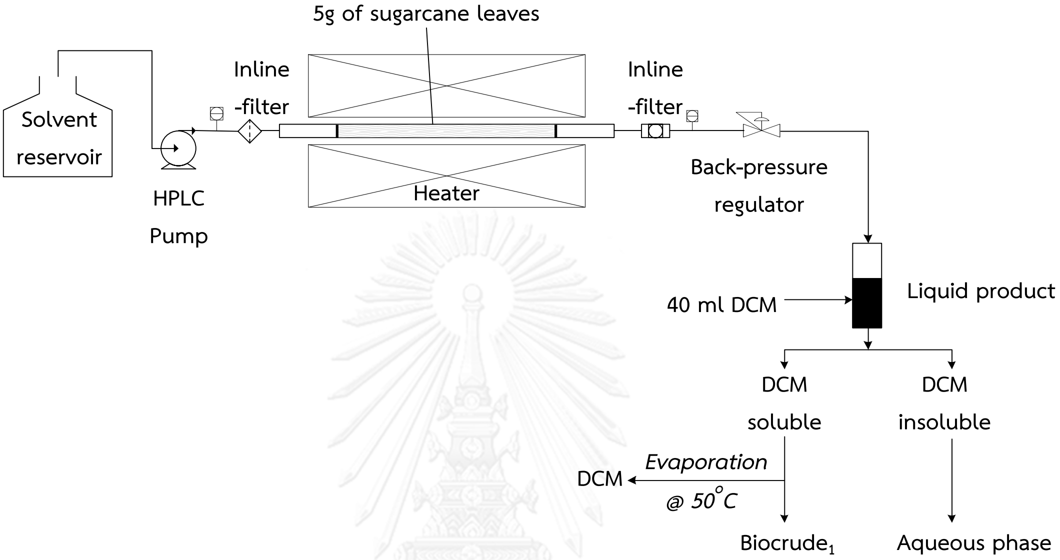

Figure 3.1. Scheme HTL of sugarcane leaves in a semi-continuous flow reactor

As reaction accomplished, the pressure would be gradually liberated until reaching to atmospheric pressure. Simultaneously, the reactor was also cooled down to room temperature. Liquid product collected at the end of back pressure regulator was serviced to a following separation process.

3.2.2. Product separation

The steps of product separation are described as the procedure below (Figure 3.2). First of all, the liquid product was rapidly extracted in separation funnel with 40 ml dichloromethane (DCM) overnight. In addition, the solution would vaporize the DCM in a rotary evaporator at 50 °C. The DCM soluble fraction was weighed and designated as biocrude$_1$. After extraction, the rest of water defined as aqueous phase contained water-soluble compounds. The oil remaining in the reactor and the solid residue was washed out using acetone until colorless. Afterwards acetone-soluble phase was evaporated under reduce pressure and then, the biocrude$_2$ was obtained. Finally, acetone insoluble fraction called as the solid residue was dried at 110 ^{o}C in 24 hours.

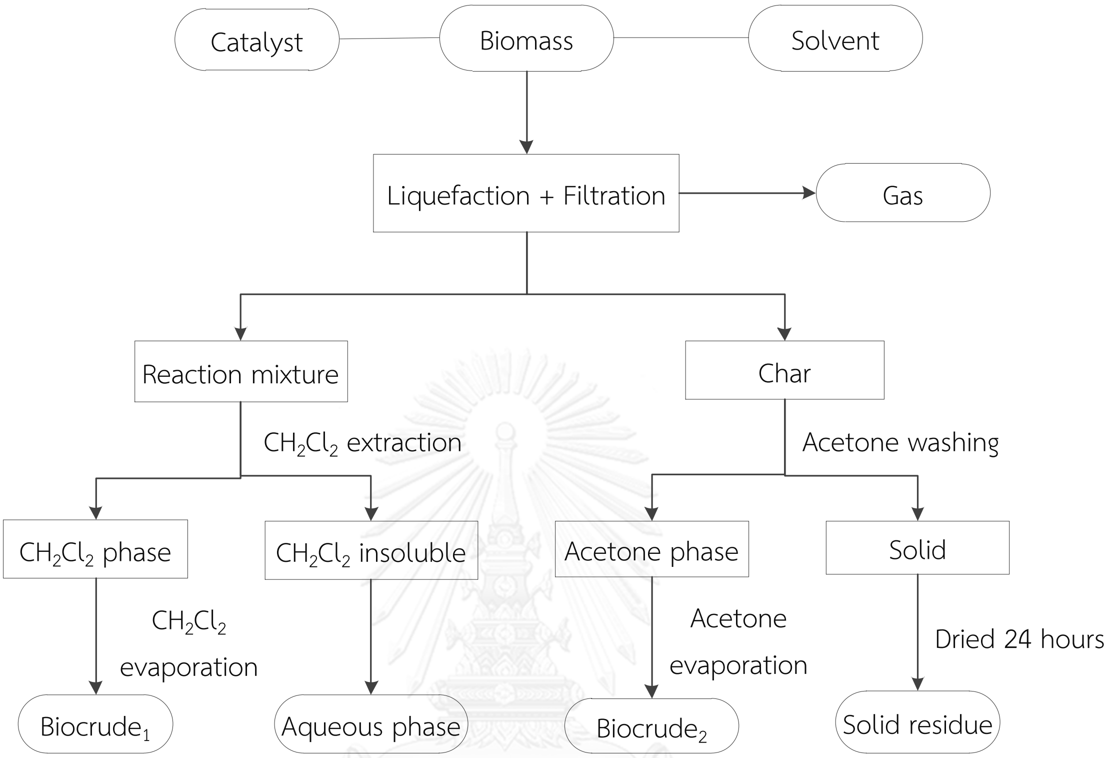

Figure 3.2. The HTL product separation procedure

3.3. Experimental parameters

It is probable to summarize the scope of experimental content as detailed in Table 3.2. It is the first time that the influences of alkaline catalyst (K_3PO_4) in mixture of water and ethanol (between 0 wt% and 3 wt%) on lignocellulosic liquefaction was comprehensively explored in a semi-continuous flow reactor at temperatures from 280 ^{o}C until 320 ^{o}C. Moreover, there is also an overall scene of the impact of K_3PO_4 on that process at different resident time which is indirectly evaluated via two flow rates of 0.5 ml/min and 1 ml/min.

As what I have just turned out in the previous session, the remarkable obstacle of the HTL was the aqueous fraction (organic water-soluble compounds). Even though, there are many academic reports detailing the positive effect of homogeneous catalysts (alkaline compounds) on the process, it seems that nobody is likely to convince completely whether their process will bring actual benefits to both economy and environment by reason of too much liquid contaminant discarded. Recently, some scientists tried to reuse initial aqueous phase as organic solvent for subsequent reactions but those resolutions will still not be thorough. That is one of the important reasons prompt me to this work. On the other hand, K_3PO_4 satisfies necessary properties of catalyst for liquefaction in theory. The more important thing is that it is possible to exist on the aqueous fraction under fertilizer (N, P, K) after the one. Therefore, the aqua phase might be used to irrigate directly biomass harvest after modifying a dose of N, P, K compounds for approaching the environmental standards.

Table 3.2. The HTL conditions of sugarcane leaves

Experimental factors	Parameters
Water/Ethanol (v/v)	100/0, 75/25, 50/50, 25/75, 0/100
Temperature (^oC)	280, 300, 320
Solvent flow rate (ml/min)	0.5, 1
Concentration of K_3PO_4 in water (wt%)	0, 1, 3
Concentration of K_3PO_4 in co-solvent (water/ethanol) (wt%)	0, 1, 3

3.4. Analytical methods

3.4.1. Characteristic of sugarcane leaves

The proximate analysis method was properly assessed by ASTM E871 - 82 in order to determine an ingredient of moisture, volatile matter, fixed carbon and ash of sugarcane leaves.

The ultimate analysis comprised of carbon, hydrogen and nitrogen content was typified by CHN analyzer [CHN628, LECO Instrument (Thailand) Ltd]. The rest (a level of oxygen) would be balanced on the others so that the total was a hundred percent.

The higher heating value (HHV) of sugarcane leaves was calculated via the proximate analysis result by an equation 3.1 [47, 48].

$$\text{HHV (MJ/kg)} = 0.3536FC + 0.1556VM - 0.0078A \qquad (3.1)$$

Where:

FC: Fixed carbon (*wt%, total-dry basis*)
VM: Volatile matter (*wt%, total-dry basis*)
A: Ash (*wt%, total-dry basis*)

3.4.2. Analysis of biocrude

3.4.2.1. Karl-Fischer titration (KF)

Karl-Fischer titration (KF) is a method for inspecting water content of oil by *METTLER TOLEDO - V20 Volumetric KT Titrator* technique as delineated in Figure 3.3. This factor influence directly quality as long as water is accredited to rise an amount of oxygen leading to decline high heating value of the biocrude. The principle of volumetric titration method is based on a chemical equation below [49].

$$ROH + SO_2 + 3\ RN + I_2 + H_2O \longrightarrow (RNH)^{\bullet}SO_4R + 2\ (RNH)I$$

Where:

ROH: Hydranal methanol dry
RN: Pyridine-containing reagents

Figure 3.3. Karl - Fischer titration apparatus (METTLER TOLEDO - V20 Volumetric KT Titrator)

3.4.2.2. Total acid number titration (TAN)

Total acid number (TAN) of the biocrude was determined by titration method (*METTLER TOLEDO* - G20 compact titrator) as labeled in Figure 3.4. The sample would be drawn up approximately 0.02 g in a specialized plastic cup and then, it was entirely diffused in 50 ml co-solvent mixed between ethanol and diethyl ether (50/50 v/v). The aim of this technique is to evaluate the influence of alkaline catalyst on the biocrude composition.

Figure 3.4. Total acid number titration apparatus (TAN) (METTLER TOLEDO – G20 compact titrator)

3.4.2.3. CHN analysis and high heating value (HHV)

Figure 3.5. CHN628, LECO Instrument (Thailand) Ltd

The carbon, hydrogen, nitrogen and oxygen content in the biocrude were characterized by a CHN analyzer [CHN628, LECO Instrument (Thailand) Ltd] as illustrated in Figure 3.5.

The higher heating value (HHV) of the biocrude would be counted from the elemental composition results by the Dulong formula in an equation 3.2 [47, 50, 51].

$$HHV_{biocrude}\ (MJ/kg) = 0.3383 \times C + 1.422 \times \left(H - \frac{O}{8} \right) \qquad (3.2)$$

3.4.2.4. Gas Chromatography/Mass Spectroscopy (GC-MS)

The main target of method is to point out differences in chemical compounds of the biocrude production under the effective catalytic liquefaction. The experimental steps comprises that firstly, the oil utterly dispersed in 2-propanol was regulated proximately 0.37 wt%. Next, the sample would be detected by the gas chromatography mass spectroscopy (GC-MS) (Agilent Technologies 7890A, GC system) as represented in Figure 3.6.

Figure 3.6. Gas chromatography mass spectroscopy (GC-MS) (Agilent Technologies 7890A, GC system)

The technique applies HP-5MS column (Agilent 19091S-433) to classify and determine oil components. The 1μL of sample is injected into the system at 300 ^{o}C. The temperature program of GC oven is automatically set up from 40 ^{o}C (0 min of holding time) until 320 °C (3 min of holding time) at a heating flow rate of 20 °C/min. Besides, a flow rate of carrier gas is 1.8 ml/min. Table 3.3 summarizes concretely the other parameters.

Table 3.3. Gas Chromatography/Mass Spectroscopy (GC-MS) parameters

Carrier gas	Helium (He)
Column	Agilent 19091S-433, HP-5MS (30 m of length, 0.25 μm of film, ID: 0.25 mm)
Injector temperature	300 °C
Oven column temperature	40 °C – 330 °C
Heating rate	20 °C/min
MS source temperature	230 °C
Run time	17 min

CHAPTER IV
RESULTS AND DISCUSSION

4.1. Property of feedstock (sugarcane leaves)

4.1.1. Proximate and ultimate analysis

Table 4.1 shows the proximate and ultimate analysis of sugarcane leaves. The result indicates that a volatile content occupies around 69.43%, followed by a fixed carbon with 12.91% of the feedstock ingredient. These are two essential parts serving to manufacture biocrude via the HTL process [25]. Another important thing is that the ash content which shrinks the reaction conversion, heating value of material (based on an equation 3.1) as well as elevate the solid contaminant. Nonetheless, the one made up approximately 7.625% of the total. There are some reasons explaining why sugarcane leaves are likely to become suitable feedstock for the HTL process.

Table 4.1. The proximate and ultimate analysis of sugarcane leaves

Analysis	wt%
Proximate (wt%, as received)	
Moisture	10.04
Volatile	69.43
Fixed carbon	12.91
Ash	7.63
Ultimate (wt%; dry, ash-free)	
Carbon	51.8
Hydrogen	9.3
Nitrogen	0.9
Oxygen*	38.0
Heating value (MJ/kg)	15.31

* *By difference*

According to the ultimate analysis, elemental compositions of sugarcane leaves were completely listed 51.8%, 9.3%, 0.9% and 38% corresponding to a load of carbon, hydrogen, nitrogen and oxygen, respectively. Comparing to some raw materials of the previous researches, barley straw [2] contained carbon (44.66%), hydrogen (6.34%) and oxygen (47.97%). Water hyacinth [52] consisted of carbon (34.98%), hydrogen (6.46%) and oxygen (56.36%) or birch wood sawdust [45] included carbon (47.6%), hydrogen (6.3%) and oxygen (45.9%). Sugarcane leave displays a prominent candidate for the HTL process due to many noticeable aspects, for example higher carbon and hydrogen content but lower oxygen than the others. As a result, it is probably to retain better qualities of the biocrude production.

4.1.2. Thermal gravimetric analysis (TGA) and differential thermal gravimetric (DTG) of sugarcane leaves

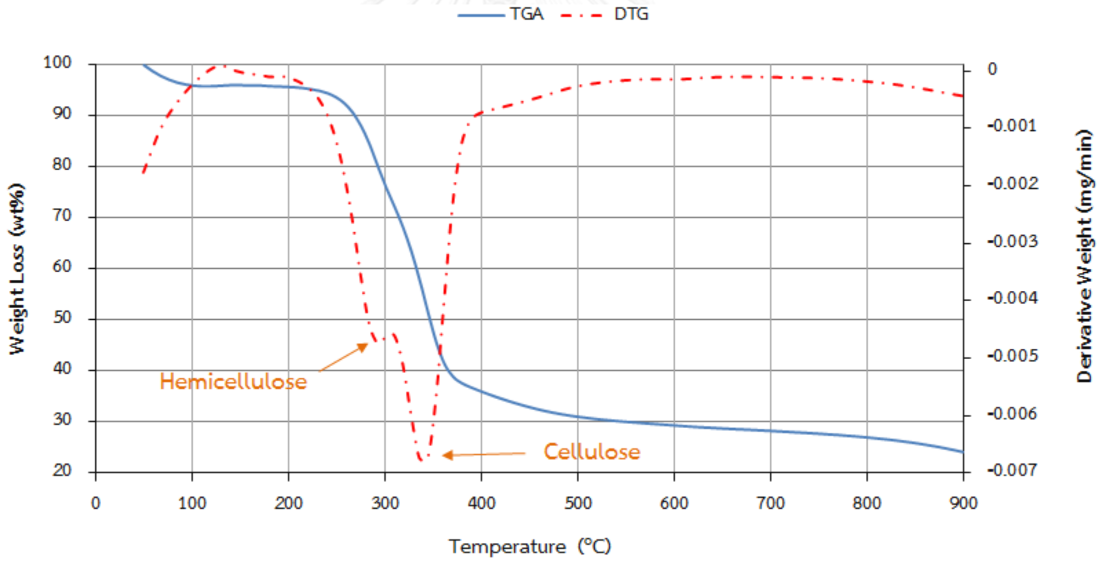

Figure 4.1. Thermal degradation behaviors and differential thermogravimetric curves of sugarcane leaves

One of the most important properties of sugarcane leaves in need of initially scrutinizing was thermal gravimetric analysis as shown in Figure 4.1. The result has been used to provide cracking behavior of feedstock and a suitable scale of temperature serving the HTL process. In general, there were three regions of the decomposition curve where the first stage (25 - 150 °C) detailed a gradual evaporation of moisture content. The mass loss at this stage was 6.1%.

The second stage disintegration of sugarcane leave started at 180 °C was entitled to terminate at the temperature around 400 °C. The weight of material declined vigorously, with roughly 50% of the total. Concretely, thermal degradation of hemicellulose and cellulose occurred between around 212 °C and 366 °C. The third stage (500 - 850 °C) was equal to the stagnant breakdown of simply lignin. It made up approximately 7% of the mass loss. The rest of mass was inflexible fixed carbon and ash content.

