Production of anhydrosugars by pyrolysis of cellulose in practical reactor

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修士論文

Production of anhydrosugars by pyrolysis of cellulose in practical reactor

九州大学大学院総合理工学府総合理工学専攻

材料理工学メジャー

化学反応工学教育分野

修士課程 2 年　ZHENHAO GAO

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Contents

Chapter 1: Introduction

1.1. Overview of biomass and energy

Currently, our world is facing the challenges of greenhouse effect and transforming reliance on fossil fuels to sustainable resources. Biomass energy is the energy which stored in biomass. It is the energy stored in biomass by green plants converting solar energy into chemical energy through chlorophyll. It usually includes wood and forest industrial waste, agricultural waste, and domestic organic waste, aquatic plants, oil plants, etc. Biomass energy has always been an important source of energy for human survival. It ranks fourth in the world's total energy consumption after coal, oil and natural gas, and occupies an important position in the entire energy system[1,2]. Biomass, as the only renewable energy that can be converted into gas, liquid, and solid energy forms, has attracted widespread attention around the world due to its advantages such as huge output, storability, and carbon cycle. Countries all over the world have placed the high-efficiency utilization of biomass energy in an important position in high-tech research and development when adjusting their national energy development strategies. Efficient utilization of biomass energy is also one of the important topics of the modern energy production and consumption revolution.

Fig. 1 clearly shows that the forecast of CO_2 emission savings of different sectors worldwide. The most promising sectors are transport and industry which can reach 29% and 32% respectively. So that should make sense, these two sectors are also among the sectors that consume the most energy and emit the most carbon dioxide. While People's policies and efforts are inclining towards decarbonization and the use of renewable materials (e.g., biomass), hence their effectiveness is the most obvious. **Fig. 2** and **3** indicate annual subsector CO_2 emission of China and Japan contrastively. Attributed to the rapid industry and economy growth during the decade, it almost increased by 8 billion tons (Gt) of CO_2 in 2011. Among them, power and heat consumption accounts for the largest part of total. About Japan, major economies in the world, as a developed country responsible for 4% of total annual CO_2 emissions in the world, experienced an increase of nearly 50% in overall CO_2 emissions during last four decades, compared with China's consumption growth is not so significantly but nonetheless the direct increase of residential consumption from 1990 to 2011 was low.

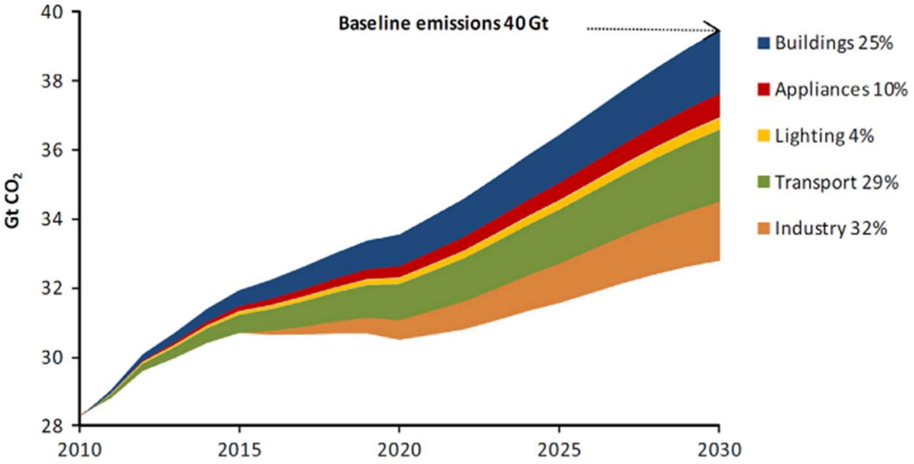


Fig. 1. The global potential of different sectors for CO_2 mitigation by 2030. ([2]) Reprinted from [2], Copyright (2003), with permission from Elsevier

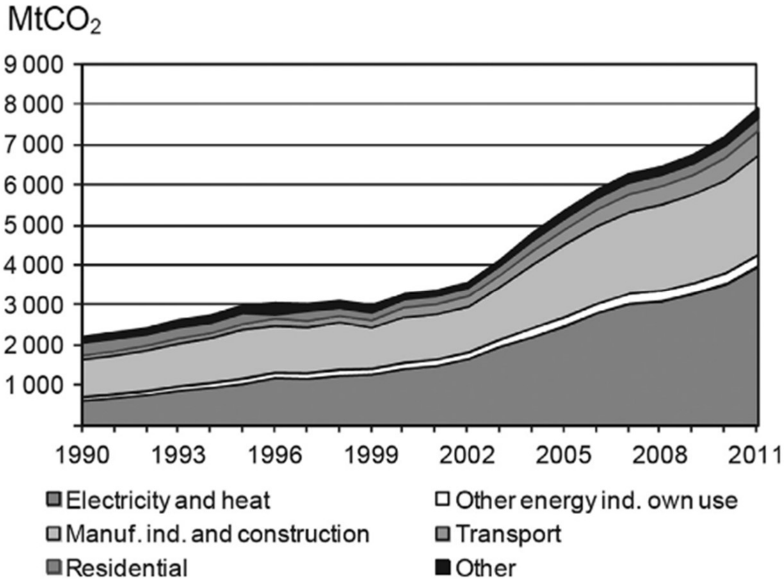


Fig. 2. Sectorial CO_2 emissions in China from 1990 to 2011. ([2]) Reprinted from [2], Copyright (2003), with permission from Elsevier

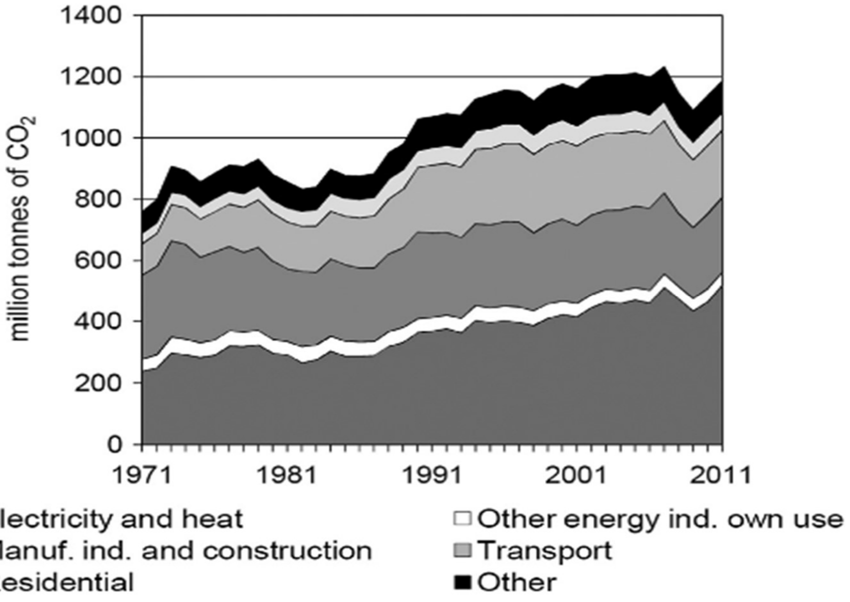


Fig. 3. Sectorial CO$_2$ emissions in Japan from 1971 to 2011. ([2]) Reprinted from [2], Copyright (2003), with permission from Elsevier

To summarize, owing to the contradiction between the increasing energy demand and energy saving and emission reduction accelerating the adjustment of energy structure and transformation is imminent should be on the agenda right away. With the overall goal of efficiently utilizing biomass resources to enhance scientific and technological innovation capabilities, promoting low-carbon economic development, and breaking through the technology and bottlenecks of emerging industries, it has formed a global development model from resource development, key core technology breakthroughs to the establishment of major product development models. The whole chain is integrated and the trend of coordinated development: diversification of resources, multi-channel raw material supply is an important guarantee for the development of industrial technology; original innovative technology inventions in the technical field, multi-technology coupling and target product regulation and high value are the future The core of technology development; the utilization of all components of biomass in the industrial chain and the high-value utilization of low-value raw materials are effective means to achieve product economy.

However, there is still a long way to go for the efficient use of biomass and its industrialization. The main factors restricting the development of biomass mainly include capital supply and cost factors, technical system bottlenecks, industrial model bottlenecks, financing bottlenecks and lack of policies. Although there have been many basic research projects on biomass energy in recent years, these researches are mainly concentrated on the traditional thermochemical conversion platform at the laboratory stage, which not only has high energy consumption and is not friendly to the environment, but also has indiscriminately damaged the structure of hemicellulose and lignin of biomass, and the derivatives formed are difficult to be effectively used, and difficult to be industrialized. In addition to the relatively mature application system of biogas for rural users, biodiesel, solid fuel and other industries are faced with sales and user problems. On the one hand, the price of biomass energy products is not competitive; On the other hand, some production-oriented users, despite their large demand, have high requirements for the stability of energy supply. Because they are worried about the unstable production of biomass energy enterprises and take a wait-and-see attitude towards the purchase of energy and chemical products, the market capacity cannot be opened since these situation, and the narrow market will cause obstacles to the cost reduction of biomass energy, leading to the inability of the industry to form a scale from raw material acquisition to technology integration, However, it is unable to stabilize production in a large amount, thus forming a vicious circle.

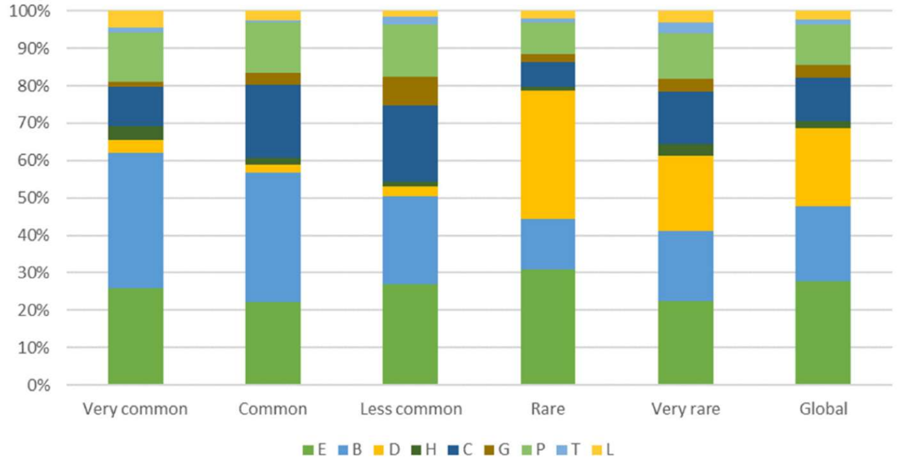


Fig. 4. Relative research intensity for each kind of bioenergy application in each group according to the classification from very common to very rare wetland vegetation: (E) Bioethanol; (B) Biogas; (D) Biodiesel; (H) Biohydrogen; (C) Combustion; (G) Gasification; (P) Pyrolysis; (T) Torrefaction; (L) Liquefaction. ([3])

Despite the above disadvantages, the advantage of the development of the biomass industry is that biomass is the only renewable carbon source on the earth, and it is also the only renewable resource that can be converted into gas, liquid, solid state and electricity; Extensive; the biomass refining industry involves many issues such as energy, environment, agriculture and ecology, vigorously developing the biomass industry is conducive to the overall planning of social and economic development; biomass energy is conducive to the establishment of a diverse energy system and energy security. I think that the development opportunities and challenges of the biomass industry are the same. On the one hand, the fossil energy reserves are limited, the greenhouse effect and environmental pollution are becoming more and more serious, and the development of new energy is imminent; with the increasingly fierce energy competition, people pay more and more attention to the use of renewable energy. Development, policies and regulations have been promulgated one after another, and the international community needs the support of clean and renewable energy for sustainable economic development and the construction of an environment-friendly society; with the rising price of fossil energy, biomass energy will have more and more competitive advantages. To sum up, there are many deficiencies in the utilization and development of biomass energy, but at the same time it has its own advantages. How to transform from the old energy model to the development of new energy is the most important thing.