These results were in good agreement with some earlier literature reviews. For instance, Blasi et al. [53] reported that the hemicellulose splintered off within a temperature range of 225 - 325 °C, proceeding with the destruction of cellulose (325 - 375 °C). The lignin content would be damaged progressively during a wide temperature of 250 - 500 °C. Other author was Yang et al. [54] researching on characteristic of the hemicellulose, cellulose and lignin pyrolysis. Their TGA results indicated that the thermal decomposition of each aforementioned component occurred mainly in temperature scope of 220 - 315 °C, 315 - 400 °C and from ambient until 900 °C, respectively.

Apart from our findings, it was recognized that most of the organic substances were crumbled during the second stage. Therefore, the catalytic liquefaction of raw material should be organized inside that area. Nonetheless, to the best knowledge of the liquefaction principal, the process was energetically conducted between 250 °C and 350 °C with correlated pressure from 10 MPa until 25 MPa. As recommended above, one of the crucial advantages of the HTL is much inferior reaction temperature to the others because it is not only thermal cracking process, but also substantial assistance of hydrolysis, dehydration, decarboxylization or alcoholysis, etc. In addition, Aysu et al. [55] explored bio-oil yield under catalytic supercritical liquefaction of Syrian mesquite (Prosopois farcta). They highlighted that the liquid products would slip down massively when raising temperature in excess of 320 °C due to transforming from biocrude into gas and lighter water-soluble components via thermal decomposition. Yuan et al. [56] were in good agreement with those deductions. All the foundations motivated me to choose a temperature range of 280 - 320 °C to study the effect of K_3PO_4 on the HTL of sugarcane leaves.

4.2. Hydrothermal liquefaction of sugarcane leaves

4.2.1. Effect of co-solvent

Compared to water, advantages of using ethanol as liquefaction solvent are much its lower critical temperature and pressure, higher yields of water-insoluble biocrude and the obtained oil with lower oxygen content, leading to higher caloric value. Nonetheless, high cost and environmental problems are the major drawbacks of organic solvent. In contrast, the water originates in natural resource, hence it is simple to collect, lower cost and facilitates recovery of inorganic substances in biomass [7]. In order to take advantage of those characteristics, the effects of co-solvent are comprehensively investigated at a liquefied temperature of 300 ^{o}C, along with two different flow rates for 2 hours operating time and without catalyst.

4.2.1.1. Effect of co-solvent at a low flow rate

The results are drawn up in Figure 4.2. It was found that the highest percentage of biocrude$_1$ was 21.24% with mixture of water and ethanol (25/75 v/v) at 300 ^{o}C and a flow rate of 0.5 ml/min, succeeded by 20.86% and 12.98% in case of a balanced co-solvent and pure ethanol, respectively. It can be clearly seen that co-solvent unveiled more positive effect on the liquefaction of sugarcane leaves than pure solvent, though there was a slight different conversion of 50/50 v/v and 25/75 v/v (water/ethanol). This is obviously favorable because ethanol is in charge of the downward critical point, dielectric constant of co-solvent and surface tension of liquefied products [42, 57]. Thereby, it advocated the extraction process during the HTL, which impulses to be dramatic down aqueous phase from 51.45% until 23.15% when lifting ethanol in the ratio of co-solvent.

On the other hand, the biocrude$_1$ was significantly plummeted in conjunction with discarding the largest solid residue (61.25%), in case of pure ethanol. It is noteworthy that free radical reactions would be remarkably discouraged as using pure ethanol owing to its weak acidity [50].

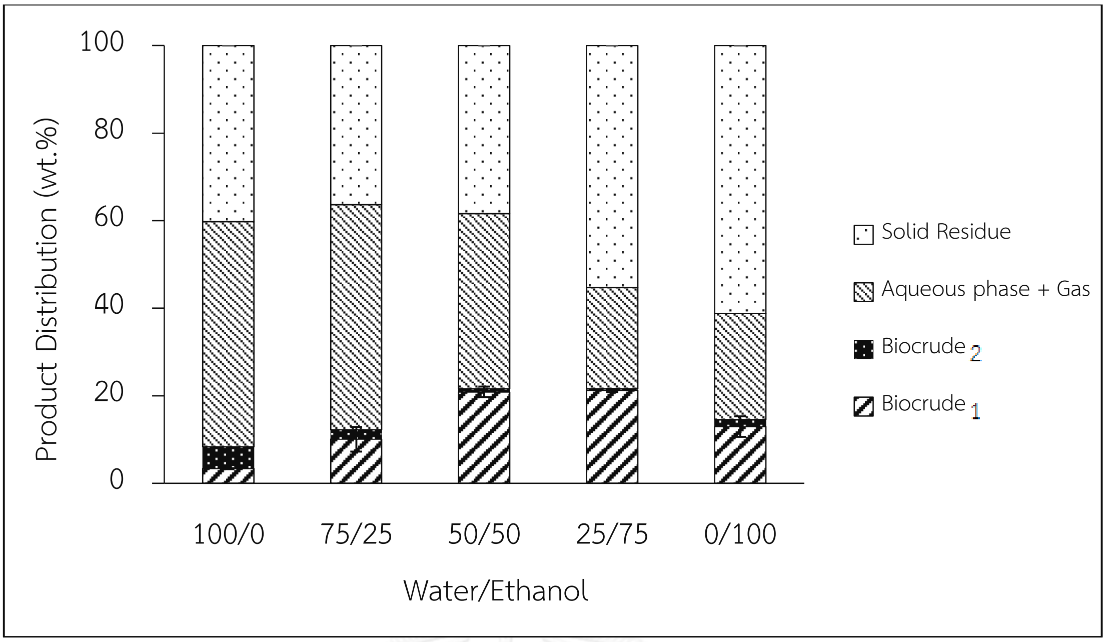

Figure 4.2. Effect ratio of co-solvent on the HTL of sugarcane leaves at 300 ^{o}C and a flow rate of 0.5 ml/min

4.2.1.2. Effect of co-solvent at a high flow rate

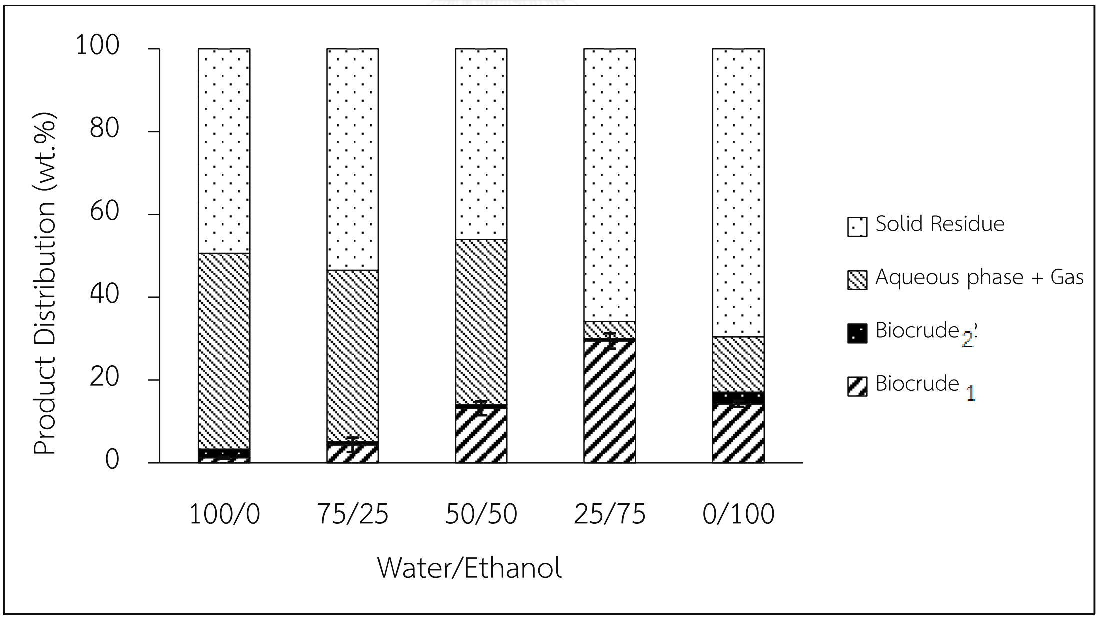

Figure 4.3. Effect ratio of co-solvent on the HTL of sugarcane leaves at 300 ^{o}C and a flow rate of 1 ml/min

As what I have just mentioned, the mixture of water and ethanol exhibited a synergistic impact on the liquefaction of biomass under many aspects. However, the synergy between co-solvent and liquefaction time was firstly probed by two flow regimes. The solvent flow rates of 0.5 ml/min and 1 ml/min stood for the resident times as 40 min and 20 min, respectively. Figure 4.3 exhibited the distribution of products derived from the liquefaction of sugarcane leave in conditions of 300 ^{o}C, various ratio of co-solvent and a flow rate of 1 ml/min.

First of all, it was worthy to recognize that the co-solvent attained the significantly positive impact on the biocrude$_1$ conversion at a short resident time. In there, the lowest percentage of oil was 1.27% and 47.21% of the aqueous fraction when a making use of pure water. It proved that the one might be disability to absorb reaction intermediates during the liquefaction at this condition. Besides, the maximum biocrude$_1$ obtained 29.47% was sustained by the minimum aqueous phase as 4.07% at a ratio of 25/75 v/v (water/ethanol). This was attributable to interactions between alcohol and some transitional compounds by the alcoholysis reaction (hydroxylalkylation) [7, 58]. Furthermore, ethanol played a role as the hydrogen donors, which enhances decomposition of the biomass (sugarcane leaves) by hydrogenolysis agents [36]. It also reinforced the dispersion of solvent into the cellulose, hemicellulose and lignin matrix as well as stabilization of free radicals [40].

Even so, the number of solid residue escalated dramatically in both cases of 25/75 (water/ethanol) and pure ethanol, with 65.87% and 69.51%, respectively. This is an apparent evidence to suggest twice that either an excess of alcohol or only alcohol could suppress radicals generation attending to decomposition of raw material [42].

In conclusion, the HTL of sugarcane leave in co-solvent proposed to combine the advantages of water and alcohol. Especially, the ratio of water/ethanol (25/75 v/v) was plausibly defined the more tremendous effect on oil conversion at a short resident time (a flow rate of 1 ml/min) than that of others.

4.2.2. Effect of temperature

Temperature is also no less crucial aspect as to the HTL. This is a key to mobilize thermal cracking process of lignocellulosic biomass. It would be examined in the range of temperatures between 280 °C and 320 °C with two flow rate systems.

4.2.2.1. Effect of temperature at a low flow rate

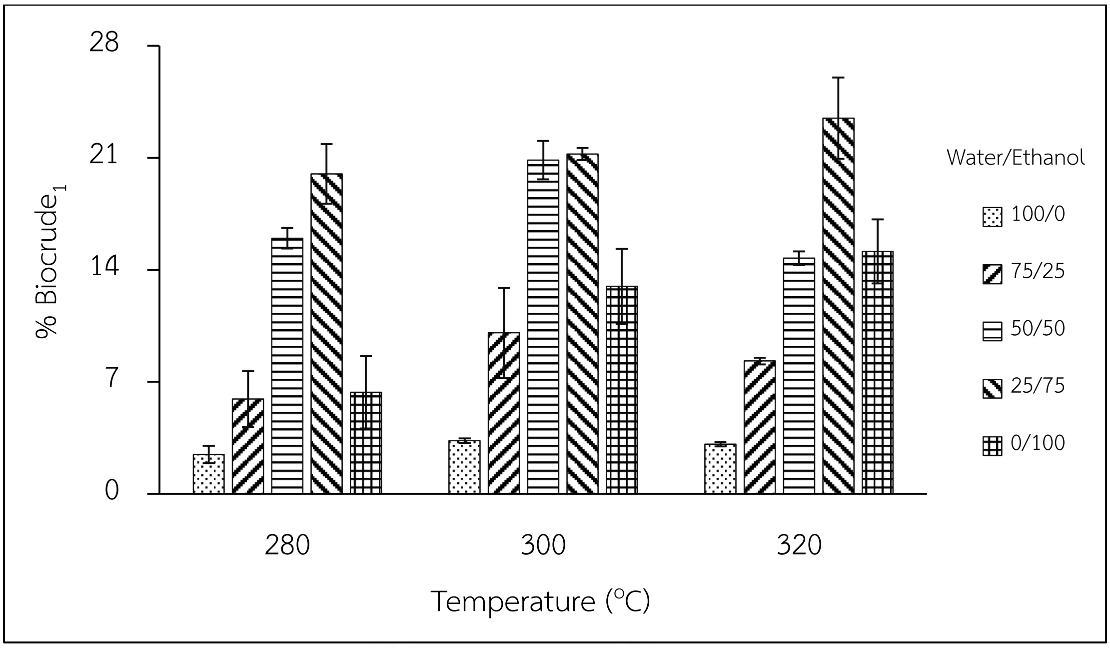

Figure 4.4. Effect temperature on biocrude$_1$ *via the HTL of sugarcane leaves at a varied ratio of co-solvent (water/ethanol) and a flow rate of 0.5 ml/min*

Figure 4.4 represented an influence of different temperatures on percentage of the biocrude$_1$ at a long resident time (a flow rate of 0.5 ml/min). The outcomes indicated that the temperature of 300 °C gained the best condition of oil conversion, with 3.33%, 10.06% and 20.86% matching ratios of co-solvent as 100/0, 75/25, 50/50 (water/ethanol), respectively. Nonetheless, the biocrude$_1$ would be sharply tumbled down when rising temperature up to 320 °C. This is obviously due to the fact that the disassociation of celluloses and lignin is only approached as the temperature ramped beneath the critical point of solvent. As mentioned above, Yuan et al. [56] also found that the biocrude might be fallen down at temperature exceeds 310 °C since gas yields and light water-soluble compounds were discarded through further thermal cracking of oil yields.

On the other hand, further raising temperature favored biocrude$_1$ yield up to 23.48% and 15.15% at 320 ^{o}C in case of 25/75 v/v (water/ethanol) and pure ethanol, respectively. The reasons were originated from too little water in co-solvent and weak acidity of ethanol [50]. It would prompt to restrict hydrogen-donor generation during the HTL. Eventually, the cracking of celluloses, hemicelluloses and lignin in sugarcane leaves must depend entirely on temperature. Moreover, another important thing is that the solvolysis of biomass components would be remarkably accelerated at relatively higher temperatures [55, 59]. In addition, the more accessible the fragments were disintegrated into a liquid oil-rich phase at those conditions. As a consequence, the density of solvent would be vigorously increased when growing in reaction temperature. We are able to speculate that the solvents were more incremental dissolving competency than normal. Thus, more and more products could be diffused into oil fraction at greater solvent's density [60].

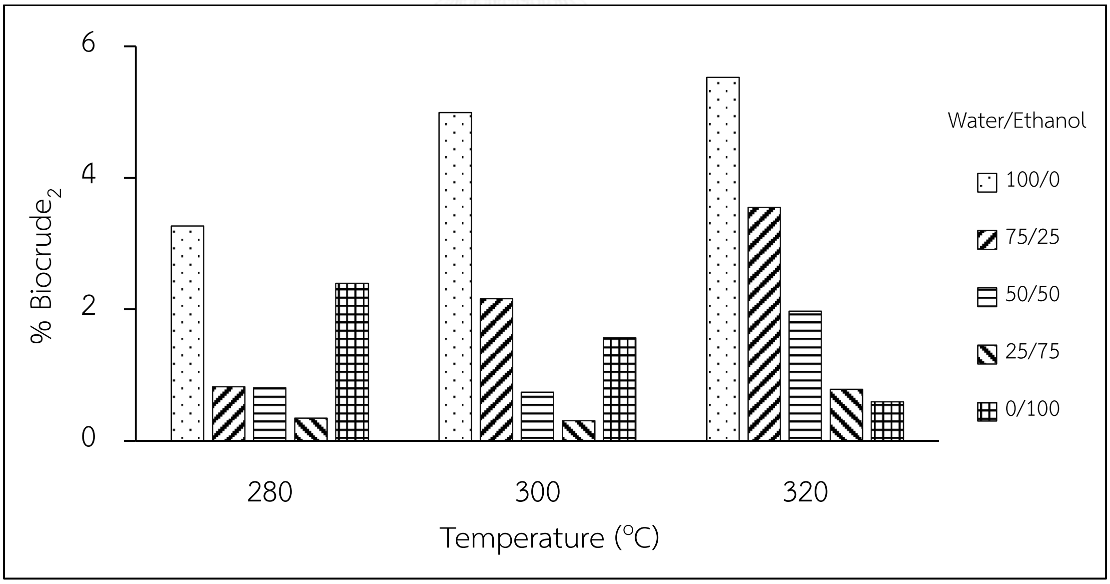

Figure 4.5. Effect temperature on biocrude$_2$ via the HTL of sugarcane leaves at a distinct ratio of co-solvent (water/ethanol) and a flow rate of 0.5 ml/min

In contradiction with the biocrude$_1$, the higher temperature and the greater number of biocrude$_2$ was monitored almost co-solvent ratios except pure ethanol via

Figure 4.5. There was an extraordinary escalation oil yield from 3.26% to 5.52% in water as pure solvent, followed by ramping up to 3.55% from 0.83% of the mixture of 75/25 (water/ethanol) in the range of 280 - 320 °C. Temperature was responsibility to co-ordinate competitive reactions during the HTL, for example hydrolysis, disintegration and repolymerization [52]. Nonetheless, depolymerization process to form lighter compounds would be more active at lower temperatures, while recombination reactions were probably to happen at higher temperatures so as to build up longer chain fragments [61]. In pure ethanol situation, the $biocrude_2$ dropped from 2.4% at 280 °C unitl 0.59% at 320 °C since this solvent would react with free radicals by the solvolysis reactions at high temperatures of 320 - 400 °C in order to convert from $biocrude_2$ into $biocrude_1$ [59].