1.2. Review of cellulose pyrolysis aiming at production of anhydrosugars (AHSs)

1.2.1. Mechanism of formation of monomer, dimer and oligomers

Biomass, especially lignocellulosic biomass, is the renewable, plentiful, reasonable neutral resource that could be used to product fuels and platform chemicals in the industry. The main components of lignocellulosic biomass are cellulose, hemicellulose and lignin which can transform into levoglucosan (LGA), levoglucosenone (LGO), furans and phenols respectively[34-40]. Among them, LGA, the main precursor of LGO, and LGO, are the cellulose monomers we are interested in because they are new sugar source with great development potential for synthesizing natural products owing to its highly functionalized structure containing essentially one chiral center[1]. Pyrolysis and liquefaction of biomass to generate bio-oil is considered to be the most promising biomass energy utilization technology due to the advantages of liquid products such as convenient storage, transportation and high energy density. Compared with slow pyrolysis, fast pyrolysis is in order to transform biomass to a maximum quantity of liquids (so called TAR)[2]. Although slow pyrolysis is well known and an established process, fast pyrolysis is mainly still in the experimental stage, used for analysis, but not suitable for practical production and still under development.[3]

Char is the main product of the typical slow pyrolysis of biomass, in which the reactants is heated slowly to temperatures between 300 and 400 °C. To the contrary, fast pyrolysis is a high temperature process in which the feedstock is rapidly heated in the absence of air, temperature carefully controlled in the range of 450~600 ℃ at atmospheric pressure. The generated gas is captured into bio-oil through a condensing unit, also the solids called char and non-condensable gases can be produced at the same time. Among the liquid products, anhydrosugars (AHSs) are the most concerned which can be classified as monomer, dimer and oligomers depending on the length of the chain. The research on cellulose pyrolysis has been carried out for nearly a century. Researchers around the world have used experiments and simulation methods to conduct extensive and sufficient research on different pyrolysis stages, and proposed many macroscopic and microscopic reaction kinetics. The widely accepted Brodio-Shafizadeh (B-S) model has illustrated pyrolysis reaction path.[4] Based on the B-S model, cellulose pyrolysis is divided into two steps, first converted into active molten intermediates (intermediate cellulose). After that, those cellulose generate oligomers and non-sugar products through depolymerization and ring cleavage. After undergoing further degradation, these oligomers converted into monomers, for instance, LGA, 5-hydroxy Methylfurfural, and other important chemical raw materials. Both oligomers and monomers experience the intra-particle diffusion and evaporation, followed that, they are transformed into oligomers or monomers in liquid product, gas and char by secondary pyrolysis[24,30-33,38]. More specifically, cellulose experiences dehydration and random bond breaking of C-0 bonds at the same time, at random along the chain. Some breakages of $C_{(1)}$-O glycosidic bonds yield hexose units that rearrange to form levoglucosan. Other breakages of C-0 bonds cause breakdown of part of the chain, yielding low-molecular products (including carbon monoxide, carbon dioxide, and water) and a carbonaceous residue[4].

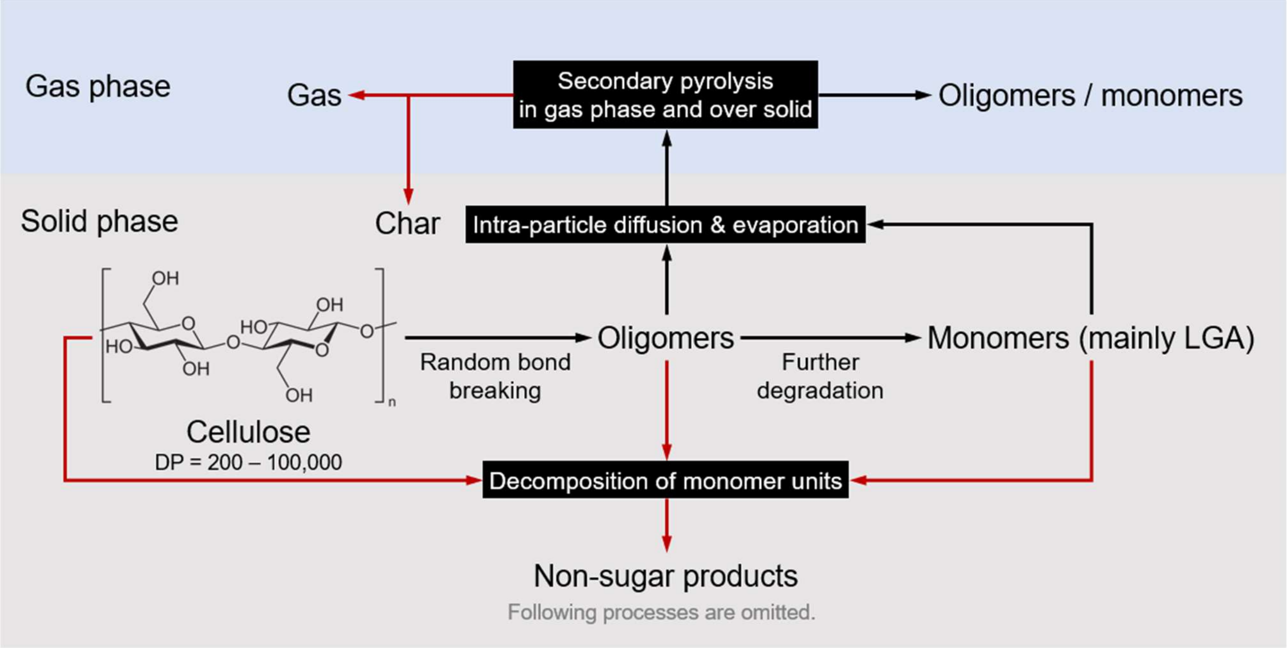


Fig. 5. Mechanism of pyrolysis of cellulose.

1.2.2. Pyrolysis of cellulose in Wire mesh reactor (WMR)

In order to provide direct insight into the two-step mechanism of pyrolysis, a type of reactor is introduced separately at this chapter. Actually, dimensions are very important parameters for pyrolysis[35]. **Fig. 6** shows an analytic pyrolyzer named Wire mesh reactor (WMR) which allows the sample as mono-layer under extremely ideal conditions to eliminate the extra-particle secondary volatiles during the pyrolysis, particularly that due to chemical interaction between pyrolyzing cellulose particles. Additionally, **Fig. 7** demonstrates the configuration of WMR and monolayer form on a wire-mesh holder. 3–5 mg of particles in a form of monolayer formed was tightly sandwiched by two layers of the wire mesh made of SUS316 stainless steel. The sample-laden wire mesh was heated at a rate of 1, 10, 100 or 1000 °C/s from ambient to a prescribed temperature in the range of 300–700 °C, and then cooled to ambient temperature at an initial cooling rate (r_c) that was calculated by the following empirical equation derived from preliminary experiments.

$$r_c = 2.6853(T_p)^{2.6715} \times 10^{-6}$$

where r_c and T_p are the initial cooling rate and the peak temperature, respectively. During the heating and cooling, the carrier gas, helium (flow rate; 5 L-stp/min), was forced to pass through the sample-laden mesh at a velocity, *ca*. 0.066 m/s, high enough to sweep the vapor of nascent volatiles away from the vicinity of the pyrolyzing particles. This forced He flow minimized the degree of the secondary pyrolysis of the volatiles over the particles. The mass of char after pyrolysis was measured. The LGA and other condensable products were cooled and condensed in a trap (≈ –190°C) that was immersed in liquid N_2. The light gases such as H_2, CO, CO_2 and C_1-C_2 gaseous hydrocarbons, which was vaporized in the trap when it was transferred to –70°C bath (methanol mixed with liquid N_2) and then sent to a gas chromatograph. The LGA, oligomers and the liquid products (not vaporized at all during the vaporization of the above-mentioned light gas) was recovered with a solvent, distilled water or methanol.

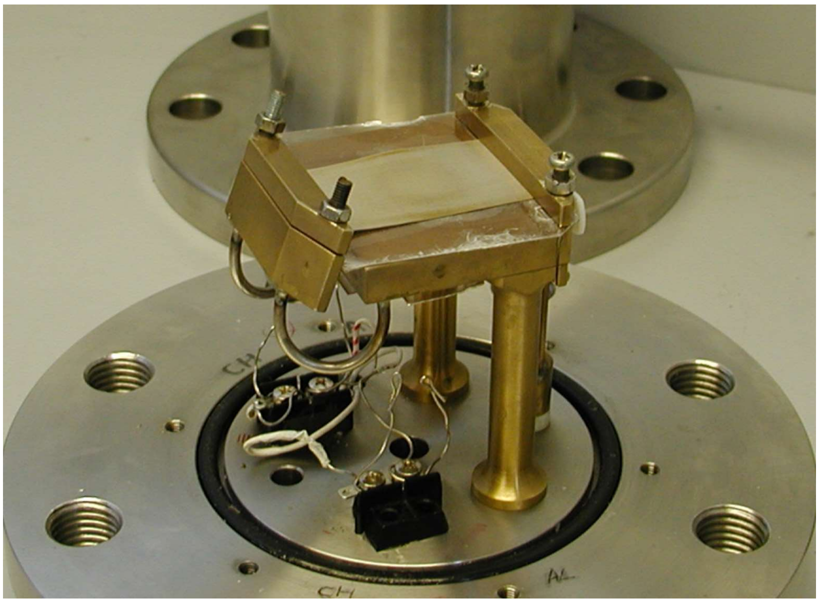
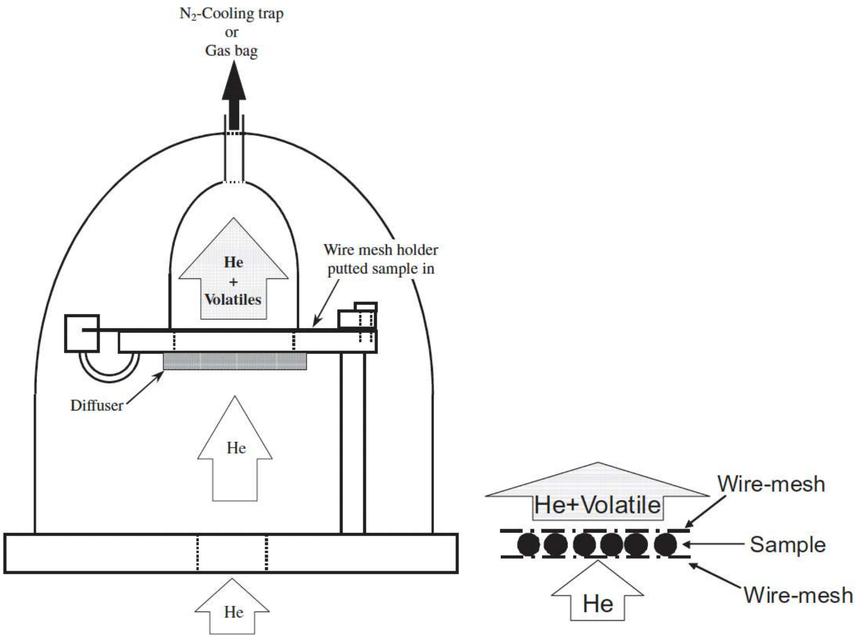


Fig. 6. Wire mesh reactor (WMR).



(a)Wire-mesh reactor (b) A monolayer form of a sample on a wire-mesh holder

Fig. 7. Schematic diagram of a wire-mesh reactor (WMR) and a monolayer form of a sample on a wire-mesh holder.

Moreover, **Fig. 8** shows mass fraction of solid (char yield) from the pyrolysis of cellulose in wire-mesh reactor and that in thermogravimetric analyzer (TGA). The heating rate was fixed at 1 °C/s for both WMR and TGA. Clear differences between WMR and TGA are seen. Firstly, the release of volatile matter occurs in WMR earlier than that in TGA regardless of the initial cellulose mass. This demonstrates that LGA and oligomers underwent the secondary pyrolysis over the pyrolyzing cellulose particles in the fixed bed (in TGA), and then physically and/or chemically adsorbed onto those particles until released from the bed. Secondary, the char yield from the pyrolysis in WMR is as small as 1 wt%-cellulose, and more importantly, clearly smaller than those from the pyrolysis in TGA. This resulted from decomposition of at least a portion of LGA and oligomers, which was deposited irreversibly on particle surfaces and incorporated into the char. In the fixed bed of TGA, due to the absence of forced gas flow, the progress of the secondary pyrolysis was thus significant.

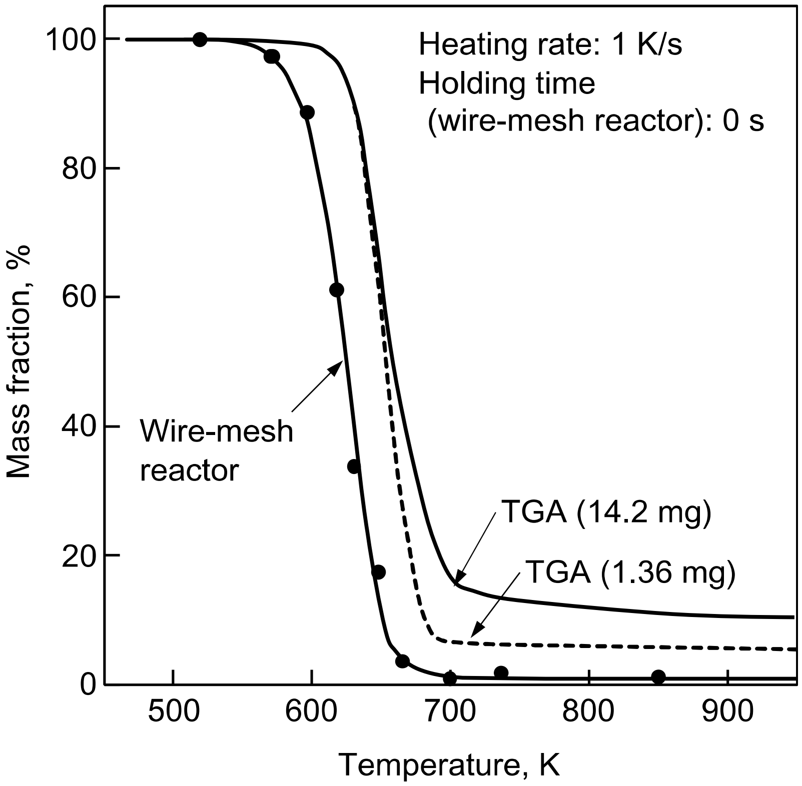


Fig. 8. Mass fraction of solid (char yield) from the pyrolysis of cellulose in wire-mesh reactor (plot) and that in thermogravimetric analyzer (TGA) (solid and dashed lines corresponding different initial mass of 14.2 mg and 1.36 mg).