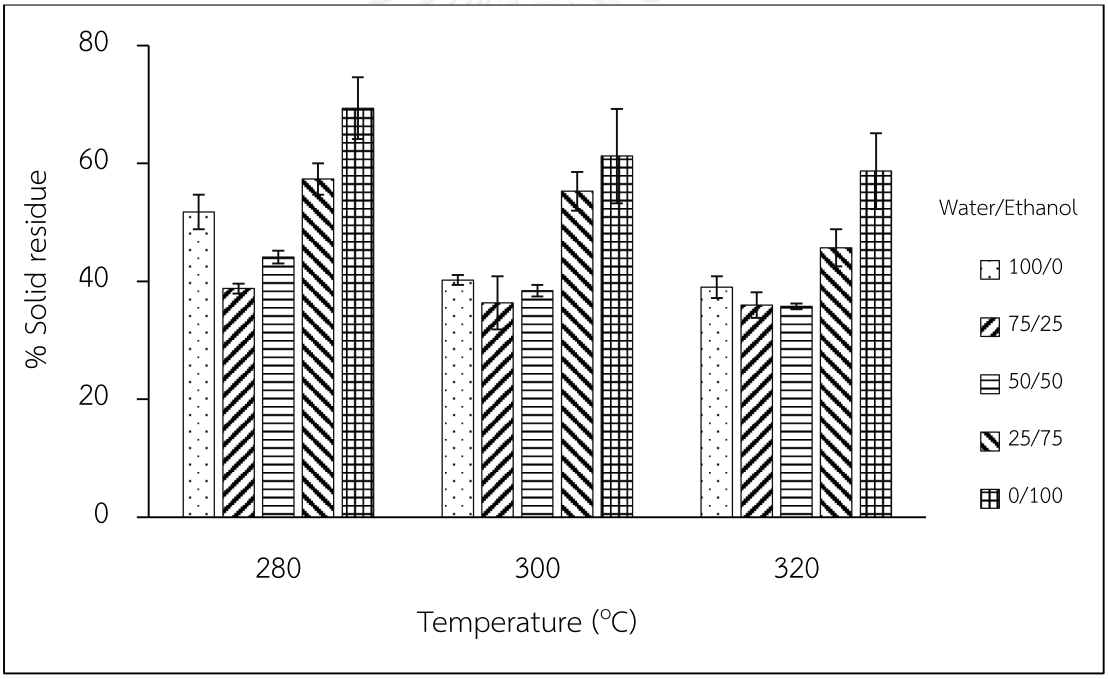

Figure 4.6. Effect temperature on solid residue via the HTL of sugarcane leaves at a diverse ratio of co-solvent (water/ethanol) and a flow rate of 0.5 ml/min

Overall, it can be clearly seen that as regards all the ratios of co-solvent, the solid residue was gradually suppressed when growing temperature. Concretely, the strongest thermal cracking of sugarcane leaves was established in the temperature area between 280 °C and 300 °C, which involves diminishing the huge solid remaining from 51.78% to 40.24% in case of pure water, or from 44.13% until 38.42% in an equal co-solvent and roughly 8.14% in pure ethanol as solvent. Notwithstanding, their cutback in further temperature would be considerably downturn, with only 1.22%, 2.67% and 2.55% standing for pure water, 50/50 v/v and pure ethanol, respectively. It is one's belief that thermal disintegration of biomass will be a dominant reaction during an initial period of the liquefaction at lower temperatures [52]. After that, either repolymerization or condensation reaction was more effective than the other process at higher temperatures. It was implied that both the biocrude product and intermediates will transform into char/coke at that conditions [57, 62].

4.2.2.2. Effect of temperature at a high flow rate

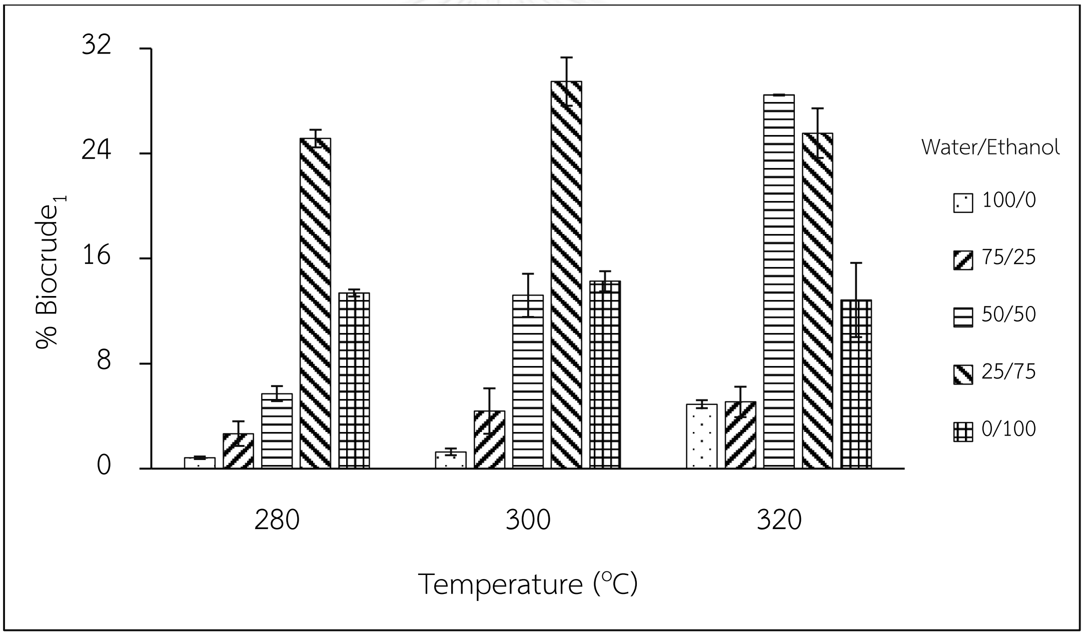

Figure 4.7. Effect temperature on biocrude$_1$ via the HTL of sugarcane leaves at a different ratio of co-solvent (water/ethanol) and a flow rate of 1 ml/min

Comparing to Figure 4.4, first of all, it is worth recognizing that the optimal biocrude$_1$ yield obtained from the conditions of 50/50 and 25/75 v/v (water/ethanol) at a shorter resident time of 20 min (a flow rate of 1 ml/min) was higher than the longer one of 40 min (a flow rate of 0.5 ml/min) in the overall view. Many researches on the HTL of lignocellulose were in agreement with our deduction [42, 63, 64]. This was attributed to the condensation and repolymerization reactions of unsaturated intermediate compounds, which might build up heavy oil or solid residue. Those reactions were vigorously stimulated when extending the reaction time [51], leading to the growth of tar/char. As a result, the curtailed liquefaction time would be more reasonable for biocrude generation than the other.

In addition, there were entirely contrary results emphasized in Figure 4.7 laying out the impact of temperature on biocrude$_1$ at a shorter resident time. Meanwhile, both pure water and 75/25 v/v (water/ethanol) as the liquefaction solvent took an upturn in the product until 4.91% and 5.08%, respectively at 320 °C. Particularly, the oil yield escalated sharply from 5.71% to 28.46% in case of 50/50 v/v (water/ethanol) when raising temperature up to 320 °C. Whereas, the rest of circumstances gained a peak of the oil conversion at 300 °C, which was depicted as 29.47% of 25/75 v/v (water/ethanol) and 14.27% of pure ethanol. Afterwards it would be slumped at a further temperature.

These might be interpreted by a significant difference in the resident time. The thermal cracking of feedstock would be restrained owing to a shorter contacting time. Thus, a role of the combination between hydrolysis and solvolysis derived from ethanol as to the HTL of sugarcane leave is literally necessary in this condition. Nevertheless, the more energetic influence of solvolysis on biomass compositions might be emerged from the upper temperatures [42, 55]. This is a reason why the higher temperature and the larger percentage of biocrude$_1$ were achieved in terms of lower 50% ethanol in co-solvent. In contrast, both hydroxyalkylation (alcoholysis) and solvolysis would be remarkably advocated in excess of ethanol as elevating temperature [7, 58]. It is feasible to transform oil product into gas or tar/char which was clearly typified in Figure 4.9. These reasons might infer the loss of biocrude$_1$ from 25/75 v/v (water/ethanol) and pure ethanol situations.

Figure 4.8 demonstrated the incidence of temperature on biocrude$_2$ at a shorter reaction time. On the whole, the oil yield collection was quite less than that of a flow rate of 0.5 ml/min. Most of them fluctuated in a narrow range of 0.3 - 3.2%. We are likely to neglect some situations having a beneath 1% of the product conversion as long as it is too hard to appraise accurately. As stated in cases of pure water and ethanol as solvent, there was a slight increase in the biocrude$_2$ product from 1.72% to 3.21% and from 1.17% until 2.11%, respectively when rising temperature. The explanation for these matters would be the much same as discussions mentioned for Figure 4.5.

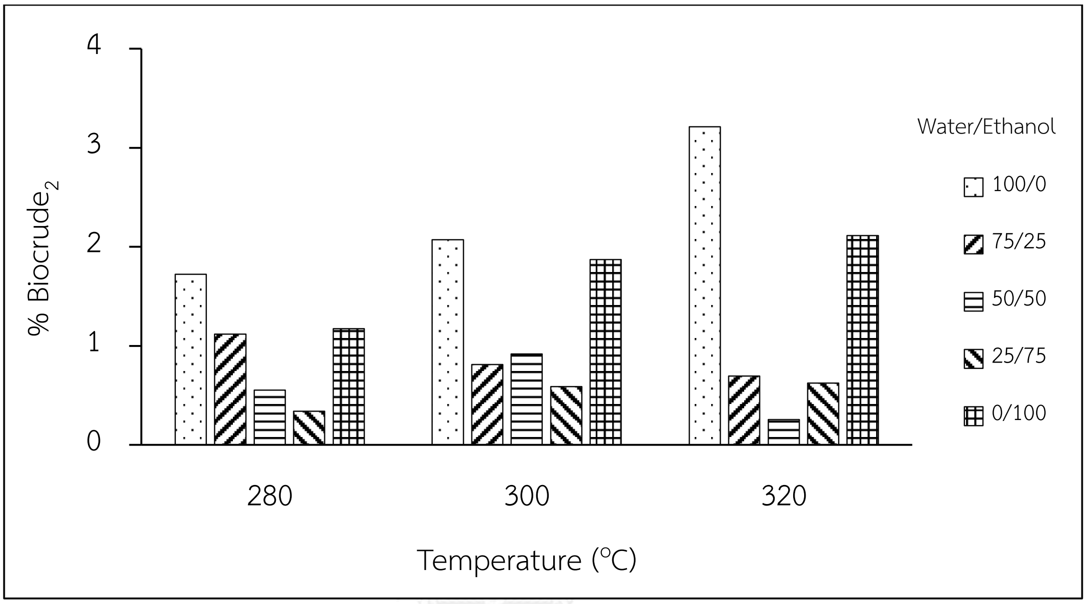

Figure 4.8. Effect temperature on biocrude$_2$ via the HTL of sugarcane leaves at an assorted ratio of co-solvent (water/ethanol) and a flow rate of 1 ml/min

Finally, the impact of temperature on solid residue was clearly denoted in Figure 4.9. The results announced that the minimal points were attained almost all of co-solvent proportions at 320 °C. Definitely, the trends of solid remaining were also similar to the former trends of Figure 4.6. However, a marked difference between a flow rate of 0.5 ml/min and 1 ml/min is the measure of abundance. In general, the leftover of a shorter resident time was much more extensive than that of the other. This is ascribed to insufficient liquefaction time to convert lignin matrix accounted for nearly 16% of dried sugarcane leaves into the valuable products [22, 42]. Besides, too brief reaction time could impede the profound thermal disintegration of long-chain fragments conducting to unbalance between degradation of the second step and repolymerization of the third step during the HTL.

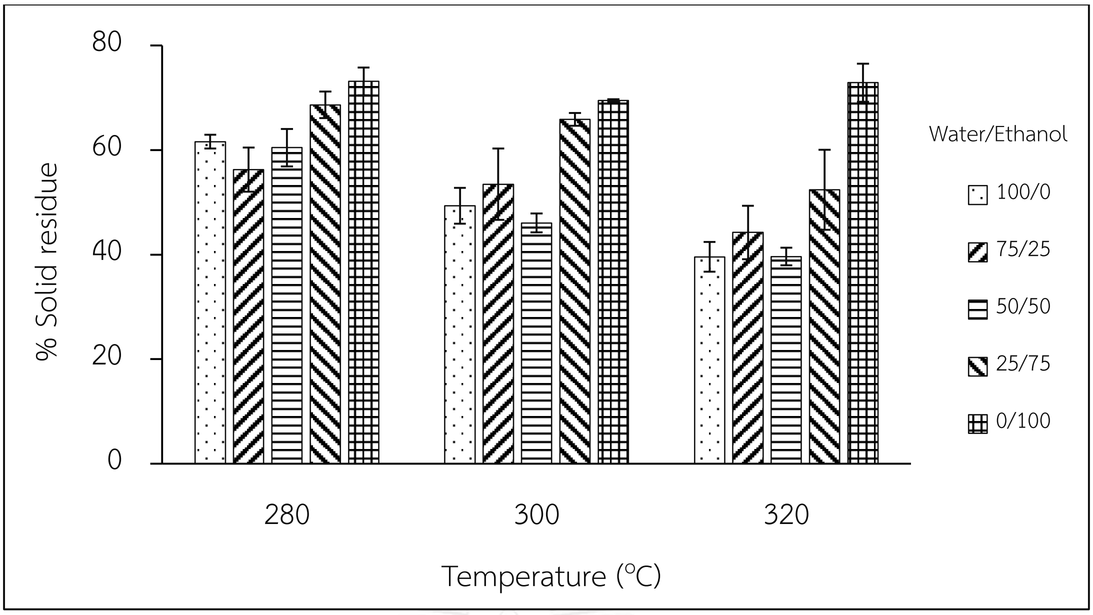

Figure 4.9. Effect temperature on solid residue via the HTL of sugarcane leaves at a various ratio of co-solvent (water/ethanol) and a flow rate of 1 ml/min

From Figure 4.9, it was found that a drastic reduction in mass of solid was observed from 61.61% at 280 °C until 39.56% at 320 °C with respect to pure water. In case of 50/50 v/v co-solvent, the enormous change in weight fraction was from 60.47% to 39.63% of residue between 280 °C and 320 °C, respectively. It gave a reliable witnesses to the defragmentation of complicated polymers into liquid oil-rich phase when accelerating temperature. Notwithstanding, an extra increase in the one would encourage in transforming of these fragments into gaseous product [65]. Especially, the maximum solid remaining was gained from pure ethanol, making up 73.15%, 69.51% and 72.91% of all the tested temperatures. This might be accounted for the weak acidity of ethanol [50] and enhancing the formation of coke/char at relatively high temperature [66].

4.2.3. Effect of K_3PO_4 in co-solvent (50/50 v/v water/ethanol)

To the best of our knowledge, catalysts play a crucial role of expediting chemical reaction rates of the HTL process. Furthermore, it still influences on eventual product distribution as well as characteristic of the biocrude [25, 64]. So far, there has been no research into the effective alkaline compound of tripotassium phosphate (K_3PO_4) on the liquefaction process yet. Therefore, the ambition of this work is to examine its consequence and operating parameters on the HTL of sugarcane leaves in ethanol-water co-solvent at two flow rate regimes. This is preliminary outcomes to step up to an integrated concept of utilizing aqueous fraction, including homogenous alkali and organic compounds as a fertilizing source (N, P, K) for the biomass cultivation.

4.2.3.1. Effect of K_3PO_4 in co-solvent at a low flow rate

The incidence of K_3PO_4 in mixture of water and ethanol (50/50 v/v) on the liquefaction of sugarcane leaves was firstly explored at varied temperatures and a flow rate of 0.5 ml/min exercising a semi-continuous flow reactor. In general, Figure 4.10 indicated an undoubtable evidence that the alkaline compound (K_3PO_4) in co-solvent performed positive impact on the biocrude$_1$.