Fig. 9 shows results of pyrolysis of cellulose in WRM at different degrees. The facts that with the increase of reaction temperature, there was decrease of yields of monomers and dimers whereas the selectivity of other oligomers increased infers it is unfavorable to product LGA at extra high temperature. Meanwhile, **Fig. 10** characterizes datum of pyrolysis of WMR and other types of reactors obtained by previous works. It describes that at high degrees of temperature the yield of LGA in fluidized bed is less than that in micro reactor which can be attributed to the extra-particle secondary reaction to a certain extent. What's more, slow pyrolysis at low temperature can enhance the yields of LGA and oligomers greatly showing strong correlation in the WMR highly suggests that LGA is decomposed from oligomers thereby boosting the intra-particle primary reaction can enhance the yield of LGA. Not only that, from the results of Westerhof et al, we can know slight extent of secondary reaction also enhance the yield of LGA. Overall, if we want to maximize the yield of LGA immensely promote the primary reaction and marginally repress the secondary reaction is a reasonable method, however, in impractical reactor.

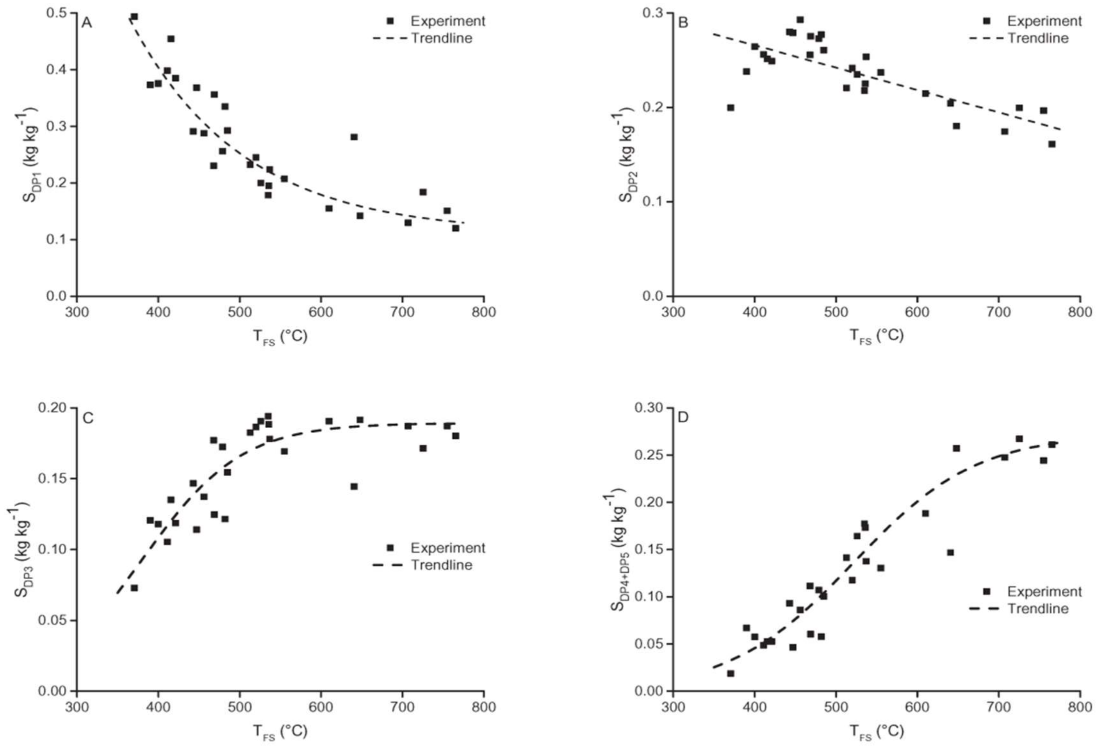


Fig. 9. A) DP1, B) DP2, C) DP3 and D) DP4+5 selectivity as function of TFS with the pressure at 5 mbar and 1 or 5 seconds holding time. ([23]) Used with permission of Royal Chemical Society, from [23], copyright 2023.

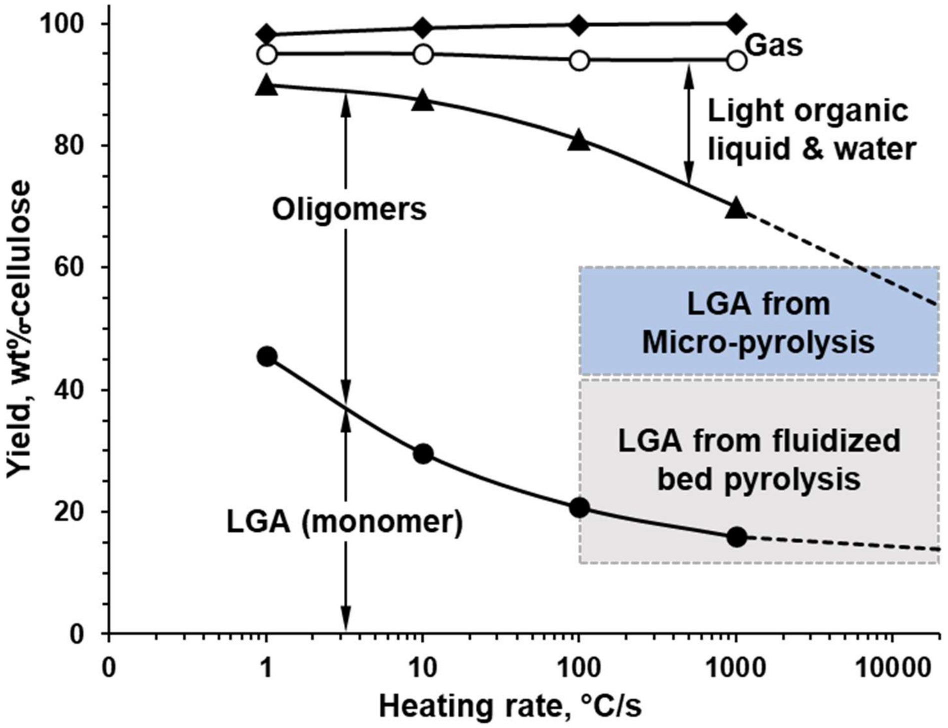


Fig. 10. Yields of LGA, oligomers and others from cellulose pyrolysis in WMR.

1.2.3. Pyrolysis of cellulose in Pyroprobe™ reactors (PBR)

At this stage, pyroprobe™ reactor (PBR) is widely used in the study of pyrolysis[9,10,11]. Automatic sample injection is adopted. Meanwhile, the automatic sampler has 48 positions and can add samples at any time. The automatic sampler is driven by a novel hybrid mechanism, which combines the reliability of the most advanced air actuator and the accuracy of the electronic stepper motor. As a type of impractical reactor, it is linked with a Mass Spectrometer which bombard the compound with electrons to pulverize it at the later section, the compounds are fragmented in a reproducible way, then the ions are separated by the MS and give the results of spectrum which are both qualitative and quantitative. Pyrolysis works in much the same way. By applying heat to a sample that is comparable to the energy of specific bonds, the molecule will fragment in a reproducible way. The number of peaks, the resolution by capillary GC, and the relative intensities of the peaks permit discrimination among many similar formulations, making pyrolysis a powerful tool in the identification of unknown samples. On the basis of B-S model, secondary reaction can be conducted in gas or liquid phase. But for PBR, it can be carried out in the gaseous phase with extremely short residence time and over solid. Although PBR is impractical reactor, it provides the reaction foundation for a model of the conversion of reactant during fast pyrolysis in real practical systems. As distinguish from the ideal and analytic case of PBR, it is impracticable of fast pyrolysis, even 1000 K/min, in practical reactor or in industrial production due to difficulty of secondary decomposition of AHSs and low selectivity to anhydro-monosaccharide, LGA. LGA is a major anhydro monosaccharide product formed during cellulose primary pyrolysis[8], and also can be generated from secondary reaction in a smaller amount as mentioned above. However, if the residence time of volatile phase is too long causing the overall yield of oligomers and monomers may decline since product cannot diffuse promptly. These products undergo secondary reaction on the surface of solid and gas phase that decreases yields of monomers such as LGA, leading the rise of mass of char and fall of weight of gas which is captured by subsequent concatenated condenser to the liquid phase contrastively. Recently, researchers did some studies in the thesis of secondary reaction[9,11]. We may be able to conservatively expect the results of effectiveness of slow pyrolysis which is practical and can be used in industrial production such as fixed bed reactor under reduced pressure for minimization of secondary pyrolysis of AHSs and maximization of their yield.

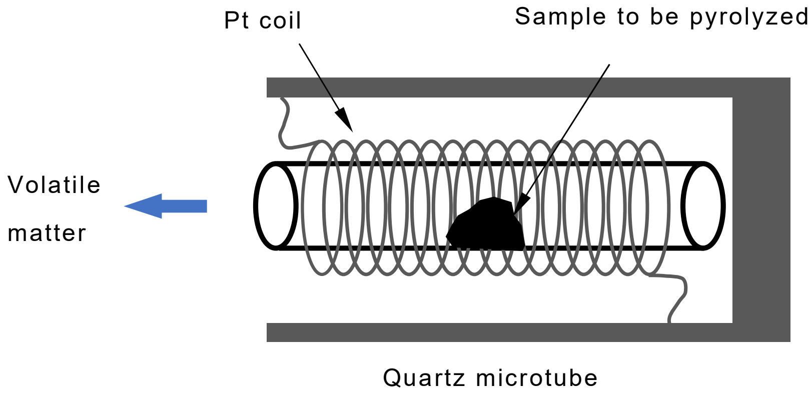


Fig. 11. CDS Pyroprobe

1.3. Review of catalytic cellulose pyrolysis aiming at production of AHSs

1.3.1. Mechanism of formation of monomers

Typically, non-catalytic pyrolysis of cellulose can obtain LGA as the main monomer product[13,14]. Several catalysts were reported to obviously improve the yield of LGO rather than LGA such as H_2SO_4, H_3PO_4 as well as lowering the reaction temperature to save energy[10,15,25-29]. In the case of catalytic rapid pyrolysis of cellulose, H_2SO_4 shows characteristic of promoting the formation of intermediate products[16]. In the two-step mechanism, according to the H_2SO_4-catalyzed reaction models shown in **Fig. 12**, the H_2SO_4-catalyzed depolymerization via C1-O1 bond scission and bridged dehydration take place through a two-step mechanism. After forming a sulfate ester intermediate by linking the sulfonic group to C1 in the first step, sulfuric is obtained with a new H achieved from 6−OH of the sulfate ester intermediate in the next stage. Immediately afterwards, LGA convers from cellulose by removing sulfonic group eventually. More than that, LGO can also be generated by LGA through dehydration reaction with acid catalyst.

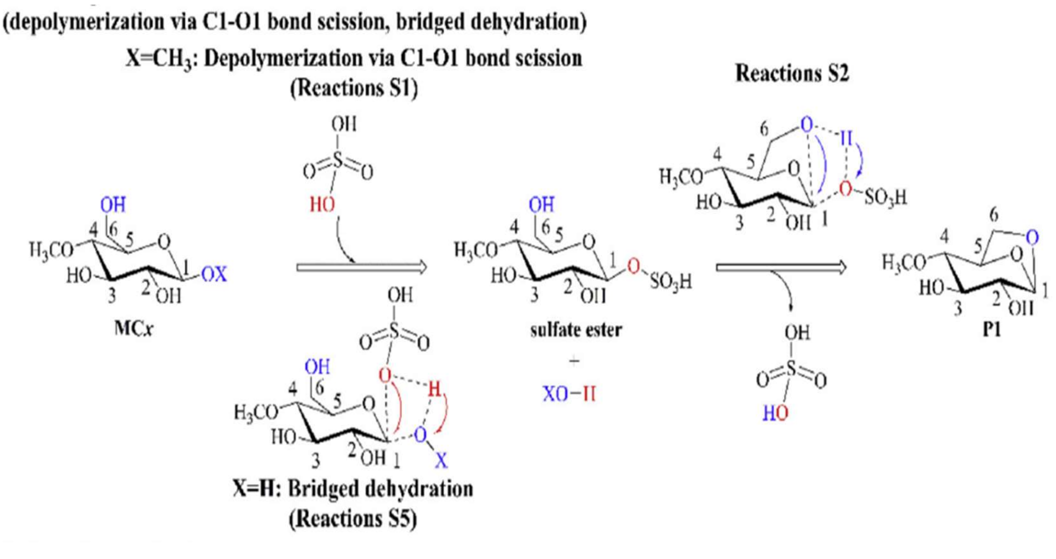


Fig. 12. Two-step mechanism of pyrolysis of cellulose with H_2SO_4. ([16]) Reprinted from [16], Copyright (2023), with permission from Elsevier

The mechanism of catalysis of phosphoric acid is similar to that of sulfuric acid[17]. As illustrated in the **Fig. 13**, under H_3PO_4 catalysis, the cellulose chain depolymerizes to form the

LGA end, which subsequently decomposes.