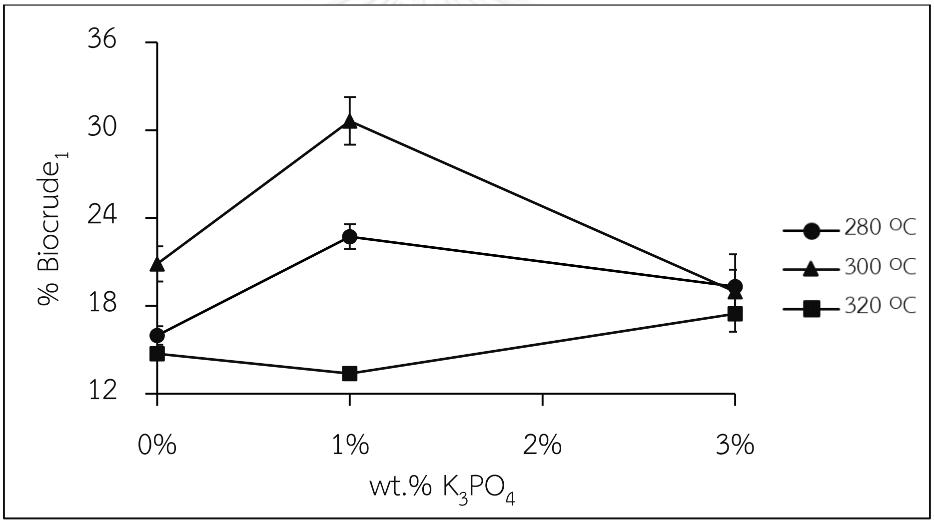

Figure 4.10. Effect of K_3PO_4 in co-solvent on biocrude$_1$ at different temperatures and a flow rate of 0.5 ml/min

The results figured out that comparing to 15.98% of the conversion in case of non-catalyst at 280 °C, the biocrude$_1$ was extensively ramped up to 22.73% in presence of 1 wt% alkaline solution, and subsequently plunging down to 19.31% at 3 wt% K_3PO_4. Moreover, the most impressive upshot is that there was a striking escalation percentage of the biocrude$_1$ from 20.86% until 30.63% when adding 1 wt% catalyst into co-solvent at 300 °C. The oil growth was accounted for closely 10% prior to suddenly remarkable decrease to 18.97% as lifting 3 wt% catalyst.

As a result, it was worth recognizing that the most reasonable catalytic proportion as to the HTL of sugarcane leaves was 1 wt% K_3PO_4 in co-solvent at 300 ^oC. Mazaheri et al. [67] informed that alkaline catalysts could rule out the creation of stable structures. Simultaneously, they would soften C-C linkages as well as enforce internal surface area and expand the segregation of structure interlinks between holocellulose and lignin matrix. Thereby, the activation energy for complicated reactions was conclusively inferior. Rustamov and his co-workers [68] also unveiled that the intermolecular interaction of glucoside bonds would become much more fragile in alkaline solution. The outcomes were concurrently implied that both alcoholysis and thermal decomposition process were strongly accelerated in medium temperatures and basic environment by a cause of its low thermal stability.

Furthermore, one of the main reasons contributing to the elaboration of the quantity of oil production is that formation of organic acids and more hydrolyzed intermediate yields were advocated during the lignocellulosic liquefaction process with alkaline catalyst [2]. Those would react with ethanol through esterification reaction producing fatty acid ethyl esters similar to biodiesel [7]. This consequence will be adequately exposed in the following GC-MS results.

In addition, the basic environment had an ability to enlarge hydrolysis of lignin matrix. A huge complicated three-dimensional biopolymer of lignin could be detached to simply monomers and monocyclic structures under the alkaline solution [69]. Besides, glucose fragments originated from the thermal cracking of cellulose and hemicellulose might break down intensely into aldehydes and acid compounds in that condition [70]. Those were some arguments spelling out the growth of $biocrude_1$.

Simultaneously, the alkaline salts were also attributed to massive cutback in the percentage of oil production when adding 3 wt% catalyst since the further breaking of $biocrude_1$ might be profoundly happened to form gaseous product at much higher basic pH condition [71]. Moreover, most of oil components would be nonpolar molecules under weak alkaline conditions. They were more easily extracted by DCM, resulting in the efficient yield collection. In contrast, those substances became deeper polar when enhancing the alkalinity, which is a mean cause of decrease in $biocrude_1$ production [72].

Besides, the biocrude$_1$ went down and up vastly at 320 °C, first declining from 14.73% to 13.38% when adding 1 wt% catalyst into co-solvent, hence jumping to 17.45% at 3 wt% K_3PO_4. The root cause was because the high temperature would be in remarkable favor of both thermal decomposition and solvolysis of biomass components [42, 59]. They became predominant reactions than the esterification between ethanol and acid components in the aqueous fraction since a much less dose of alkaline catalyst (only 1 wt% of solution) would create insufficiently organic acids serving those reactions [2, 73].

Nonetheless, the biocrude$_1$ production wrested the upturn in conversion at a solution of 3 wt% from the modest downturn at 1 wt% catalyst. These outcomes resembled the report of Singh et al. [52] highlighting that there was a drastic escalation of bio-oil yield from 12% with 0.5 N K_2CO_3 to 19% with 1 N K_2CO_3 or from 14% until 19% corresponding to 0.5 N and 1 N KOH, respectively.

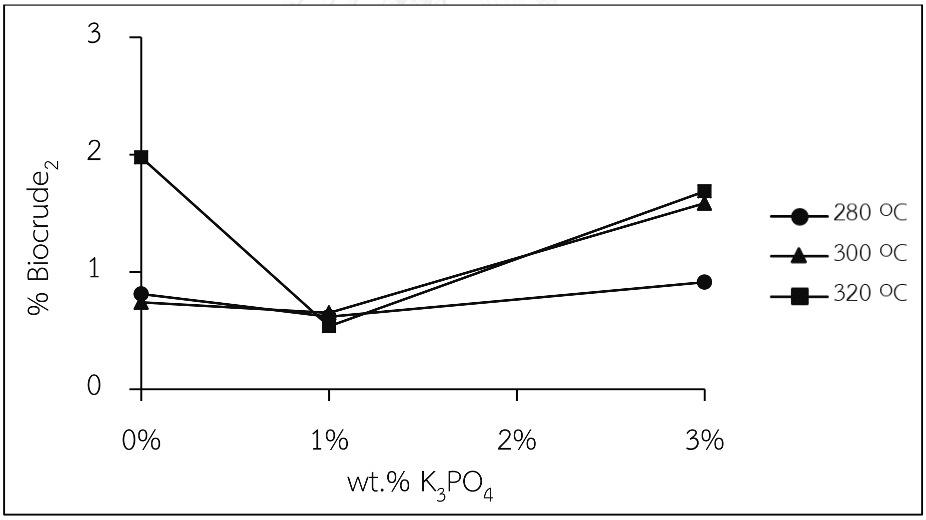

Figure 4.11. Effect of K_3PO_4 in co-solvent on biocrude$_2$ at different temperatures and a flow rate of 0.5 ml/min

The influences of K_3PO_4 in co-solvent on biocrude$_2$ production in temperatures of 280 - 320 °C, along with a flow rate of 0.5 ml/min were fully emphasized by Figure 4.11. Overall, it can be clearly seen that the fluctuation of biocrude$_2$ between 0.54% and 1.97% was not worthy considering when comparing to biocrude$_1$. Notwithstanding, the biocrude$_2$ had a tendency to escalate a little in presence of 3 wt% catalyst at higher reaction temperature. This is due to the fact that the strengthening of pH environment conducted to further breakdown either the biocrude$_1$ or lighter components into unstable intermediate fragments via the decarboxylisation reaction or retro-aldol condensation [26, 45]. Afterwards they would associate simply with each other to produce longer-chain compounds under greater temperature condition [61].

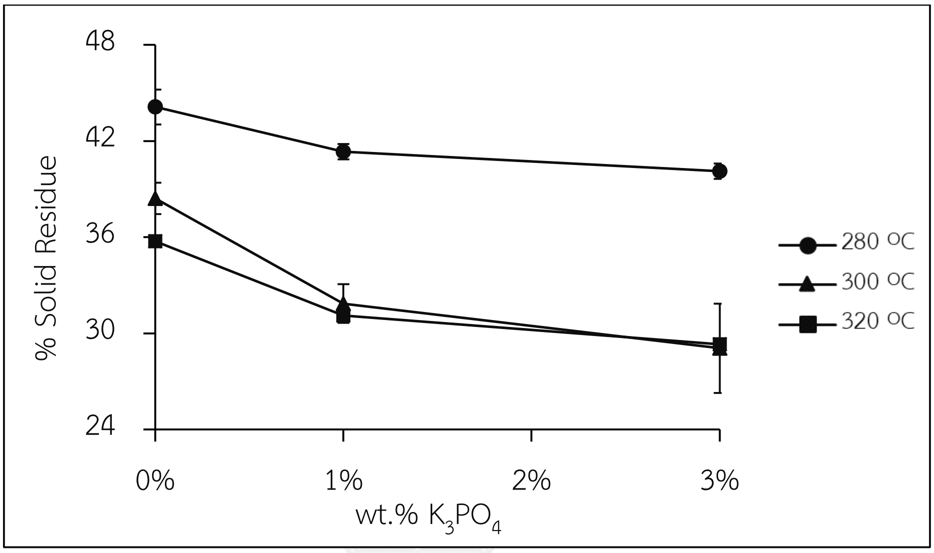

Figure 4.12. Effect of K_3PO_4 in co-solvent on solid residue at different temperatures and a flow rate of 0.5 ml/min

Figure 4.12 laid out the incidence of K_3PO_4 in co-solvent on solid remaining. It was found that the minimal product was roughly 29% of the total at both temperatures of 300 °C and 320 °C in case of 3 wt% catalytic solution. Besides, the drastic shrinkage of residue fraction was made up around 2.8%, 6.56% and 4.64% standing for 280 °C, 300 °C, 320 °C, respectively when comparing between 1 wt% catalyst and non-catalyst run. These might be since dehydration of transitional monomers would be forbidden and substituted by decarboxylisation reactions as the addition of alkaline salts. There is no denying the fact that the dehydration process might eliminate a high extent of oxygen. However, it also generated parallel unsaturated fragments which effortlessly reconnect to tar/char [26]. Besides, some reports affirmed that the alkaline catalyst has not only an ability to inhibit formation of char/tar during the HTL process but also sharp decrease in the solid yield when a larger dozen of catalyst [74, 75].

On the other hand, there were no enormous changes the residue content between catalyst and non-catalyst run at 280 °C as attached in Figure 4.12. Moreover, the highest one was acknowledged with 44.13% in an absence of K_3PO_4 at that temperature. Subsequently, it dipped slightly into 41.33% and 40.12%, corresponding to 1 wt% and 3 wt% catalyst run, respectively. This might be owing to the fact that there was a limitation of thermal cracking reaction at low temperatures within the period of liquefying sugarcane leaves. Once again the temperature took a crucial responsibility for the HTL process.

4.2.3.2. Effect of K_3PO_4 in co-solvent at a high flow rate

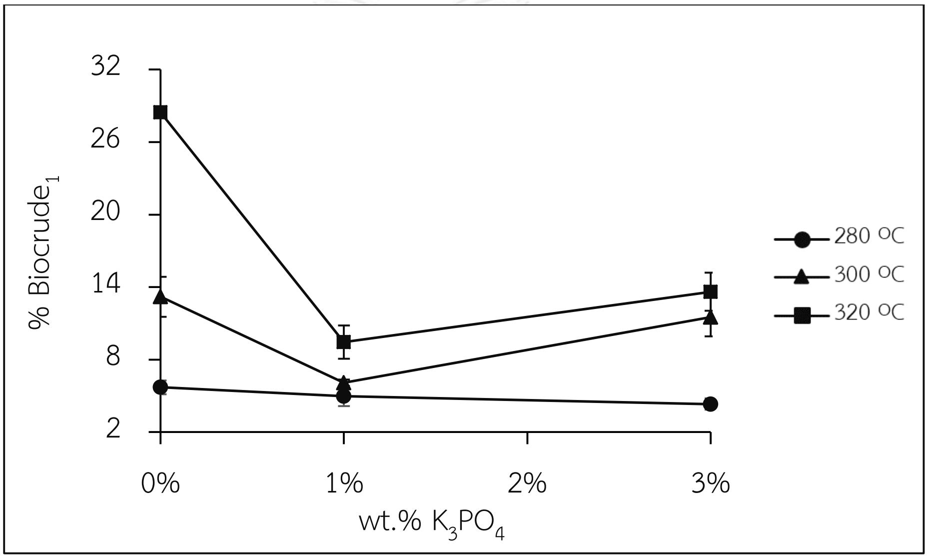

Figure 4.13. Effect of K_3PO_4 in co-solvent on biocrude$_1$ at different temperatures and a flow rate of 1 ml/min

As far as what I referred in a previous session, the alkaline catalyst (K_3PO_4) in co-solvent played a key role in the HTL of sugarcane leaves. It lighted up undoubtedly a sharply positive effect on escalation in the huge amount of biocrude$_1$ and cutback in solid residue at a variety of temperatures and a longer resident time (a flow rate of 0.5 ml/min). Those outcomes were in an agreement with almost prior researches on the lignocellulose liquefaction executed in solution of alkali and pure water, for instance Zhu et al. [2], Singh et al. [38], Huang and his colleagues [65] or Nazari's group [45], etc.

On the contrary, Hafez et al. [42] found that there was an even negative influence of alkaline solution (Na_2CO_3) in solvent on the biocrude production via fast liquefaction (5 min) of giant miscanthus feedstock. The result was proved that it is an impossible to take no notice of the interaction between liquefaction time and the catalytic efficiency.

Figure 4.13 epitomized the relation of K_3PO_4 and a shorter resident time (a flow rate of 1 ml/min) to $biocrude_1$ production over the HTL of sugarcane leaves at numerous temperatures. It was generally admitted that adding alkaline catalyst (K_3PO_4) into the mixture of water and ethanol displayed unfavorable effect on yield capacity at a flow rate of 1 ml/min. The most noteworthy changes transpired at high temperature. Definitely, at 320 ^oC, the $biocrude_1$ was down markedly from 28.46% in case of non-catalyst to 9.45% when dissolving 1 wt% K_3PO_4, followed by suddenly reaching 13.62% in term of 3 wt% catalyst. These observations were also the similar to the temperature of 300 ^oC. The extreme reduction in weight of oil was recorded from 13.2% until 6.09% matching with 0 wt% and 1 wt% alkali, respectively before moderate shooting up again to 11.53% in 3 wt% situation.

The key explanation is possibly because the catalyst was supposed to be secondary promoter in the liquefaction process [76], hence it was also in favor of depolymerization/degradation reactions of hemicellulose and cellulose. Nonetheless, in case of the shorter liquefaction time, the degradation of initial oil yield became predominate to produce lighter fragments or gas due to its low thermal stability. Even so, it was not enough reaction time for condensation or repolymerization of small intermediate compounds into more stable ones (final product). Moreover, the alkaline solution also leveled up reaction rate of carbon-carbon scission, leading to provoke more gaseous product out [77].

In contrast, when lifting to 3 wt% catalyst, the degree of $biocrude_1$ was higher than that of other. Like the previous spelling out, an adequate alkaline concentration promoted formation of an abundant acidic components developing a volume of oil by the esterification reaction. Nevertheless, there was no typical change the percentage of $biocrude_1$ with closely 5% conversion in term of 0 - 3 wt% catalyst at a low temperature of 280 ^oC owing to a lack of reaction time and thermal energy.

In accordance with Figure 4.14, the biocrude$_2$ proportion was evaluated an interaction between catalytic concentrations and distinct temperatures at a flow rate of 1 ml/min. In a general view, the mass of biocrude$_2$ stemmed from two flow rate regimes was much less than biocrude$_1$. It is too difficult to argue which the condition will be better than another since they went up and down in a narrow scale. Therefore, we might only focus on the potential lines.

It can be noticed that all of them rose steadily when raising an alkaline concentration. The highest oil yield were reached 2.9%, 1.57% and 1.73% at 3 wt% catalyst from only beneath 1% of conversion in non-catalyst case between 280 °C and 320 °C, respectively. Zhang et al. [78] found that a high alkalinity improved hydrolysis of cellulose/hemicellulose and ester bonds in the complex lignin matrix by detaching its glycosidic linkage, which constitutes much more organic acids [79]. It is one's belief that an excess unstable monomers (acids, hydroxyl group, aldehyde, etc.) discarded in aqueous phase under higher alkaline concentration would elevate the reconnection process into heavy oil (the biocrude$_2$).