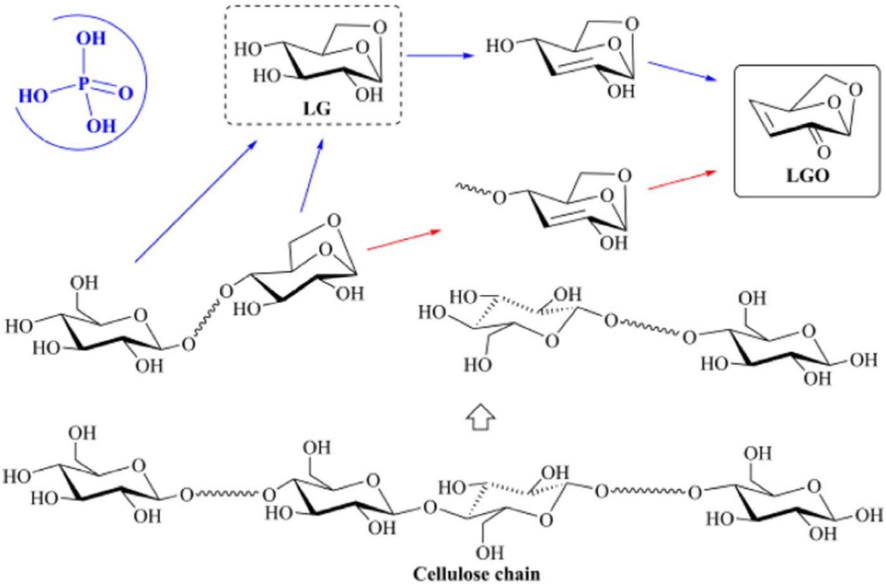


Fig. 13. Mechanism of pyrolysis of cellulose with H_3PO_4. ([17]) Reprinted from [17], Copyright (2023), with permission from Elsevier

1.3.2. Research progress of fast pyrolysis of cellulose with catalysts

As mentioned above, acid catalysis can product both LGA and LGO. **Table. 1** illustrates LGA/LGO yield of fast pyrolysis of cellulose in PBR at the range of 300~500 ℃. As shown in the **Table. 1**, loading very small amount of mineral acid can greatly increase yield of LGA/LGO, much more than that from non-catalytic pyrolysis. However, loading too much acid catalyst will reduce their yields. The results could be explained by the fact that increasing the loading contents to a greater extent not only promotes ring-breaking and dehydration of anhydrosugars, but also improves the conversion of the polysaccharides. Meanwhile, doping these catalysts can markedly decrease the temperature of pyrolysis with higher yield of monomers.

Table. 1. Yields of LGA and LGO from catalytic pyrolysis of cellulose.

Catalyst	Temperature/℃	Reactor	LGA yield/wt%	LGO yield/wt%	References
H_2SO_4/0.1wt%	300	CDS pyroprobe	33.3	9.8	[18]
H_2SO_4/0.1wt%	500	CDS pyroprobe	27.5	4.1	[18]
H_3PO_4/0.5wt%	500	CDS pyroprobe	58.1	8.7	[19]
H_3PO_4/1wt%	500	CDS pyroprobe	25.2	29.8	[19]
H_3PO_4/0.5wt%	350	Vertical flow reactor	0.06	22.3	[19]
H_2SO_4/0.1wt%	300	CDS pyroprobe	36.8	11.5	[10]
H_2SO_4/2.75%	300	CDS pyroprobe	9.1	2.2	[10]
H_3PO_4/1wt%	500	CDS pyroprobe	25.2	29.8	[19]
H_3PO_4/0.5wt%	500	CDS pyroprobe	40	22	[20]
H_3PO_4/2wt%	500	CDS pyroprobe	16	34	[20]

Additionally, it was recorded that acid catalysts also can promote the yields of LGA and LGO from lignocellulose. It is widely accepted that thermal-induced or AAEMs catalyzed decarboxylation, decarbonylation and pyranose ring-breaking reactions are predominantly responsible for the formation of non-condensable gases and light oxygenates causing the decline of yields of monomers[10,15,18]. Then it is inferred that H_2SO_4 combined with the AAEMs to the sulfates called passivation in raw biomass is a main actor of rise of yields of monomers with previous people's understanding of acid catalysts.

1.4. Current problems and prospects

Presently, most of the researches on pyrolysis were under analytic conditions which were so idealized with providing constructive theoretical data but if we aim to use these datum to apply on an actual industrial production, this is almost impossible to achieve, for instance, rapid pyrolysis at the rate of 1000 ℃/s, very thick film of feed even mono-layer. At present, the thermal efficiency of wood biomass pyrolysis technology is only about 30%, and the pyrolysis process will release a large amount of carbon dioxide, causing pollution to the environment should be considered. Thus, given that the scale of industrialization, we have to adopt a low consumption and high efficiency scheme, even better than traditional fossil energy. Overall, as mentioned about the urgency of energy structure transformation above, this study aimed to investigate the catalytic pyrolysis of cellulose and lignocellulosic biomass in practical reactor providing transitional theoretical basis.

Chapter 2: Non-catalytic Pyrolysis of Cellulose

This chapter introduces our previous work, and also make a foreshadowing for the later study of acid catalytic pyrolysis. In particular, the purpose is to investigate effectiveness of slow pyrolysis in fixed bed reactor at reduced pressure and ambient for maximization of AHSs yield.

2.1. Experimental

As illustrated in **Fig. 14**, 0.1 g or 1.0 g of samples are placed on the quartz boat in the FBR. Then the dimensions of the samples are shown in the **Fig. 15** and **16**. The temperature conditions of pyrolysis are peak degree is in the scale of 360-420 °C, 10 ℃/s of the heating rate, holding time is 10min. Pressure set to 3 kPa or 102 kPa for comparison. The N_2 flow rates were 200 mL/min at 3 kPa and 500 mL/min at 102 kPa respectively. Conventionally, on the one hand, condensable gases were collected by aerosol filter and cold trap (-70℃), on the other hand non-condensable gases were analyzed by micro GC and collected by gas bag at the end of the device. After pyrolysis in such FBR, compounds in the liquid products were qualified by HPLC.

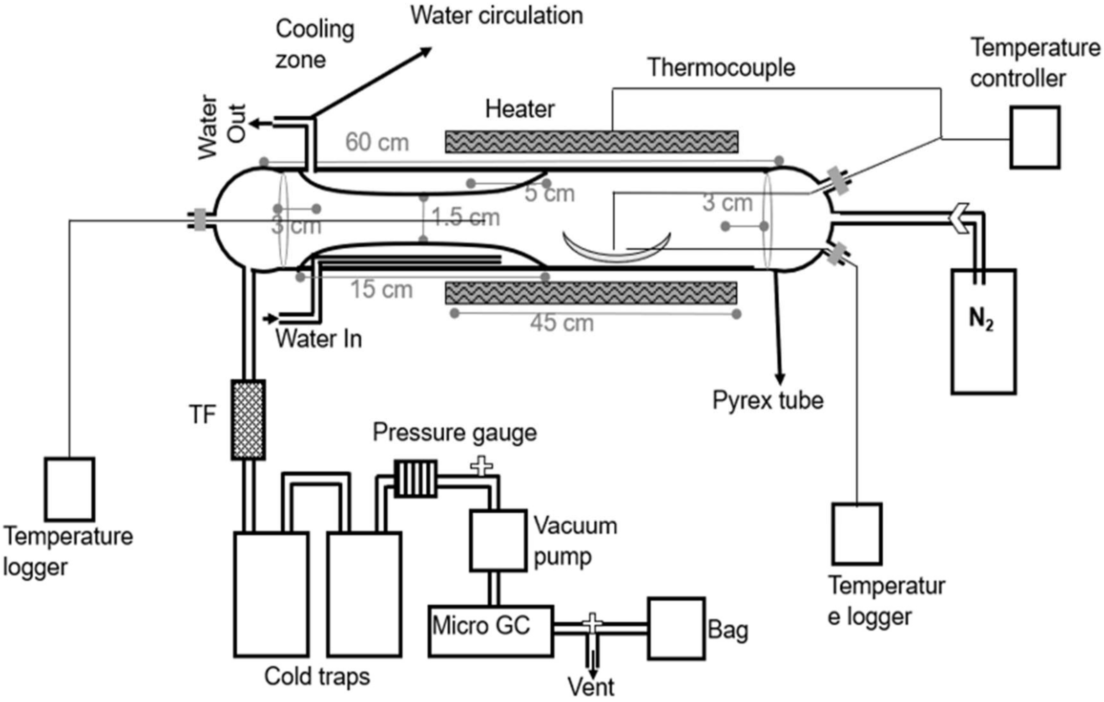


Fig. 14. Thumbnail of reaction equipment.

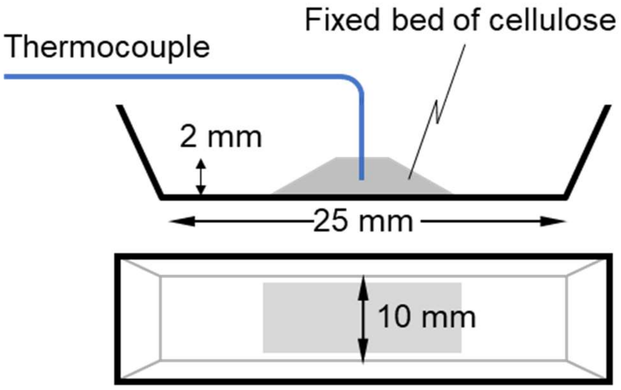


Fig. 15. Configuration 0.1g of cellulose in the quartz boat.

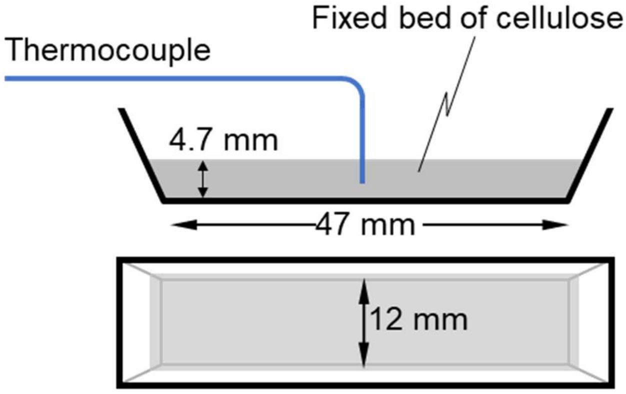


Fig. 16. Configuration 1.0 g of cellulose in the quartz boat.

Last but not least, considering the oligomers are difficult to identify or quantify since we do not have standard samples, we subjected the entire portion of the collected liquid products to acid-catalyzed hydrolysis. For purpose of hydrolysis, 1 mL of mother solution dilute to 10 mL may result in the loss of color. **Fig. 17** and **18** show the images of products collected from different sections (reactor(R), thimble filter (TF), cold trap (CT)) by MeOH after pyrolysis and hydrolysis respectively.

Next, we quantified the glucose, and determined 'hydrolyzable' oligomers according to the following equation. Also, the yield of dimer was quantified by the same HPLC.

Yield of Oligomers = Yield of total glucose – Yield of LGA

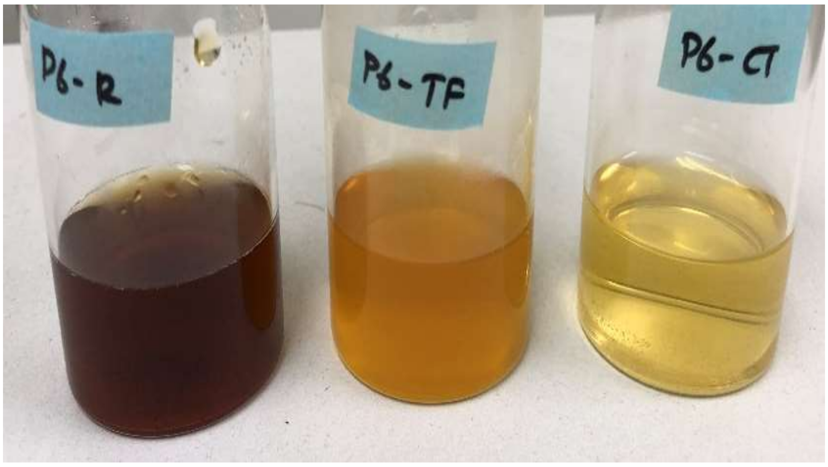


Fig. 17. Products collected from different sections after pyrolysis.

Fig. 18. Products collected from different sections after hydrolysis

2.2. Results and discussions

2.2.1. HPLC, GC chromatogram

From **Fig. 19** to **24** describe that the HPLC chromatogram plainly about the results of HPLC chromatogram of pyrolysis of 0.1 g cellulose at 372 °C, 3.1 kPa collected from different sections after pyrolysis and hydrolysis. Meanwhile, the positions of peak of glucose and LGA are clearly marked in the graphs. We can find that there is very tiny peak of glucose and large peak of LGA conversely obtained from reactor and thimble filter shown in the figurations. As mentioned earlier, from this fact we can draw a conclusion that rather than glucose LGA are main products which is the most obvious advantage and characteristic. After hydrolysis there is none of LGA shown in the graphs as we expected suggesting that our method mentioned early can approximately estimate the yields of oligomers and monomers. Additionally, the results obtained by GC is also shown in the figurations below. Although the results from these two analysis methods were not entirely consistent, in the meantime we cannot conduct evaluation of which is more accurate about them, the similar trends before and after hydrolysis could be discovered.

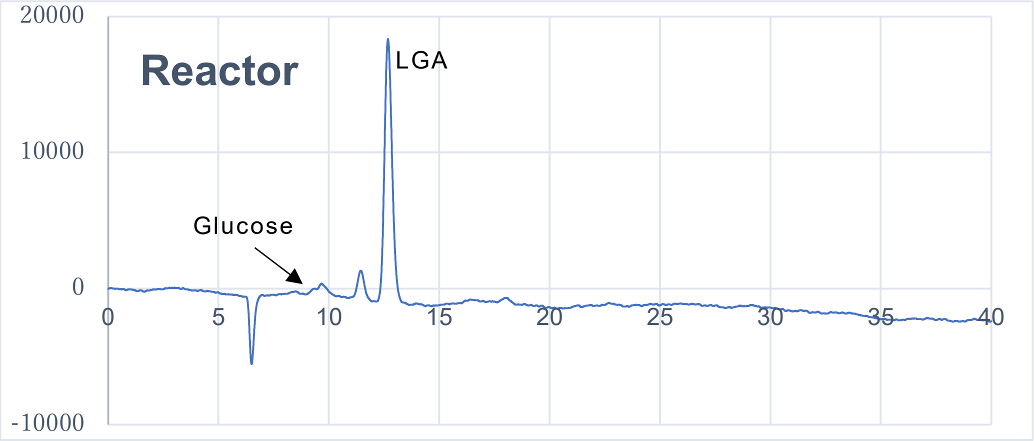


Fig. 19. HPLC chromatogram of pyrolysis of 0.1 g cellulose at 372 °C, 3.1 kPa collected from reactor after pyrolysis.

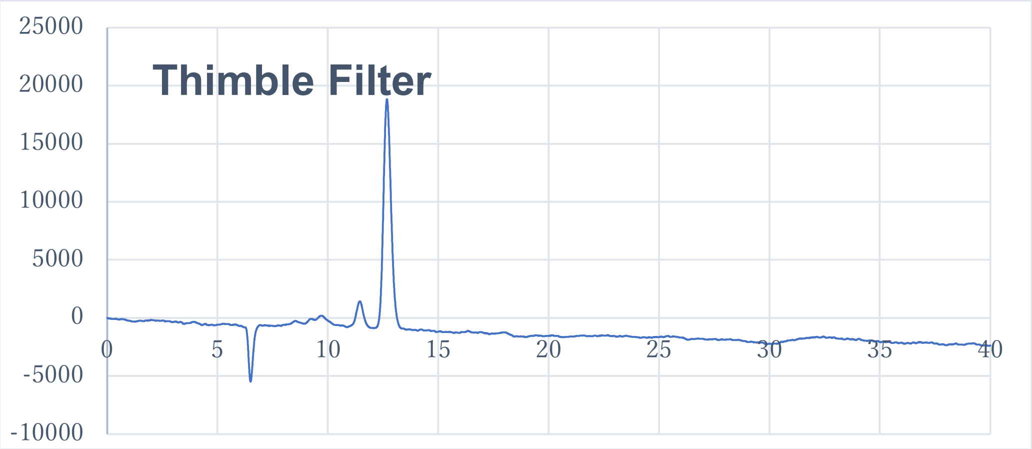


Fig. 20. HPLC chromatogram of pyrolysis of 0.1 g cellulose at 372 °C, 3.1 kPa collected from thimble filter after pyrolysis.

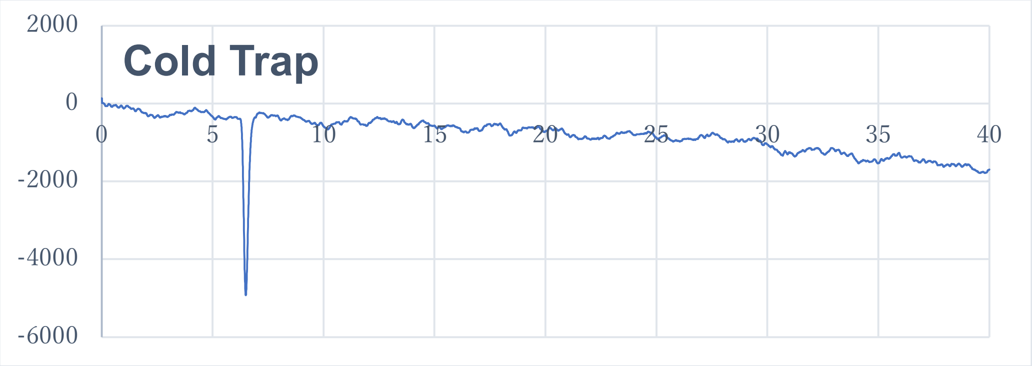


Fig. 21. HPLC chromatogram of pyrolysis of 0.1 g cellulose at 372 °C, 3.1 kPa collected from cold trap after pyrolysis.

Fig. 22. HPLC chromatogram of pyrolysis of 0.1 g cellulose at 372 °C, 3.1 kPa collected from reactor after hydrolysis.

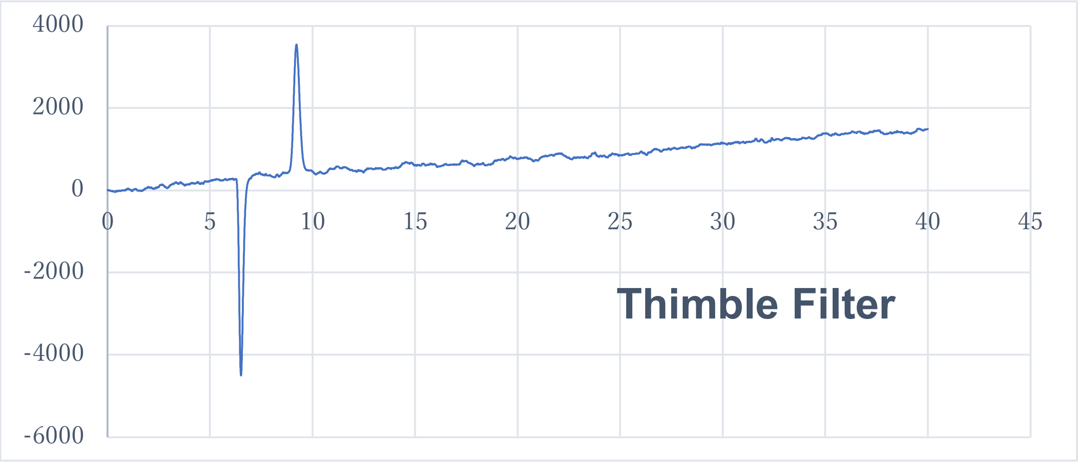


Fig. 23. HPLC chromatogram of pyrolysis of 0.1 g cellulose at 372 °C, 3.1 kPa collected from thimble filter after hydrolysis.

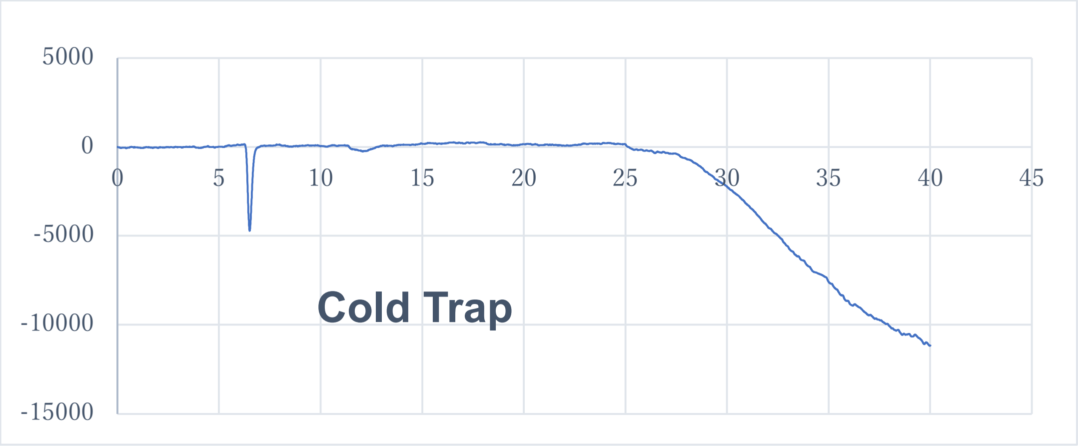


Fig. 24. HPLC chromatogram of pyrolysis of 0.1 g cellulose at 372 °C, 3.1 kPa collected from cold trap after hydrolysis.

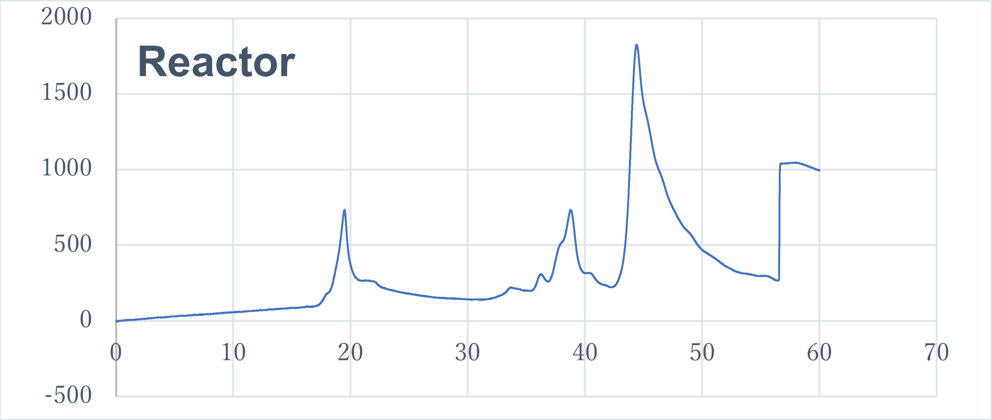


Fig. 25. GC chromatogram of pyrolysis of 0.1 g cellulose at 372 °C, 3.1 kPa collected from reactor after pyrolysis.

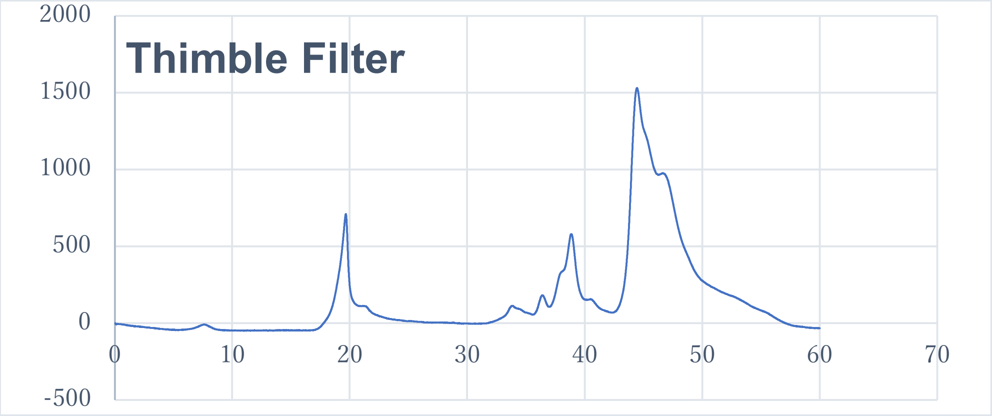


Fig. 26. GC chromatogram of pyrolysis of 0.1 g cellulose at 372 °C, 3.1 kPa collected from thimble filter after pyrolysis.