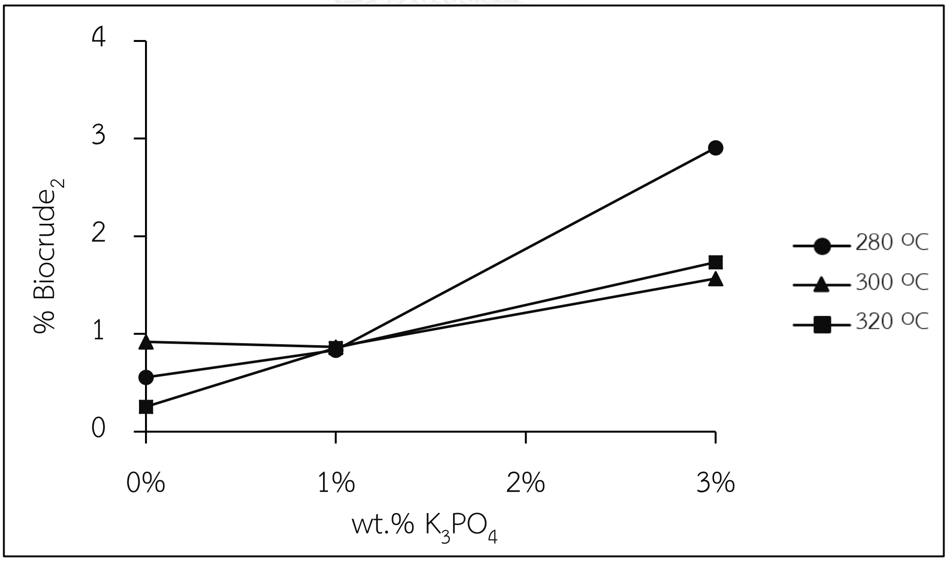

Figure 4.14. Effect of K_3PO_4 in co-solvent on biocrude$_2$ at different temperatures and a flow rate of 1 ml/min

Finally, the consequence of alkaline compound and temperatures for solid residue conversion was symbolized in Figure 4.15. On the whole, both 1 wt% and 3 wt% catalyst were found to be effective for massive decrease in the percentage of solid. Evidentially, the greater reaction temperature and the lower in weight of solid were identified at a shorter resident time associated with the addition of catalyst.

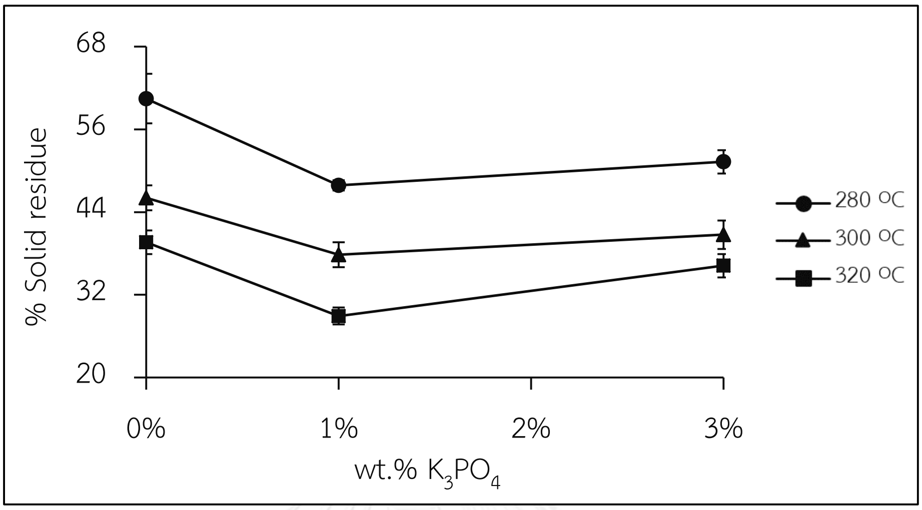

Figure 4.15. Effect of K_3PO_4 in co-solvent on solid residue at different temperatures and a flow rate of 1 ml/min

The minimum marks were 47.89%, 37.81% and 28.93% coinciding with temperatures of 280 – 320 °C, respectively in term of 1 wt% K_3PO_4. Yin et al. [80] delved into the liquefaction pathways of cellulose via many environments. They discovered that the intermediately unsaturated components (e.g. 5-HMF, organic acids, etc.) being primary elements would be dehydrated and reconstructed into the solid residue under a neutral condition. However, the dehydration reactions might be restricted in presence of the denser pH value [26]. As a result, the solid residue dwindled extraordinarily on account of utilizing alkaline solution which approaches an arrangement and stabilization of small fragments, hence it could abolish formation of char or solid production [70].

On the other hand, an apparently divergence from two flow rate regimes is that the solid residue was accidentally rocketed to 51.29% at 280 °C, prolonged by 40.72% and 36.23% matching temperatures of 300 °C and 320 °C at a flow rate of 1 ml/min while the catalytic solution climbed up to 3 wt%. In much the same as a preceding explanation, one of the prime causes departures from the abundance of unsaturated monomers under the superior alkalinity, which might be more accessible to recombine sensitive molecules to the tar/char production. Another important thing is that the catalysts were assumed responsibility for neutralizing any leftover organic acids during the HTL process [2], whereas in fact, our liquefaction time was too abridged to counteract thoroughly. It was also confirmed by Huang et al. [65] that the repolymerization process would prevail against depolymerization during the HTL of rice husk at a higher dosage of catalyst and 20 min resident time.

4.2.4. Effect of K_3PO_4 in pure water

In order to entirely appreciate an efficiency of K_3PO_4 in different solvents, the catalytic liquefaction of sugarcane leaves was also organized in pure water as solvent, along with two flow rates.

4.2.4.1. Effect of K_3PO_4 in pure water at a low flow rate

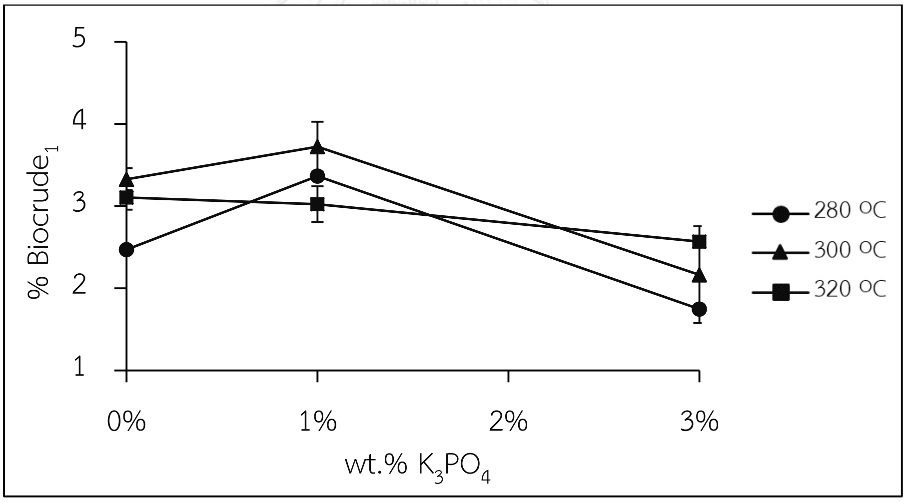

Figure 4.16. Effect of K_3PO_4 in water on biocrude$_1$ at different temperatures and a flow rate of 0.5 ml/min

The influence of alkaline concentrations (wt% K_3PO_4) in pure water on the biocrude$_1$ production at different temperatures and a flow rate of 0.5 ml/min were exposed in Figure 4.16. First of all, nothing is more important than the fact that the catalytic liquefaction realized in pure water was much less persuasive than that of co-solvent.

Secondly, it seemed that there was no effect of K_3PO_4 solutions on the biocrude$_1$ conversion, stagnating at the same level (approximately 3% of the total) in whole concentrations at 320 ^oC. Nonetheless, rather different events took shape at 280 ^oC in which the oil yield jumped to 3.37% at 1 wt% K_3PO_4 in water prior to coming down enormously to 1.75% at 3 wt.% alkaline solution. The largest amount of biocrude$_1$ was recorded at 1 wt% catalyst at 300 ^oC, with 3.72% of the oil conversion, thereafter dipping into 2.16% at 3 wt% solution. An explanation of those matters is probably that the alkali could promote disintegration of glycosidic linkages in sugarcane leaves. Otherwise, potassium salts might also facilitate the recombination of light oil yield, simultaneously expedite the polarity of aqueous fraction, which was assigned to intensify phase separation between oil fraction and water soluble phase [81].

Many authors interpreted the best performance of alkaline-promoted lignocellulosic liquefaction by the mechanism blow [16, 45]:

- Firstly, there was a combination between hydroxyl ion and CO originated from breaking cellulose/hemicellulose to create the formate ion

$$OH^- + CO \longrightarrow HCOO^-$$

- Secondly, the dehydration of vicinal hydroxyl groups in a carbohydrate would be strongly encouraged to make its enol, which were combined with each other into ketone by isomerization reactions:

$$CH(OH)\text{-}CH(OH)\text{-} \longrightarrow \text{-}CH{=}C(OH)\text{-} + HOH \longrightarrow \text{-}CH_2\text{-}CO\text{-} + HOH$$

- Thirdly, it is feasible to cut freshly formed carbonyl group into the interrelated alcohols, formate ion and carbon dioxide

$$HCOO^- + \text{-}CH_2\text{-}CO\text{-} \longrightarrow \text{-}CH_2\text{-}CH\text{-}(O^-)\text{-} + CO_2$$

$$\text{-}CH_2\text{-}CH\text{-}(O^-)\text{-} + HOH \longrightarrow \text{-}CH_2\text{-}CH\text{-}(OH)\text{-} + OH\text{-}$$

That is an adequate reason why the alkaline catalysts have an ability to reinforce biomass the HTL conversion as well as diminish heavier oil formation as labeled in Figure 4.17. The results unveiled that the biocrude$_2$ slumped down massively from 3.27% without catalyst to 2.52% and 0.96% in terms of 1 wt% and 3 wt% K_3PO_4 solution, respectively at 280 ^oC and a flow rate of 0.5 ml/min. With respect to a temperature of 300 ^oC, the minimal oil 2 product, which departed from 4.99% in catalytic absence, was 1.33% of the conversion in 3 wt% catalyst. Nonetheless, the fluctuation was manifested in the biocrude$_2$ yield at 320 ^{o}C. It went up and down in narrow size of nearly 5%.

The root causes are that alkaline salts sponsored the biomass degradation process into small unstable substances [26]. Subsequently, they might be benignly reconnected to heavier oil by retro-aldol condensation, whereas the catalyst was exploited for the neutralization of those unsaturated one as well as cutback in repolymerization reactions [2]. Those competition led to decrease in the biocrude$_2$ in this circumstance.

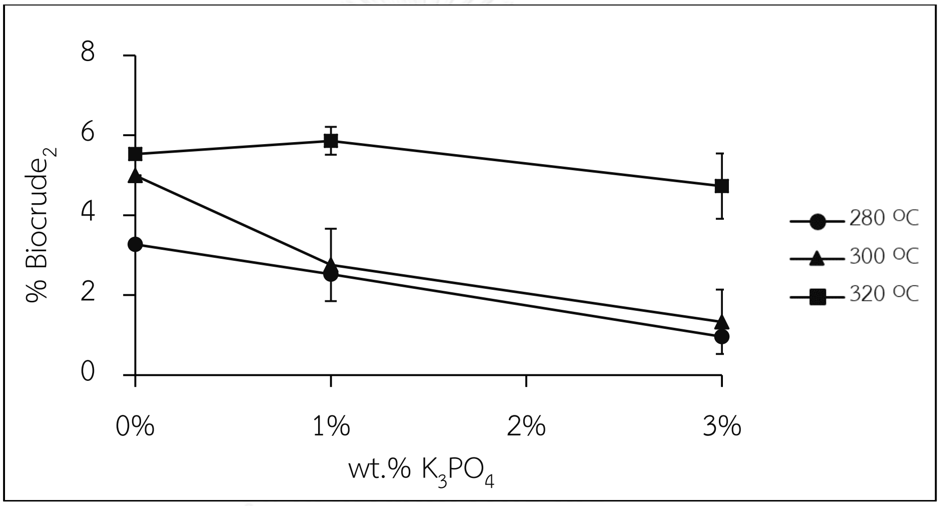

Figure 4.17. Effect of K_3PO_4 in water on biocrude$_2$ at different temperatures and a flow rate of 0.5 ml/min

The consequences were in good agreement with several earlier researches. For instances, Sing et al. [52] studied the effect of catalytic concentration (KOH and K_2CO_3) on the liquefaction of water hyacinth. It was found that a drastic reduction of bio-oil 2 was measured from 12% in blank situation until 6% and 5% of the conversion when adding into 0.5 N K_2CO_3 and KOH, respectively. Afterwards the lower percentage of oil yield and the higher dosage of catalyst were detected as 3% at 1 N K_2CO_3 and 4% at 1 N KOH. Another interesting literature review is Singh and his colleagues [38]. They defined that both KOH and K_2CO_3 were proved to be influential in upgrading the HTL of wheat husk at 280 ^{o}C for 15 min. In particular, there was a severe shrinkage of bio-oil 2 from 20% without catalyst to 16% with KOH solution and 9% of the total in presence of K_2CO_3.

There was down markedly in weight of the solid residue through a catalytic impregnation at a flow rate of 0.5 ml/min and a varied temperature as sketched in Figure 4.18. Evaluating between non-catalyst and catalyst run, the depth of recession in solid content was turned out proximately 8.38% at 280 °C, abided by 2.55% at 300 °C. The rest of temperature was 6.2% of the conversion. Besides, the minimal points were 39.27%, 31.49% and 29.92% at the temperatures of 280 - 320 °C, respectively in 3 wt% catalyst.

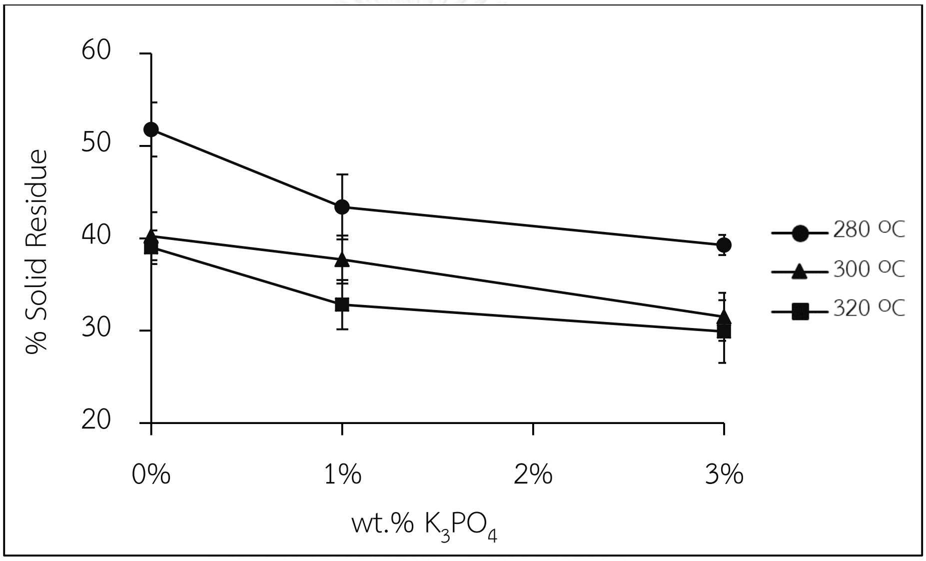

Figure 4.18. Effect of K_3PO_4 in water on solid residue at different temperatures and a flow rate 0.5 ml/min

The alkali has been reported to prohibit formation of solid residue from reconstruction reactions of unsaturated intermediate constituents [65]. Additionally, it also had an advantageous decomposition of macromolecular lignin, leading to generate organic components [52]. Moreover, the temperature always exists a spectacular relationship with the thermal cracking reactions, which is exceedingly supported at a relatively upper temperature. As a result, the greater temperature and the smaller solid residue were recognized in Figure 4.18.

4.2.4.2. Effect of K_3PO_4 in pure water at a high flow rate

Similarity to the last circumstance, K_3PO_4 specified a negative incidence to the $biocrude_1$ production at a shorter resident time as portrayed by Figure 4.19. On the whole, it seemed like that the consequences did not discriminate obviously from each other at temperatures of 280 °C and 300 °C. They went up and down approximately 1% of the conversion, no matter which the catalytic concentration was. These issues could be inferred from a quite inferior reaction temperature and short reaction time that affiliated with some weak properties of water as the liquefaction solvent, namely higher dielectric constant (e.g. 18.66 of dielectric constant at 330 °C, 35 MPa) and critical point, lower ability to extract nonpolar compounds than the other solvent [41, 82]. Those defects progressed to a deficiency of energy serving to thermal breaking of carbon-carbon bonds in complex lignocellulose matrixes as well as a shortage of contacting between catalytic dissolution and raw material.