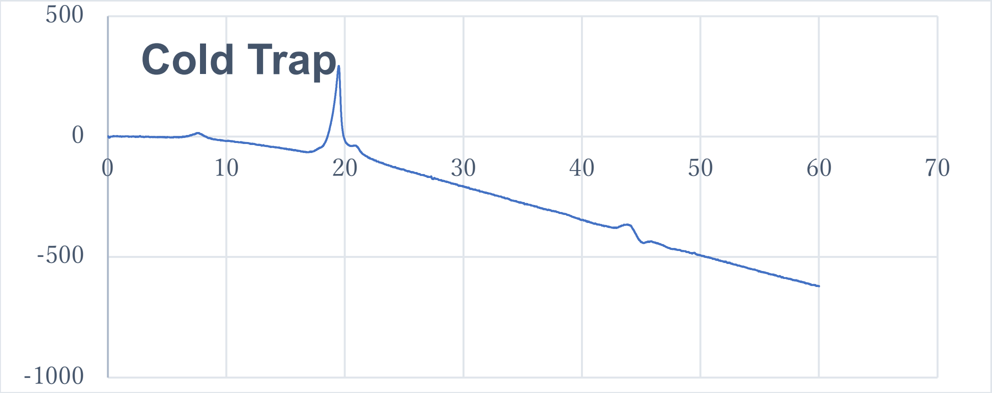


Fig. 27. GC chromatogram of pyrolysis of 0.1 g cellulose at 372 °C, 3.1 kPa collected from cold trap after pyrolysis.

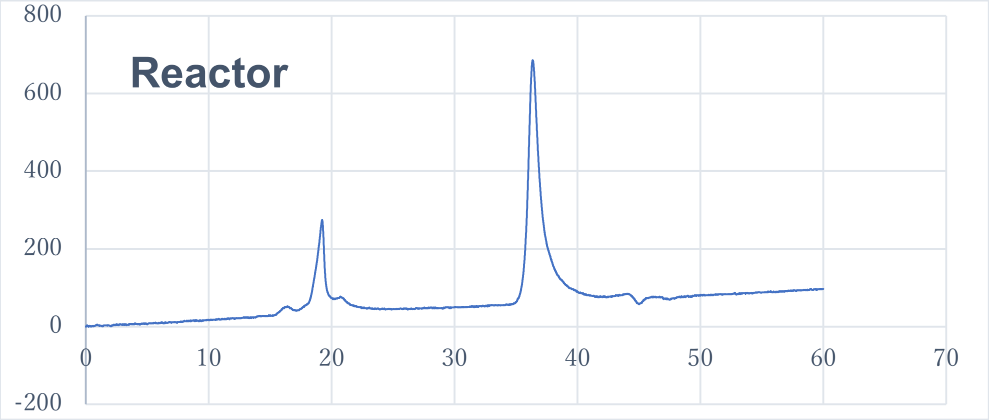


Fig. 28. GC chromatogram of pyrolysis of 0.1 g cellulose at 372 °C, 3.1 kPa collected from reactor after hydrolysis.

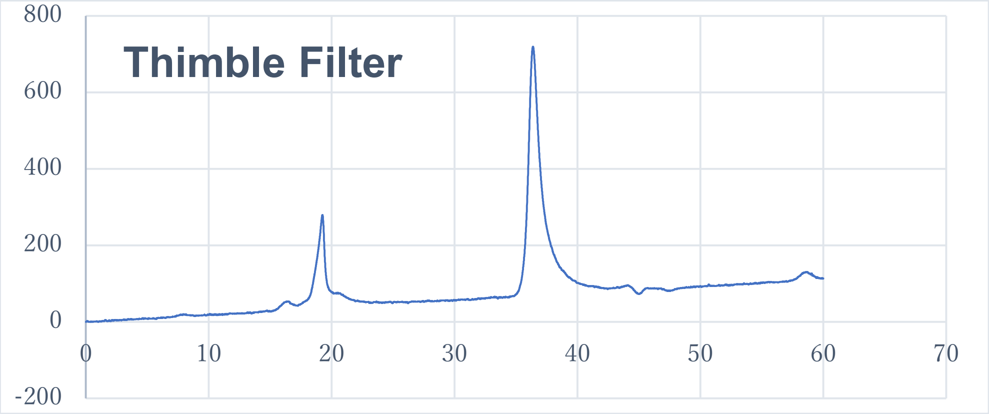


Fig. 29. GC chromatogram of pyrolysis of 0.1 g cellulose at 372 °C, 3.1 kPa collected from thimble filter after hydrolysis.

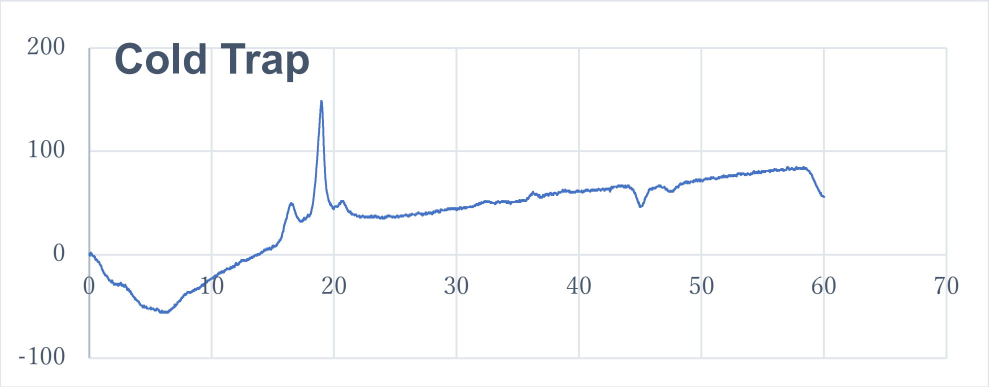


Fig. 28. GC chromatogram of pyrolysis of 0.1 g cellulose at 372 °C, 3.1 kPa collected from cold trap after hydrolysis.

2.2.2. Yield of AHSs

Fig. 29 and **Table. 2** demonstrate the yields of AHSs after pyrolysis while **Fig. 20** and **Table. 3** show them after acid hydrolysis at 360 ℃~420 ℃. We can know that before acid treating there were LGA, dimer and other oligomers mixed in the products while they underwent to glucose entirely after acid treating again. Not only that after acid hydrolysis the total yields of were marginally higher than that of not subjected by acid. This may be due to some of compounds or bigger pieces of oligomers in the original product convert into monomers. What's more the yields of AHSs at different degrees were slightly distinct from each other which recorded as 50~60%.

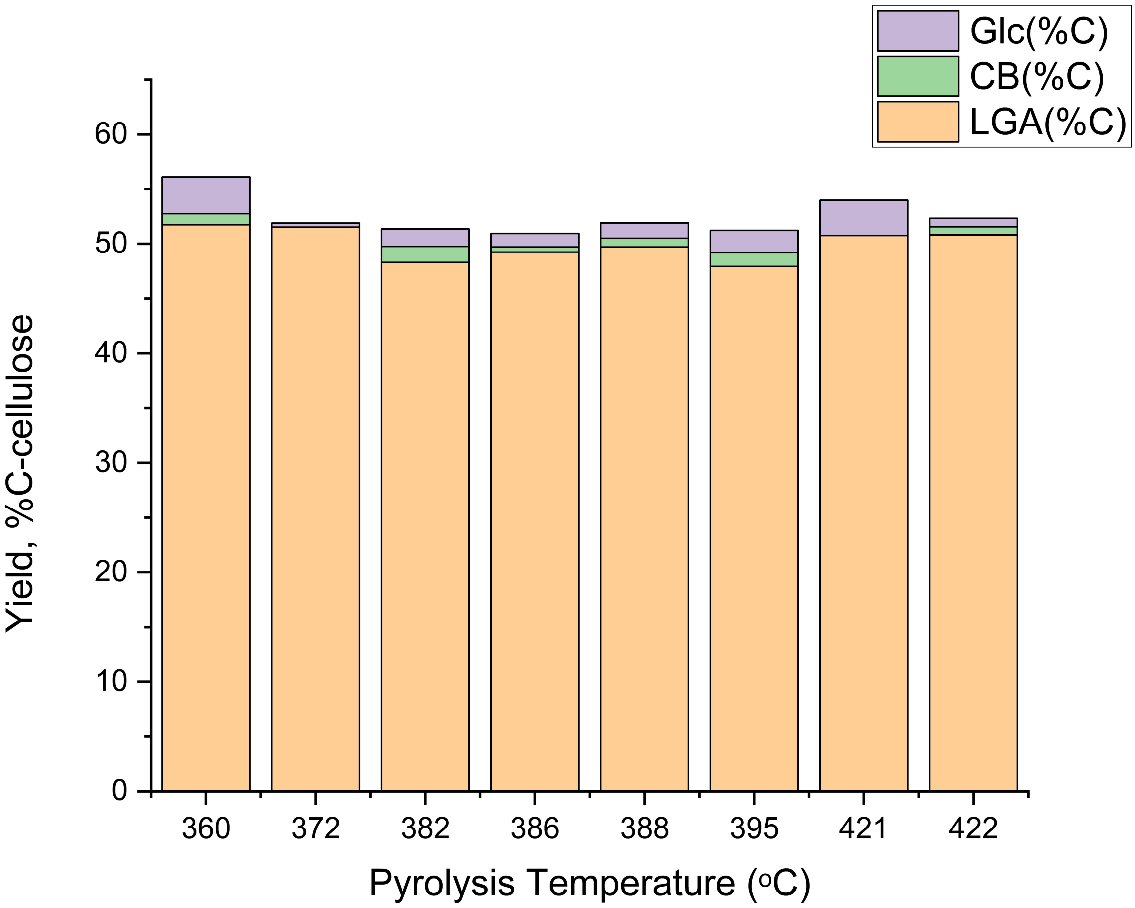


Fig. 29. Yields of AHSs from pyrolysis of cellulose at different temperature after pyrolysis.

Table. 2. Yields of AHSs from pyrolysis of cellulose at different temperature after pyrolysis.

Temperature	LGA (%C)	CB (%C)	Glc (%C)
360 (°C)	51.73	1.05	3.32
372 (°C)	51.5	0	0.37
382 (°C)	48.3	1.46	1.58
386 (°C)	49.25	0.45	1.233
388 (°C)	49.7	0.79	1.41
395 (°C)	47.95	1.24	2.03
421 (°C)	50.75	0	3.24
422 (°C)	50.8	0.747	0.799

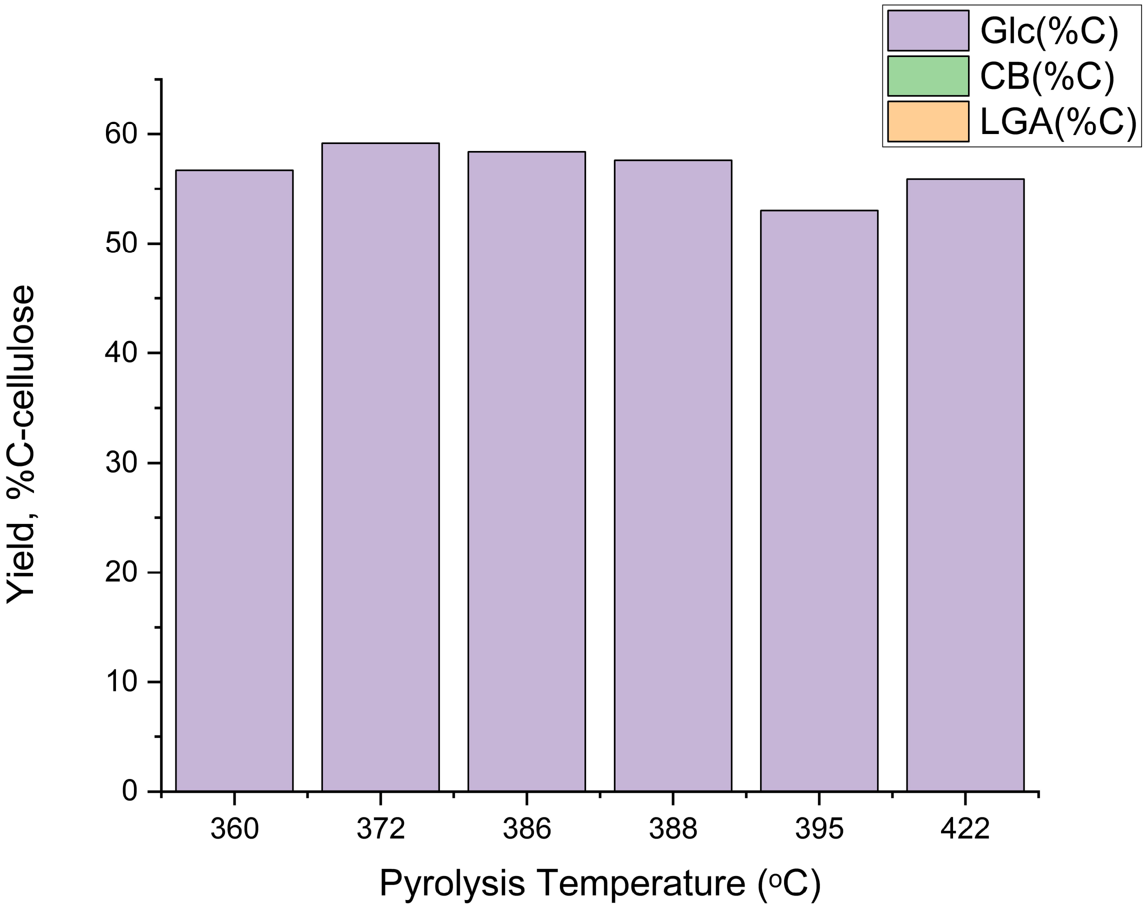


Fig. 30. Yields of AHSs from pyrolysis of cellulose at different temperature after hydrolysis.