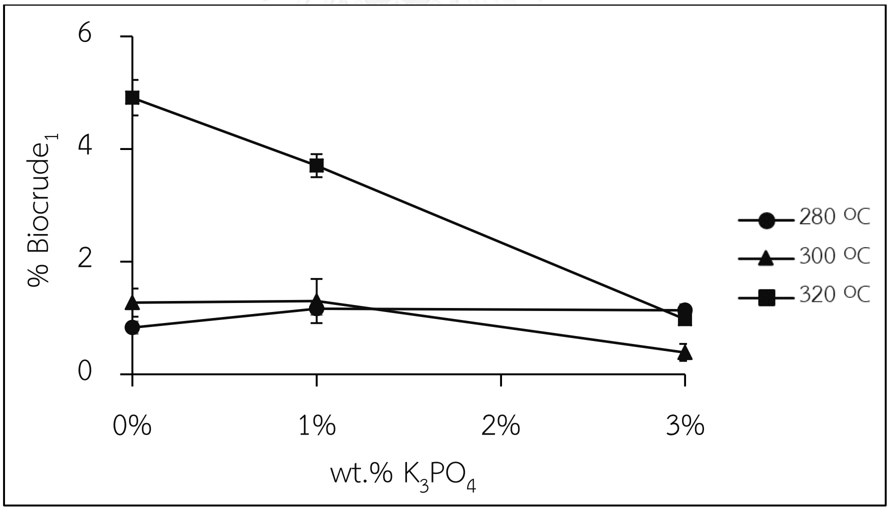

Figure 4.19. Effect of K_3PO_4 in water on $biocrude_1$ at different temperatures and a flow rate 1 ml/min

On the other side, the yield descended slightly from 4.91% in blank catalyst to 3.71% in 1 wt% solution, subsequently dipping into 0.98% of the total with 3 wt% catalyst at 320 °C. This might be interpreted by an increment in the thermal degradation of feedstock at high temperature, concurrently it also resonated with strong alkalinity so as to speed up carbon-carbon cleavages into gaseous products [77].

Likewise the former issue, the solution of catalyst in water pointed out an opposite impact on $biocrude_2$ conversion as delineated in Figure 4.20. The volume of oil product was no intensive change at 280 °C, with only 1.7% of the conversion; even so, it was supplied either 1 wt% or 3 wt% alkaline catalyst. Notwithstanding, the downward trend was disclosed at the upper temperatures. For examples, the $biocrude_2$ dwindled humbly from 2.07% in a blank test to 0.84% at 3 wt% K_3PO_4 at 300 °C. Typically, the product was as great as 3.21% at 320 °C in non-catalyst run, though it diminished suddenly to 0.9% in an existence of 3 wt% catalyst. All of the root causes to explain those matters were sufficiently cited in the discussions above.

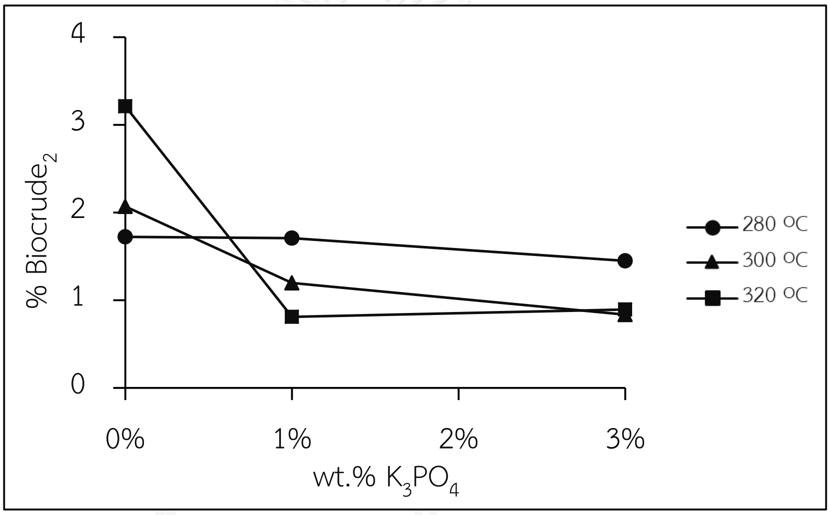

Figure 4.20. Effect of K_3PO_4 in water on $biocrude_2$ at different temperatures and a flow rate of 1 ml/min

Lastly, the solid remaining subsided colossally at high temperatures with present of alkaline catalyst as manifested in Figure 4.21. The mass loss of 12.75%, 10.2% and 11.71% between 280 °C and 320 °C, respectively were laid out when comparing between non-catalyst and 1 wt% catalyst operated. The minimal solid was 22.51% of the total at 320 °C and 3 wt% solution. These consequences were valuable clues asserting an impressive fragmentation of biomass in water as the solvent liquefaction.

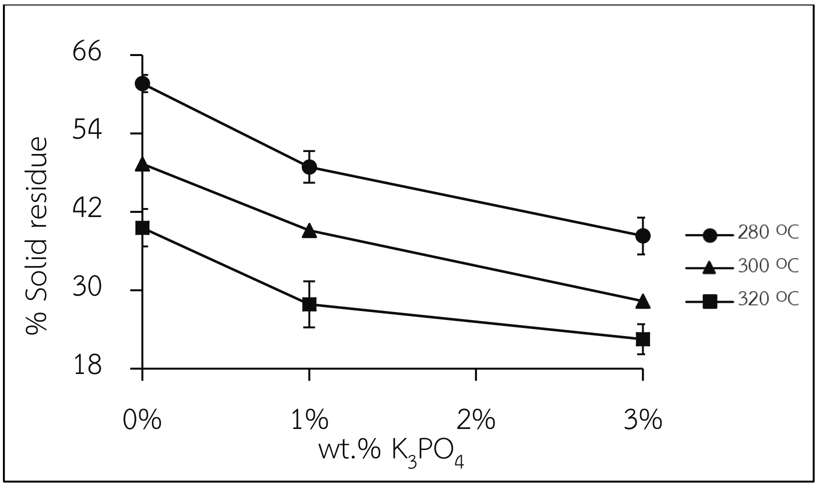

Figure 4.21. Effect of K_3PO_4 in water on solid residue at different temperatures and a flow rate 1 ml/min

It is believed that the alkali would reacted as hydrolytic agents for the disassociation of macromolecular lignin in biomass [83]. Besides, it was also participated in transferring from cellulose and hemicellulose to organic matters by cleaving glycosidic bonds [52]. Nevertheless, to the best of knowledge, these polar components were too difficult to disperse into oil phase because of some disadvantageous qualities of pure water. That is a reason justifying decrease the huge amount of feedstock via the HTL, whereas the oil production are still much less than the others.

4.3. Characteristic of biocrude

4.3.1. Total acid number titration (TAN) and Karl-Fischer titration (KF)

The total acid number (TAN) is a chemical technique to measure how much acidity exists on the oil production. It is determined by a dose of potassium hydroxide (ml) used to neutralize utterly the acidic compounds in 1 gram oil. The purpose of Karl-Fischer titration (KF) is to appraise the quantity of inherent water in the one. Both of them play an important role in the oil characterization. In fact, the TAN is required as low as acceptable for storage and transportation. It is implied that higher TAN than ASTM standard could bring about operational obstacles and corrosion during a long period of depository [84].

The quality of biocrude$_1$ was wholly analyzed via a couple of methods as illuminated in Table 4.2. Ordinarily, it is not probably to deny the fact that a downward trends in both the water content and TAN of oil yield were examined by using the catalytic liquefaction. Firstly, in case of 1 wt% K_3PO_4 impregnated with water, TAN fell off estimably 39.904 remarks (from 68.592 mg KOH/g to 28.688 mg KOH/g). Thereafter, it restored a little to 35.147 mg KOH/g at 3 wt% catalyst. However, as reported by dissolving the catalyst into co-solvent (50/50 v/v water/ethanol), there was a gradual tumble of TAN indicator from 70.482 without catalyst to 54.136 and 46.856 mg KOH/g standing for 1 wt% and 3 wt% alkali executed, respectively.

Table 4.2. Property of biocrude$_1$ in different concentration of K_3PO_4, 300 ^oC and a flow rate of 0.5 ml/min

Solvent	C_{K3PO4} (wt%)	Water Content (wt%)	TAN (mg KOH/g)
Water	0%	7.455	68.592
	1%	4.023	28.688
	3%	5.881	35.147
Ethanol/water (50/50 v/v)	0%	4.725	70.483
	1%	4.245	54.136
	3%	1.190	46.856
Ethanol	0%	3.987	51.227

The main reasons were credited to drop off total acids on account of their neutralization reactions with alkaline catalyst. Zhu et al [2] proved the point over GC-MS analysis results of catalytic liquefaction of barley straw. His outcomes declared that carboxylic acids inside the biocrude plunged deeply from 29.19% until 23.81% when evaluating between non-catalyst and catalyst, respectively. Furthermore, some acids might be disintegrated to carbon dioxide and water in base environment [77]. Even so, the stronger alkalinity and the more forceful hydrolysis of biomass were paid attention to rocket up an ingredient of acid compounds [79]. That progressed to rehabilitate the

TAN a bit at 3 wt% catalyst in water, whereas it continued to plummet in co-solvent due to facilitating the esterification reactions between organic acids and alcohols [7].

There are always an adjacent interaction between TAN and water content of oil. Definitely, the moisture dwindled constantly from 7.455% to 5.881% in term of water as the liquefaction solvent and from 4.725% until 1.19% corresponding to co-solvent when the comparison of blank test and 3 wt% catalyst, respectively. The cutback in water content were an absolutely suitable to descend TAN of the oil product due to some principles above.

Those results were extremely appropriate to many researches. For instance, Shakya et al. [85] elucidated that the moisture of bio-oil originated from the HTL of pavlova declined from 10.14% without catalyst to 8.15% with Na_2CO_3 at 250 ^oC. These appeared a similar to liquefy isochrysis being raw material at the catalytic conditions. Precisely, the reductions in water content were listed 0.67%, 5.64% and 3.96% catching up the temperatures of 250 ^oC, 300 ^oC and 350 ^oC, respectively. Wang et al. [86] enlightened us about the decrement in an inherent water (from 9% to 8%) and TAN (from 176 until 100 mg KOH/g) of the oil, which was gathered from litsea cubabe seed liquefaction over the blank and alkaline catalyst test.

Finally, taking unused catalyst circumstances into consideration, the pure ethanol is the best condition as regard the HTL of sugarcane leaves, with only 3.987% of water and lower TAN (51.227 mg KOH/g). These were much less than that of both pure water and co-solvent. Something else should mention that there was no significant difference in the TAN between pure water and water/ethanol as the liquefaction solvent. On the contrary, an uninterrupted decrease in the ingredient of moisture in oil were recorded from 7.455% in term of pure water until 4.725% of an equal co-solvent and furthermost in pure ethanol.

Those could be explained by a hydrogen donor. The hydrogens created from sub-/supercritical alcohol played the role as a hydrogenolysis agent to break down biomass and a deoxygenation agent to remove oxygen via H_2O formation [87]. The polarity of biocrude would be farther if it consisted a bit of the oxygen content, which urged to elaborate an ability to absorb water.

In brief, the biocrude manufactured from the HTL process contained too much acid components to serve in real, even though the ones lessened significantly under the catalytic liquefaction. The oil product did not satisfied the standard commercial fuel yet, such as: TAN ≤ 0.5 as regard to gasoline, diesel and biodiesel [88]. Thus, that is the urgent problem for liquefaction scientists to handle nowadays.

4.3.2. CHN analysis and high heating value (HHV)

Another important characteristic is an elemental composition and high heating value as clarified in Table 4.3. First of all, the comparison between the ultimate analysis of sugarcane leave and its biocrude production, we are possibly to terminate that the efficiencies of the HTL process is to manufacture oil acquiring a far top of carbon content (around 59 – 65 wt%) as well as lesser oxygen (26 - 33 wt%) rather than estimably 52 wt% carbon and 38 wt% oxygen of the feedstock. Those made the product achieve higher heating value (24 - 29 MJ/kg) from only 15.31 MJ/kg of raw material.

Secondly, regarding the blank test, there was not striking change in an ingredient of the biocrude$_1$ between pure water and mixture of ethanol/water as liquefaction solvent. Those values were approximately 60 wt%, 6.5 wt%, 0.4 wt% and 33 wt% corresponding to the carbon, hydrogen, nitrogen and oxygen content, respectively. Thereby, the HHV of a couple of situations resembled as 23.8 MJ/kg. These issues were in harmony with the resemblance between water content and TAN as mentioned in Table 4.2.

In accordance with pure ethanol, it exhibited the best candidate for liquefaction solvent. Its oil possessed the utmost of HHV (27.949 MJ/kg), along with higher carbon and hydrogen (64.259% and 7.729%, respectively) than the others. The minimal oxygen involved only 27.379% of the total, which was ascribed to deoxygenation reactions during the HTL, namely [60, 89]:

- The shrinkage of oxygen content was owing to dehydration reactions liberating CO/CO_2.

- Ethanol, polar protic solvent, could supply the hydrogen-donors or hydrogen free radicals, which probably reacted with oxygen of feedstock to proceed water.

Thirdly, the dissolution of K_3PO_4 to pure water, the larger dozen of carbon and hydrogen and the smaller oxygen content were inspected in Table 4.3. The proportion of carbon sloped abruptly from 60.398% without catalyst until 65.327% with 1 wt% catalyst, hence slightly down to 62.279% in term of 3 wt% alkaline solution. In mean time, there was a steady upturn in the hydrogen, from 6.436% of non-catalyst runs to 7.961% and 8.151% in presence of 1 wt% and 3 wt% K_3PO_4, respectively. In particular, a profound depletion of oxygen reached 26.309% at 1 wt% catalyst from 32.857% in blank condition. Afterwards it resumed hiking up to 29.25% in 3 wt% solution case.

Table 4.3. The elemental composition of biocrude$_1$ production at 300 ^oC and a flow rate of 0.5 ml/min

Solvent	C_{K3PO4}	Element composition in biocrude$_1$ (wt%)				HHV (MJ/kg)
		C	H	N	O*	
Water	0%	60.398	6.436	0.310	32.857	23.791
	1%	65.327	7.961	0.403	26.309	28.838
	3%	62.279	8.151	0.320	29.250	27.551
Ethanol/water (50/50 v/v)	0%	60.000	6.530	0.412	33.058	23.755
	1%	59.426	6.785	0.446	33.343	23.878
	3%	63.940	7.965	0.469	27.626	28.137
Ethanol	0%	64.259	7.729	0.633	27.379	27.949

* By difference

Therefore, the maximum HHV of biocrude$_1$ was 28.838 MJ/kg at 1 wt% catalyst, succeeded by 27.551 MJ/kg of 3 wt% alkali. Even then, they were still superior to 23.791 MJ/kg of the blank test. In common knowledge, we have three processes to get rid of oxygen, comprising of decarbonylation, decarboxylation and dehydration reactions. Among them, the ways not only conserving the hydrogen content but also dismissing as much as possible oxygen content would be preferred the HHV of biocrude. And both decarbonylation and decarboxylation took delight in those conditions [55]. Besides, Toor et al. [26] declared that the alkaline catalysts were in favor of the decarboxylation and water gas shift reactions, hence the generation of H_2 and CO_2 would be facilitated in abundant CO.

In another way, the elimination of CO_2 was also expedited under the interaction between unstable hydroxyl radicals and CO [2]. In there, like what I explained above, the stronger alkalinity and the denser amount of unsaturated intermediate ones were confirmed by many researches. The carbon monoxide could be produced at lower temperature by an eradication of aldehyde from an initial decomposition stage of biomass [90]. Those led to slip down the oxygen content as well as climb up the HHV of oil in existence of alkaline substance. Nonetheless, both oxygen content and HHV were a little downward at 3 wt% K_3PO_4. That might be ascribed to an excessive organic components in the high alkalinity.

As regards the impregnation of K_3PO_4 in co-solvent, it was recognized that there was no distinct properties of the biocrude$_1$ between non-catalyst and 1 wt% catalyst operated. Those values were roughly 60%, 6.53% and 33.058% denoting the dosage of carbon, hydrogen and oxygen, respectively, which entailed to proximately 23.8 MJ/kg of the HHV. Notwithstanding, both the carbon and hydrogen content elevated massively to 63.94% and 7.965%, along with diminishing a lot of the oxygen down to 27.626% at 3 wt% alkaline solution. These issues implied to scale up the topmost HHV of 28.137 MJ/kg. It was deduced that either the utilization of ethanol as the liquefaction solvent or high alkalinity approached deoxygenation reactions during the HTL of sugarcane leaves.

4.3.3. Gas Chromatography/Mass Spectroscopy (GC-MS)

4.3.3.1. The GC-MS results of biocrude$_1$ in terms of non-catalyst and catalyst run

The difference of biocrude$_1$ composition involving in a complex mixture of hydrocarbons were totally probed by the GC/MS as designated in Figure 4.22. The NIST mass spectral bibliography was used to identify the name and typical structure of chemicals. Table 4.3 expounded on the comparison of peak area (%) for each component in the biocrude$_1$ from the liquefaction of sugarcane leaves at 300 ^{o}C, a flow rate of 0.5 ml/min and catalyst or non-catalyst (K_3PO_4).

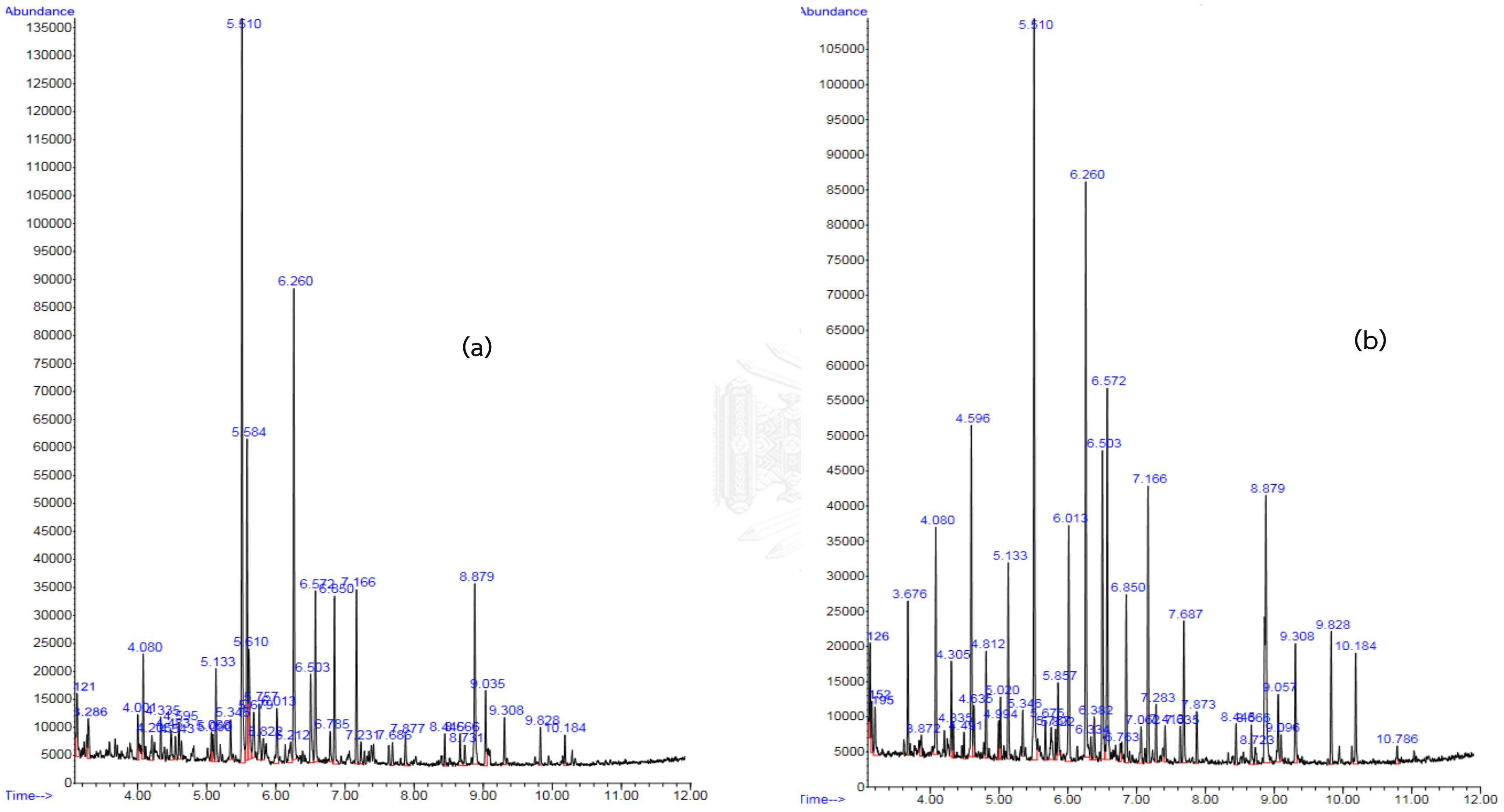

*Figure 4.22. The GC-MS chromatograms of biocrude$_1$ obtained from the HTL of sugarcane leaves with **(a)** non-catalyst and **(b)** 3 wt% catalyst in co-solvent at 300 °C and a flow rate of 0.5 ml/min*

Table 4.4. List of biocrude$_1$ compositions obtained from the HTL of sugarcane leaves with catalyst and without catalyst in ethanol-water co-solvent at 300 ^{o}C and a flow rate of 0.5 ml/min

No	Retention time (min)	Tentative compound	% Area	
			0 wt% K_3PO_4	3 wt% K_3PO_4
1	3.121	3-methoxy-2-butanol	1.95	-
2	3.126	Ethyl 2-hydroxybutanoate	-	1.29
3	3.195	4-hydroxy-butanoic acid	-	1.05
4	4.08	3-methyl-1,2-cyclopentanedione	2.43	3.42
5	4.305	2-hydroxy-3,4-dimethyl-2-cyclopenten-1-one	-	1.48
6	4.483	2-methoxy-6-methyl-pyrazine	1.02	-
7	4.491	2-tetrahydrofurylmethyl ester	-	0.4
8	4.543	Methyl 2-furoate	0.6	-
9	4.595	4-methoxy-phenol	0.97	5.21
10	5.133	4-ethyl-phenol	2.25	2.95
11	5.345	2-hydroxyphenol	1.13	0.68
12	5.51	2,3-dihydro-benzofuran	18.88	11.77
13	5.584	5-hydroxymethyl-2-furfural	8.55	-
14	5.675	3-oxohexanedioic acid diethyl ester	-	0.67
15	5.757	Ethyl (2E)-4-methyl-2-pentenoate	1.83	0.9
16	5.857	2-methyl-1-penten-3-ol	-	1.14
17	6.013	4-ethyl-2-methoxyphenol	2.04	4.24
18	6.26	2-methoxy-4-vinylphenol	11.83	9.22

19	6.334	2-ethylcyclohexyl ester	-	0.38
20	6.382	2-methyl-1,4-benzenediol	-	0.79
21	6.503	2,6-dimethoxy-phenol	3.01	5.64
22	6.85	3-hydroxy-4-methoxy-benzaldehyde	4.5	2.77
23	7.686	4-(2-hydroxyethyl)-2-methoxyphenol	0.67	-
24	7.877	5-dimethoxybenzaldehyde	0.9	-
25	8.445	4-hydroxy-3,5-dimethoxybenzaldehyde	0.78	-
26	8.666	2,6-dimethoxy-4-(2-propenyl)phenol	0.94	0.69
27	8.879	4-((1E)-3-hydroxy-1-propenyl)-2-methoxyphenol	5.74	7.37
28	9.035	Methyl 3-phenyl-2-propenoate	2.06	-
29	9.308	Ethyl 3-(4-hydroxyphenyl) prop-2-enoate	1.25	2.1
30	9.828	Ethyl (2E)-3-(4-hydroxy-3-methoxyphenyl)-2-propenoate	0.91	2.52
		Total area (%)	74.24	66.68

The values were integrated from the distribution of chromatographic each compound’s area out of the total ion chromatogram. These portion only represented relatively the individual magnitude and would not be the substantial concentration.

It was noticeable that 2,3-dihydro-benzofuran with content up to 18.88% of the total area was the largest amount among the oil components in absence of catalyst, accompanied by 2-methoxy-4-vinylphenol (11.83%), 5-hydroxymethyl-2-furfural (8.55%), 4-((1E)-3-hydroxy-1-propenyl)-2-methoxyphenol (5.74%), 4-hydroxy-3-methoxybenzaldehyde (4.5%) and 2,6-dimethoxy-phenol (3.01%). In 3 wt% alkaline catalyst loading, the major constituents were also 2,3-dihydro-benzofuran (11.77%), 2-

methoxy-4-vinylphenol (9.22%), 4-((1E)-3-hydroxy-1-propenyl)-2-methoxy-phenol (7.37%), 2,6-dimethoxy-phenol (5.64%), 4-methoxy-phenol (5.21%) and 4-ethyl-2-methoxyphenol (4.24%).

In general, it seemed like that there was a close resemblance of chemical compounds between two biocrude$_1$ over the GC/MS results. This deduction was also perceived by Zhu et al. [2] via FTIR analysis of oil products derived from the liquefaction of barley straw in alkaline environment (K_2CO_3). Interestingly, the comparative outcomes of biocrude$_1$ in Table 4.3 figured out that a huge loss of 2,3-dihydro-benzofuran was exactly 7.11%, followed by 2.66% of 2-methoxy-4-vinylphenol and 1.73% of 3-hydroxy-4-methoxybenzaldehyde. Particularly, the complete disappearance of 5-hydroxymethyl-2-furfural was tracked in 3 wt% catalyst situation, even though it ever made up to 8.55% in non-catalyst run.

Those might be set down by prohibiting against dehydration reactions of the monomers in superior alkalinity (3 wt% K_3PO_4). In the meantime, decarboxylisation process would substitute for the ones in that condition [2, 26]. Apart from Figure 4.23, it can be clearly seen that some furfurals, phenols and its derivatives were discernibly curtailed by the removal of dehydration pathway under the alkaline environment, which devoted to the remarkable diminution of solid residue (tar/char). Those arguments were in good agreement with Sinag's research into biomass decomposition in subcritical water [91]. They asserted that almost all of acids, esters and furan derivatives were constituted by thermal disintegration of cellulose and hemicellulose. Although alkali salts facilitated the breakdown of organic matters, it would also negatively influence on the formation of furfurals amount.

Additionally, a meager increase in area of short-chain compounds were also scrutinized by the biocrude$_1$ compositions between non-catalyst and 3 wt% catalyst operated, respectively. For instance, a dosage of 4-methoxy-phenol rose from 0.97% until 5.21%. An expansion of 4-ethyl-2-methoxyphenol and ester's derivative (9.828 min) were up to 4.24% and 2.52% in existence of catalyst. A peak of 2,6-dimethoxy-phenol attained 5.64% in that circumstance while the one had just been 3.01% without catalyst. Meanwhile, most of them were phenol compounds and derivatives, which proved that the alkali played a crucial role in thermal degradation of lignin.

It was approved by Xu et al. [92] that phenol and its derivatives, for example: benzestrol, hexastrol, 4-(1,1-dimethylpropyl)-phenol, etc. were generally arisen by breaking down the aryl ether bonds in complex lignin matrix. Besides, the unsaturated compounds manufactured from hydrolysis of cellulose and hemicellulose might endure the condensation/cyclization process, which excited the formation of phenolic derivatives under basic conditions.

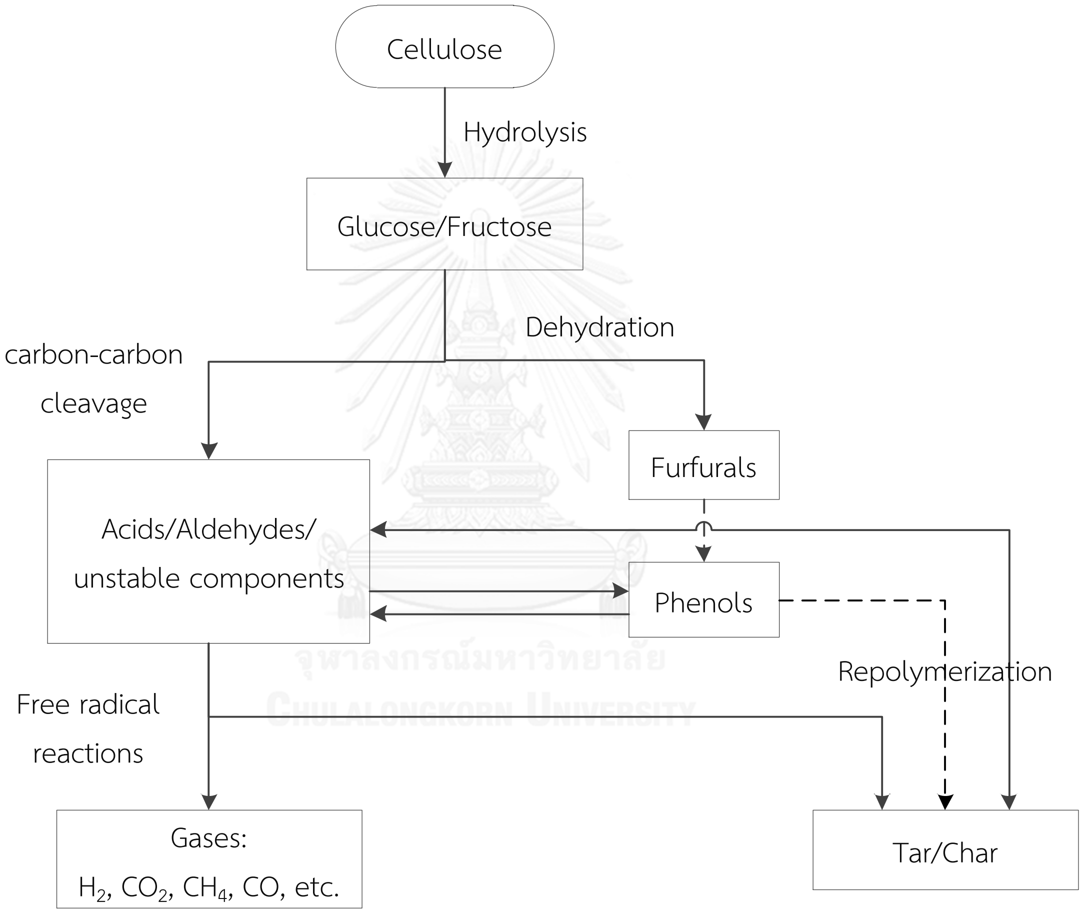

Figure 4.23. Reaction network of hydrothermal biomass degradation [26, 93]

Lastly, the appearance of ester compounds in the biocrude$_1$ ascertained that the presence of ethanol in the HTL was favorable to transform intermediate organic acids into their corresponding esters [42]. According to Table 4.3, it was noticeable that even the ones did not make up a huge amount of peak area, for examples: ethyl (2E)-4-methyl-2-pentenoate (1.83%), methyl 3-phenyl-2-propenoate (2.06%), etc. in without catalyst condition. But, they were diversified and many types, hence it was accounted for 6.65% out of the total area.

On the other side, the addition of 3 wt% K_3PO_4 advocated hiking the number of some esters. The area of ethyl 3-(4-hydroxyphenyl) prop-2-enoate was from 1.25% to 2.1%. An upturn in ethyl (2E)-3-(4-hydroxy-3-methoxyphenyl)-2-propenoate was verified from 0.91% until 2.52%. In particular, a lot of fresh components were cropped up in the biocrude$_1$, such as ethyl 2-hydroxybutanoate (1.29%), 3-oxohexanedioic acid diethyl ester (0.67%), and so forth. In consequence, the sum area of esters in case of using alkaline catalyst arrived at 9.4% out of the total. That was the overwhelming evidence resulting in the existence of esterification reactions during the catalytic co-solvent liquefaction process.

4.3.3.2. The GC-MS results of biocrude$_1$ and biocrude$_2$ production

Figure 4.25 claimed the visibly distinct compositions between biocrude$_1$ and biocrude$_2$ gathered from 1 wt% catalytic liquefaction of sugarcane leaves at 300 ^{o}C and a flow rate of 0.5 ml/min by means of the GC/MS technique. Overall, it was recognized that all the ingredients of biocrude$_1$ distributed in a retention time of 3 – 9 min. Nevertheless, those of biocrude$_2$ dispensed after 10 min. The proofs were simply to persuade us that the abundant longer-chain molecules and more complexly structural compounds existed on the biocrude$_2$ product than that of another.

The major component of biocrude$_1$ detailed in Table 4.5 was 2-methoxyphenol (15.2%), succeeded by 2,6-dimethoxyphenol (14.69%), 4-acetyl-2,6-dimethoxyphenol (8.8%), 2,3-dihydro-benzofuran (7.25%), phenol (5.8%), 2-methoxy-4-vinylphenol (5.6%), etc. As mentioned above, these products were corollary of lignin disruption by the hydrolysis reactions, which was catalyzed by the high pH environment [26]. Likewise, Liu et al. [94] turned out the hydrolysis pathways of lignin during the hydrothermal conversion of walnut shells with the alkaline condition as depicted in Figure 4.24. They also certified that the C-O ester linkages (α-o-4 and β-o-4) of lignin would be deeply split into transitional methoxy phenolic compounds by the strong alkalinity in water.