Table. 3. Yields of AHSs from pyrolysis of cellulose at different temperature after hydrolysis.

Temperature	LGA (%C)	CB (%C)	Glc (%C)
360 (°C)	0	0	56.7
372 (°C)	0	0	59.18
386 (°C)	0	0	58.4
388 (°C)	0	0	57.6
395 (°C)	0	0	53.01
422 (°C)	0	0	55.9

Fig. 31 and **32** illustrate yields of AHSs from cellulose in FBR at different conditions of 0.1g or 1.0 g of sample and 3.1 kPa or 101 kPa after pyrolysis or after hydrolysis. What is pictured in the graphs is that when the mass of the samples increased the yield of LGA decreased to little extent while magnifying the pressure from 3.1 kPa to 101kPa the yield of that declined around 30%. Also, it recorded that 0.1 g of cellulose generated mildly beyond 6% of glucose after hydrolysis than that of after pyrolysis. On the other hand, 0.1g of cellulose at 101 kPa provide 2.4 times higher char than that at 3.1 kPa. Based on the results of enhancing the mass of cellulose from 0.1 g to 1.0 g or the pressure from 3.1 kPa to 101 kPa declined the LGA yield, we can know that since there was a quite scale of sample which signifies multi-layer of particles in the case of FBR, it had a mighty negative effect of the extra-particle secondary pyrolysis on the yields of LGA and oligomers. If we aim to increase the yield of LGA in FBR, we can consider about reducing pressure to minimize the impact of secondary reaction.

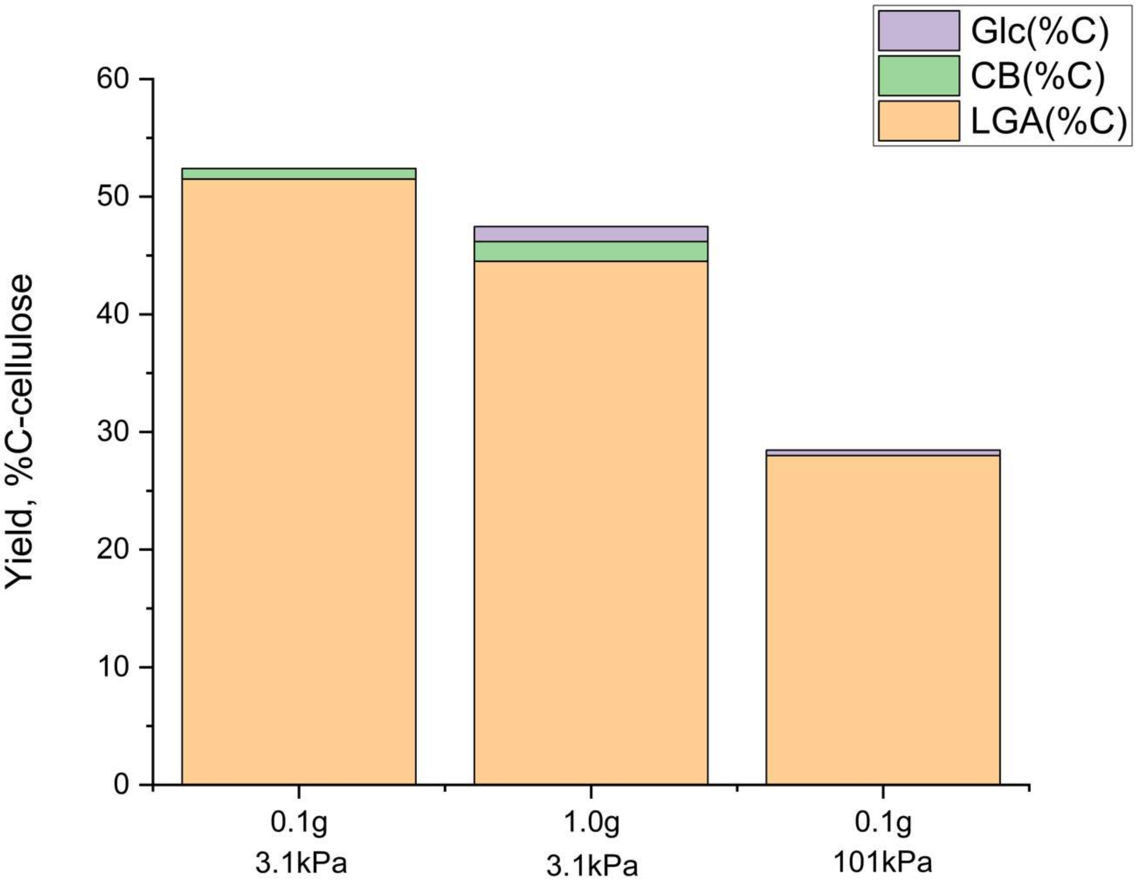


Fig. 31. Yields of AHSs from cellulose pyrolysis in FBR at different conditions.

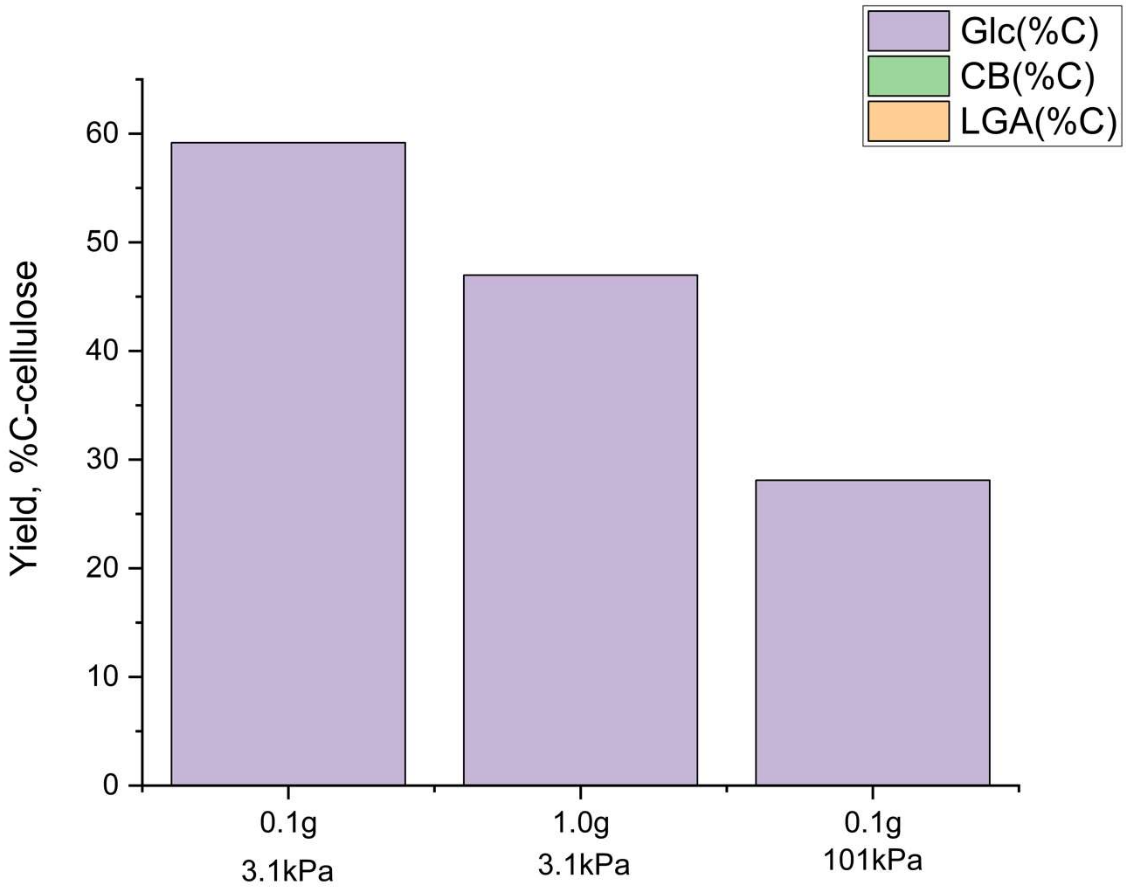


Fig. 32. Yields of AHSs from cellulose pyrolysis in FBR at different conditions after hydrolysis.

Chapter 3: Catalytic Pyrolysis of Cellulose

3.1. Experimental

3.1.1. Experimental reagents

The following are the main reagents and analysis instruments used in this study.

<reagent>

Cellulose (microcrystalline, powder, Aldrich)
Sulfuric acid (95.0+%, Wako)
Magnesium Sulfate (Anhydrous, 95+%, FUJIFILM Wako)
Potassium Sulfate (Powder, FUJIFILM Wako)
Levoglucosan (FUJIFILM Wako)
Levoglucosenone (CIRCA)
Acetone (FUJIFILM Wako)
aerosol filter (ADVANTEC, ID 20 mm, OD 22 mm, L 90 mm)

3.1.2. Specific process of experiment

<A. test the optimum acid-washing (AW) conditions and AAEMs contents >

a. AW

To investigate the impact of AAEMs on CD separately, it is necessary to know their contents in original CD. The first thing I need to do is exploring the optimum AW conditions because there is no paper specific to my sample to do similar research. After crushed into the size of 212 μm~600 μm, the samples were dried whole night until the mass was constant in the vacuum oven under 40 ℃. Then these dried CD underwent AW in the sulfuric acid solution (pH ≈ 1) with acid solution and CD ratio of 50 under ambient temperature which was aim to prevent the samples from hydrolysis. The only variable is the AW time which lasted for 2h, 4h, 6h and 8h respectively. After AW, the samples were washed by water until the filtered water was neutral.

b. Ashing

Muffle furnace (FO100, Yamato scientific) was used in next progress. **Fig. 33** shows the image of the machine. Following the AW-CDs were dried and ashed, the amounts of 100mg of the samples were placed on the platinum (Pt) boat and put into the furnace carefully. By means of temperature programming to adjust the temperature conditions during ashing progress. More specifically, raised the temperature from 25 ℃ to 300 ℃ at a rate of 3 ℃/s, after reaching 300 ℃, heating rate decreased to 1 ℃/s so as to prevent metal ions from volatilizing. The hold time is set to 5 hours.

c. Analysis

Next, ashed samples were dissolved into solutions with the method of acid digestion (1M HF&1M HNO_3)[21]. Followed that the solutions containing the ions of samples were analyzed by ion chromatograph (IC, Shimadzu), a kind of liquid chromatograph (LC) for analyzing contents of anions and cations revealed in **Fig. 35**. Methanesulfonic acid (MSA, 0.004M) with flow rate as 0.6 mL/min was employed as mobile phase, when the oven temperature was 40 ℃. The analysis time for each sample was 12 min. The above process is described briefly in the **Fig. 34** and **Fig. 36**.

Fig. 33. Muffle furnace.

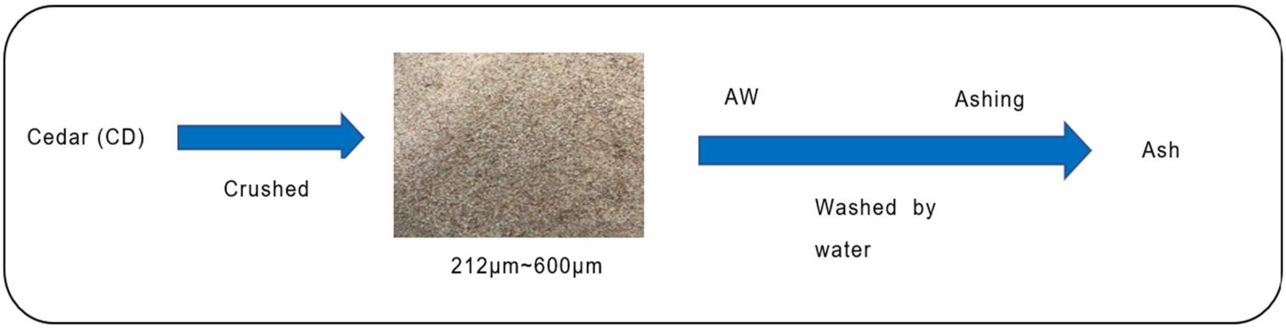


Fig. 34. Flow chart of ashing.