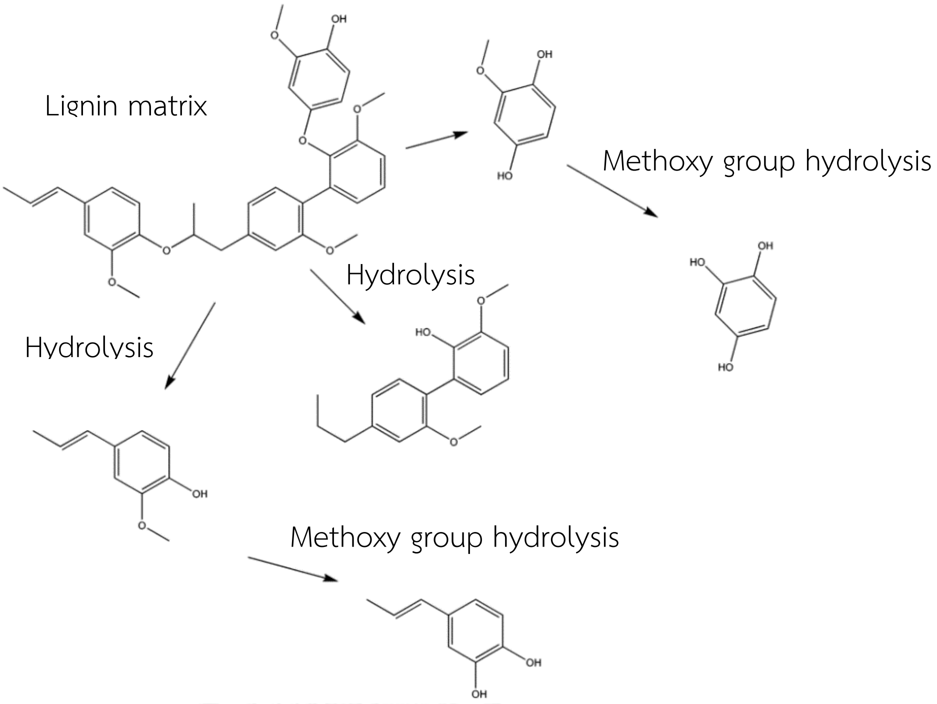

Figure 4.24. The schematic diagram of lignin degradation

Regarding the distribution of biocrude$_2$, most of peaks shifted to higher retention time between 9.95 min and 16.799 min in the GC/MS result. Especially, the largest compound of the one was 2-methyl-3-phenylindole ($C_{15}H_{13}N$), with 23.45% of the total area, followed by phthalic acid-di (2-propylpentyl) ester ($C_{24}H_{38}O_4$, 19.54%), 2-ethylacridine ($C_{15}H_{13}N$, 6.83%), 3,5-ditert-butyl-4-hydroxycyclohexa-2,4-dien-1-one ($C_{14}H_{22}O_2$, 6.49%), so forth. It was definitely seen that all of them were extremely heterogeneous compounds with long-chain molecules and multiple aromatic rings. Those chemicals were renovated by self-condensation and cyclization reactions of unsaturated components (organic acids, alcohols, aldehydes, ketones, etc.). In report on the lignin liquefaction, Lin et al. [95] concurred that the intermediate reactions with aliphatic side chains became much more active and thus, they condensed with each other into the multi-condensed yield during the HTL process.

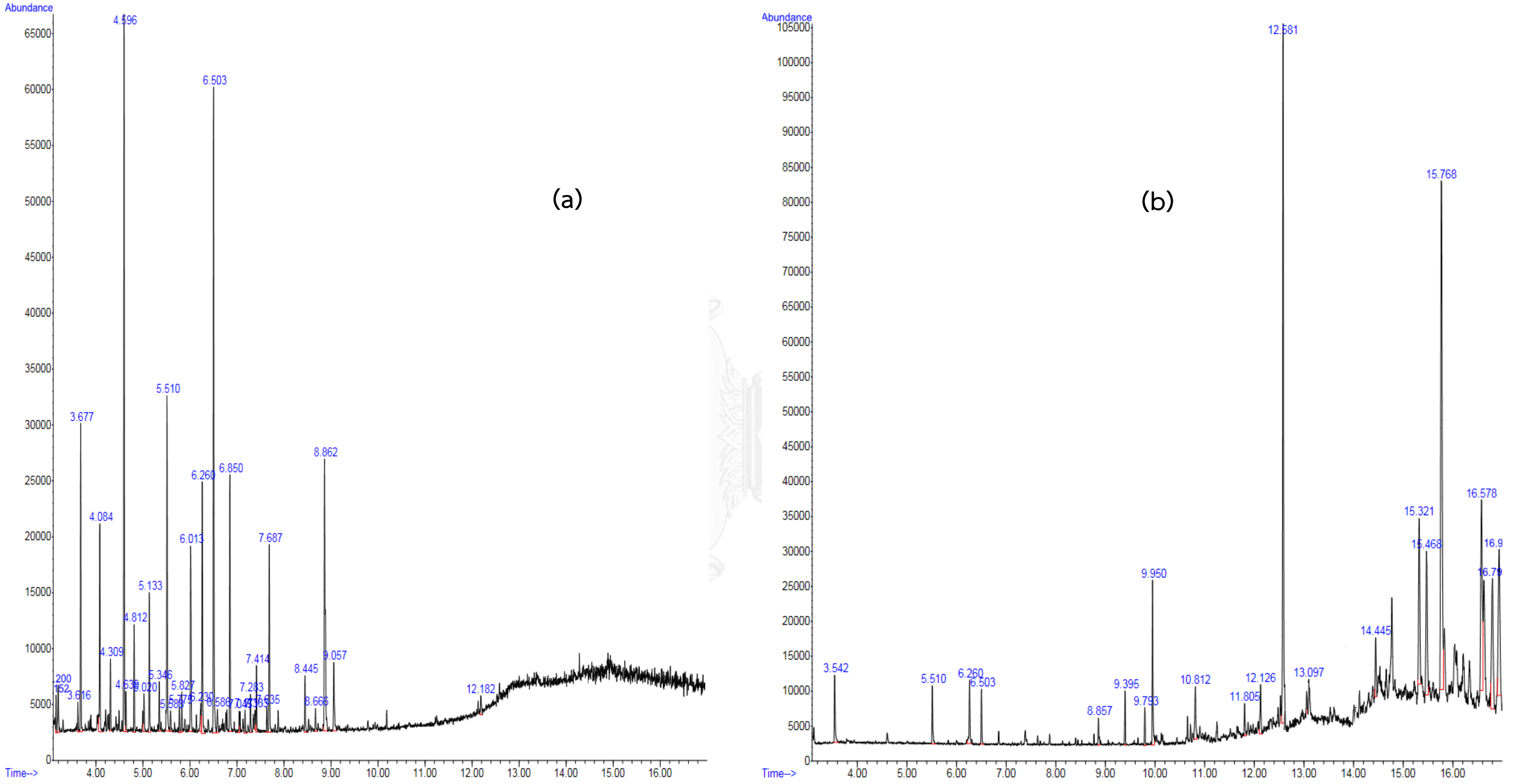

Figure 4.25. GC-MS spectrums of biocrude$_1$ ***(a)*** *and biocrude$_2$* ***(b)*** *from the HTL of sugarcane leaves with 1 wt% K_3PO_4 in pure water at 300 °C and a flow rate of 0.5 ml/min*

Table 4.5. List of biocrude$_{1\ \&\ 2}$ compositions obtained via the HTL of sugarcane leaves with 1 wt% K_3PO_4 in water at 300 °C and a flow rate of 0.5 ml/min

No	Retention time (min)	Tentative compound	% Area	
			Biocrude$_1$	Biocrude$_2$
1	3.2	Butyrolactone	1.16	-
2	3.542	Glycerin	-	1.88
3	3.677	Phenol	5.8	-
4	4.084	3-methyl-1,2-cyclopentanedione	4.36	-
5	4.309	3,4-dimethyl-2-hydroxycyclopent-2-en-1-one	1.43	-
6	4.596	2-methoxyphenol	15.2	-
7	4.812	3-ethyl-2-hydroxy-2-cyclopenten-1-one	2.05	-
8	5.133	4-ethyl-phenol	2.72	-
9	5.346	2-hydroxylphenol	1.02	-
10	5.51	2,3-dihydro-benzofuran	7.25	1.47
11	6.013	4-ethyl-2-methoxyphenol	4.66	-
12	6.26	2-methoxy-4-vinylphenol	5.6	1.71
13	6.503	2,6-dimethoxyphenol	14.69	1.27
14	6.85	3-hydroxy-4-methoxybenzaldehyde	5.51	-
15	8.862	4-acetyl-2,6-dimethoxyphenol	8.8	-
16	9.793	Methyl 10-methylundecanoate	-	0.85
17	9.95	n-hexadecanoic acid	-	3.82
18	12.581	Phthalic acid-di(2-propylpentyl) ester	-	19.54
19	15.321	3,5-ditert-butyl-4-hydroxycyclohexa-2,4-dien-1-one	-	6.49

20	15.468	7-dihydro-3,6-dimethyl-4-benzofuranone	-	6.06
21	15.768	2-methyl-3-phenylindole	-	23.45
22	16.799	2-ethylacridine	-	6.83
		Total area (%)	80.25	73.37

Furthermore, there was a fall in the number of 2,3-dihydro-benzofuran from 7.25% to 1.47% or 2-methoxy-4-vinylphenol (a loss of 3.89%). Especially, the tremendous shrinkage of 2,6-dimethoxyphenol was observed from 14.69% until 1.27% when comparing between the biocrude$_1$ and biocrude$_2$, respectively. Those reductions resulted in altering single aromatic ring to composite compounds. The findings were almost similar to Singh et al. [52] examining on the liquefaction of water hyacinth in catalytic conditions (KOH and K_2CO_3). Their ^{1}H NMR spectral distribution of functional groups in bio-oil 2 epitomized that the aliphatic content occupied roughly 90% of the total product. Otherwise, they also laid out the stunning increment of aliphatic compounds in the bio-oil 2 (acetone soluble fraction) because of employing a variety of alkaline catalysts.

CHAPTER V

CONCLUSIONS AND RECOMMENDATION

5.1. Conclusion

Taking everything into account, there are some appreciable consequences achieved from my thesis on the catalytic liquefaction of sugarcane leave in ethanol-water co-solvent.

5.1.1. Raw material

The bountiful resource, evasion of the human food-chain as well as environmental troubles arisen from the direct combustion of agricultural waste, etc. made sugarcane leave become a suitable feedstock for the thermal conversion processes. Moreover, the higher percentage of volatile and fixed carbon and the lower ash fraction were some necessary conditions for the HTL. In contrast, the existence of gigantic oxygen content in the initial material was a major impediment heading the HHV of the biocrude production down.

5.1.2. Hydrothermal liquefaction of sugarcane leaves

First of all, the mixture of water and ethanol (25/75 v/v) was the best ratio of co-solvent as regards the liquefaction of sugarcane leave, with 29.47% of the biocrude$_1$ conversion at 300 ^{o}C, a flow rate of 1 ml/min without catalyst. Besides, a cutback in the amount of biocrude$_1$ product was disclosed in term of excess water, whereas the solid residue would be rocketed up whenever the redundant ethanol owing to its weak acidity. A more interesting thing is that the biocrude$_2$ assembled from the solid remaining was not worth considering.

Secondly, according to a flow rate of 0.5 ml/min, the optimal liquefied temperature was 300 ^{o}C as to ratios of co-solvent having beneath 50% ethanol. Regarding the rest of curriculums, the biocrude$_1$ would increase significantly at higher temperature. However, those results in case of 1 ml/min flow rate were exactly the opposite to what happed before. The contradiction was attributed to the difference of resident time.

Thirdly, the addition of K_3PO_4 into co-solvent behaved positive effect on the quantity of biocrude$_1$ in the long holding time. Typically, the product attained approximately 30.63% at 300 ^oC, a flow rate of 0.5 ml/min in presence of 1 wt% catalytic solution. Simultaneously, the stronger alkalinity and the lower oil conversion were also observed at 3 wt% catalyst. In the contrary, K_3PO_4 exposed the absolutely negative influence on the HTL of sugarcane leaves when rising the flow rate to 1 ml/min, which was adopted by a profound downgrading of the biocrude$_1$ production the whole conditions.

Fourthly, in much the same as the alkali in co-solvent, the presence of K_3PO_4 in pure water still figured out a couple of divergent aspects, including a favorable impact on the oil conversion at the inferior flow rate and an adverse effect at the superior one. Besides, it certainly would be right to confirm that the efficiency of alkaline compound in co-solvent were much higher than that of pure water when evaluating an accumulation of the oil yield between two those situations.

Lastly, the influences of resident time, which is an important factor in the process, were concretely investigated via a variety of solvent flow rates. It obviously altered effects of the other parameters such as temperature, co-solvent and the addition of alkaline catalyst. For instance, both the conditions of K_3PO_4 in co-solvent and water, the catalyst performed dramatically positive effect on the biocrude yield at a longer resident time. Whereas, the oil production would decrease significantly when reducing the contacting time. In addition, the short resident time in association with the high ethanol concentration in co-solvent facilitated biocrude generation in terms of non-catalyst.

5.1.3. Characteristic of biocrude production

It was undeniable the fact that either the dissolution of K_3PO_4 in mixture of water/ethanol or pure water as the liquefaction solvent played an important role in the drastic depletion of moisture content, TAN and oxygen content of the biocrude$_1$ yield via the HTL of sugarcane leave. That was a key cause explaining why the higher HHV and the better qualities of oil were spotlighted. Notwithstanding, those HHV were still much lesser than petroleum products due to the existence of a whole lot of organic compounds leading to the abundant oxygen.

In addition, there was not a remarkable difference of functional groups in the $biocrude_1$ between non-catalyst and catalyst run via the GC/MS technique. Nevertheless, the appearance of fresh ester components contributed to the enhancement of the oil capacity in attendance of alkaline catalyst (K_3PO_4) and ethanol. Otherwise, we were probable to distinguish the $biocrude_2$ from the other by the schematic distribution of constituents. It was revealed that all the ingredients of $biocrude_2$ were long-chain molecules associated with a complex cluster of aromatic rings.

5.2. Recommendation

Even though we accomplished the spectacular success in this work, there are still some drawbacks of the property of biocrude production. Therefore, in order to optimize the catalytic liquefaction of sugarcane leave, I bravely suggest some solutions, namely:

- Investigating the effect of K_3PO_4 in a various ratio of co-solvent merged with initial gas (hydrogen) on batch reactor.
- Studying the other solvent extraction having an ability to dissolve as much as possible organic compounds in the aqueous fraction. For instances: butanol (4 of polarity and 0.43% solubility in water) or chloroform (4.1 of polarity and 0.815% solubility in water) might be instead of DCM (3.1 and 1.6%, respectively).

Exploring the influence of K_3PO_4 in co-solvent on the other feedstock possessing a larger nitrogen content than sugarcane leaves in order to assess the competence in denitrogenation. Apart from those results, we are able to control a reasonable quota of alkali and feedstock to recover aqueous fraction as standard fertilizer source (N, P, K)

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APPENDIX

APPENDIX A

CALCULATION OF BIOCRUDE PRODUCTION

The conversion of biocrude_1, biocrude_2, and solid residue were accurately counted by the following equations, respectively:

$$\%\text{Biocrude}_1\ (\text{wt\%}) = \frac{(\text{wt.of biocrude}_1) \times 100\%}{\text{wt.of daf. feedstock}}$$

$$\%\text{Biocrude}_2\ (\text{wt.\%}) = \frac{(\text{wt.of biocrude}_2) \times 100\%}{\text{wt.of daf. feedstock}}$$

$$\%\text{Solid residue (wt\%)} = \frac{(\text{wt.of solid residue - wt. of ash})}{\text{wt.of daf. feedstock}} \times 100\%$$

$$\%\ [\text{Aqueous phase + gas] (wt\%)} = 100\% - \%\text{Biocrude}_1 - \%\text{Biocrude}_2 - \%\text{Solid residue}$$

Where:

daf.	: dry, ash-free basis
wt.of biocrude_1	: weight of biocrude_1
wt.of biocrude_2	: weight of biocrude_2
wt.of daf.feedstock	: weight of dry-ash free sugarcane leaves

Besides, the experiments were repeated several times so as to calculate the average of results.

APPENDIX B

CALCULATION OF HIGH HEATING VALUE

The high heating value of sugarcane leaves was calculated via the proximate analysis result by the equation below [47, 48]

$$\mathrm{HHV}\ (\mathrm{MJ/kg}) = 0.3536\mathrm{FC} + 0.1556\mathrm{VM} - 0.0078\mathrm{A}$$

Where:

HHV	: high heating value (MJ/kg)
FC	: Fixed carbon (*wt%, total-dry basis*)
VM	: Volatile matter (*wt%, total-dry basis*)
A	: Ash content (*wt%, total-dry basis*)

The high heating value of biocrude production would be determined by the elemental composition method by the Dulong formula [47, 50, 51].

$$\mathrm{HHV}_{\mathrm{biocrude}}\ (\mathrm{MJ/kg}) = 0.3383 \times \mathrm{C} + 1.422 \times \left(\mathrm{H} - \frac{\mathrm{O}}{8}\right)$$

Where:

$\mathrm{HHV}_{\mathrm{biocrude}}$	: high heating value (MJ/kg)
C	: Carbon content (wt%)
H	: Hydrogen content (wt%)
O	: Oxygen content (wt%)

VITA

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