Fig. 35. Ion chromatograph.

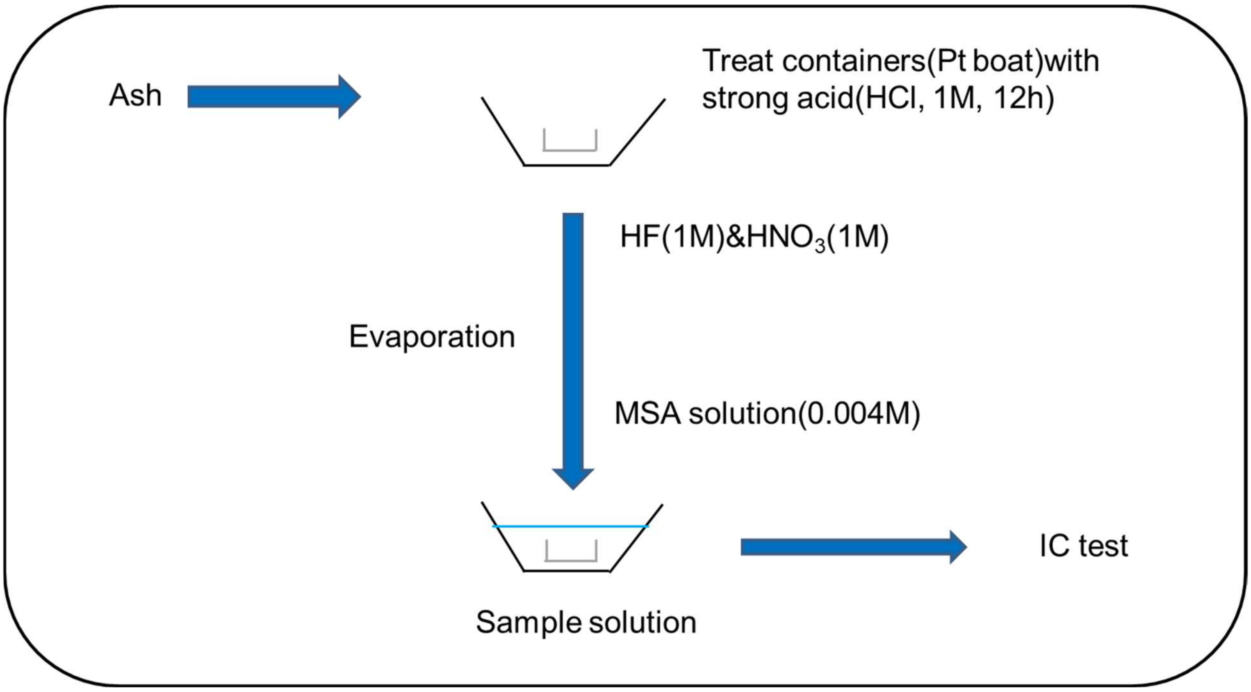


Fig. 36. Flow chart of quantification of AAEMs

<B. Catalytic pyrolysis of CD and cellulose >

a. Catalytic pyrolysis of CD

Catalysts were loaded onto the samples as the amounts of 5 g with the method of impregnation (ultrasonic, 2 h). Next, samples underwent 48 h of atmosphere dry and vacuum dry further. After the samples were dried, 0.7 g amounts of the solid samples were laid on the quartz boat then rapidly pushed into the quartz FBR. The conditions were similar with non-catalytic pyrolysis mentioned above. The flow rate of N_2 was 300 mL/min. During the pyrolysis, the temperature heated from ambient temperature to 320 ℃ at a rate of 10℃/min. Since the temperature reached peak, it was holding for 1h. On the one hand, the condensable gas products were captured by a series of condenser containing aerosol filter, cold trap (-70 ℃). On the other hand, the non-condensable gases were filled into the gas bag. The thumbnail of FBR is pictured in **Fig. 37**.

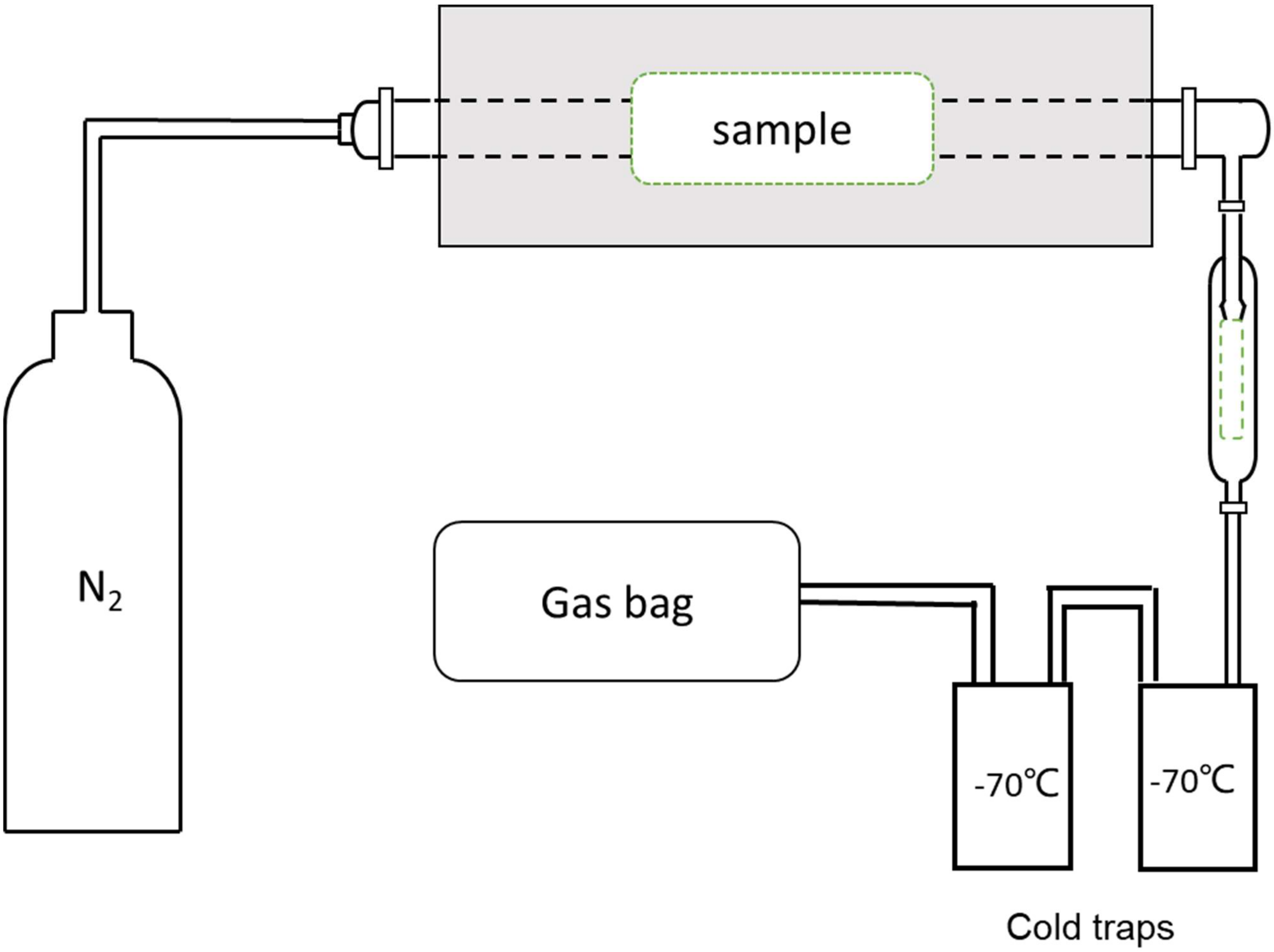


Fig. 37. Thumbnail of FBR

b. Catalytic pyrolysis of cellulose

Loading method of catalysts are same as that on CD. Next, 1 g amounts of samples were placed on the quartz boat slightly with the dimensions of length of 5 cm, width of 1.2 cm and thickness of 5 mm. They were also pyrolyzed at the same temperature and nitrogen flow rate as CD.

c. Analyze the products

The captured condensable products were dissolved in acetone then qualified contents especially AHSs by high performance liquid chromatograph (HPLC, Shimadzu) equipped with a refractive index detectors (RID) commonly used to detect carbohydrates. H_2SO_4 aqueous solution (5 mM) with flow rate as 0.6 mL/min was employed as mobile phase. The analysis time for each sample was 40 min. The column (BIO RAD, 300 mm*7.8 mm) was heated in the oven maintaining the temperature of 35 ℃. Finally, the non-condensable gases were quantified with an Agilent 490 Micro gas chromatograph (GC).

Fig. 38. High performance liquid chromatograph (HPLC) used in study.

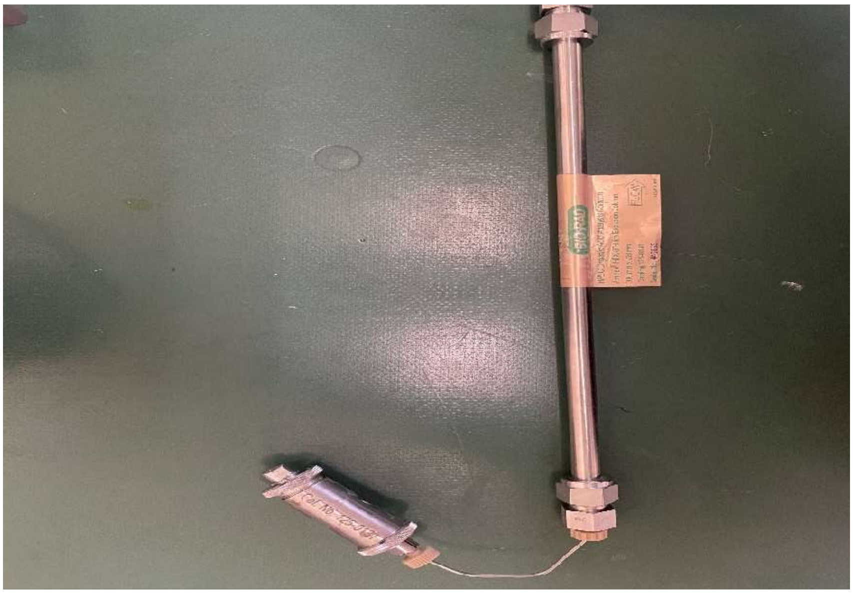


Fig. 39. Column equipped with HPLC.

3.2. Results and discussions

3.2.1. The optimum acid-washing (AW) conditions and AAEMs contents

Through IC analyzing, the removal rate of AAEMs and those contents were investigated as **Table. 4** and **5** illustrate. The results show the fact that 2 h of AW can remove most amounts of AAEMS recorded as over 95%. It seems that 2 h of AW is enough to leach AAEMs although further AWs such as 4 h, 6 h, 8 h marginally improve the removal rate which are negligible and can save time simultaneously. AW mentioned in the subsequent study means two hours of acid washing. The contents of AAEMs in original cedar are small even no more than 0.1 wt% are found out from **Table. 3**. However, it's these tiny amounts of ingredients that affect the yields of AHSs greatly[10,15].

Table. 4. Removal rate of AAEMs by AW applying on CD.

	2h	4h	6h	8h
Na^+/%	97.2	97.4	99.1	99.0
K^+/%	96.3	96.6	98.8	99.8
Mg^{2+}/%	96.2	97.2	97.3	97.4
Ca^{2+}/%	95.3	96.6	96.6	96.7

Table. 5. Original AAEMs contents.

	Na^+	K^+	Mg^{2+}	Ca^{2+}
Contents/wt%	0.026	0.066	0.007	0.085

3.2.2. Trends between tar and char

Fig. 40, **41** and **Table. 6**, **7** show the trends of yields changes between char and total liquid product legibly. In case of pyrolysis of AW-CD, loading extremely low concentration of sulfuric acid solution or sulfates solution matched with the original contents of metal ions affects slightly on yields of solid and liquid product while loading a bit more acid, for instance, 0.5 wt% on the CD can visibly enhance the yield of liquid product reached 52.9 wt% or a bit more contents of sulfates can ascent the yields of them. On the contrary, the yield of solid product declines to bottom records of 36.4 wt%. Similar tendencies are pictured in **Fig. 41**. Above facts indicates that H_2SO_4 could reinforce the decomposition of cellulose inside the pyrolyzing particle and hinder the extra-particle secondary reaction at the same time, however, too much loading of acid may promote the charring so that result in decline of the liquid yield but increase of the solid yield. Loading the sulfates of their contents matched with them in original cedar gave the impact marginally. But loading sulfates to more extent lead to augment of liquid products. The unanticipated results about loading sulfates on the samples may be speculated that the sulfates or their derivatives like acids formed by combining with carboxylic acids catalyze the formation of liquid light components.

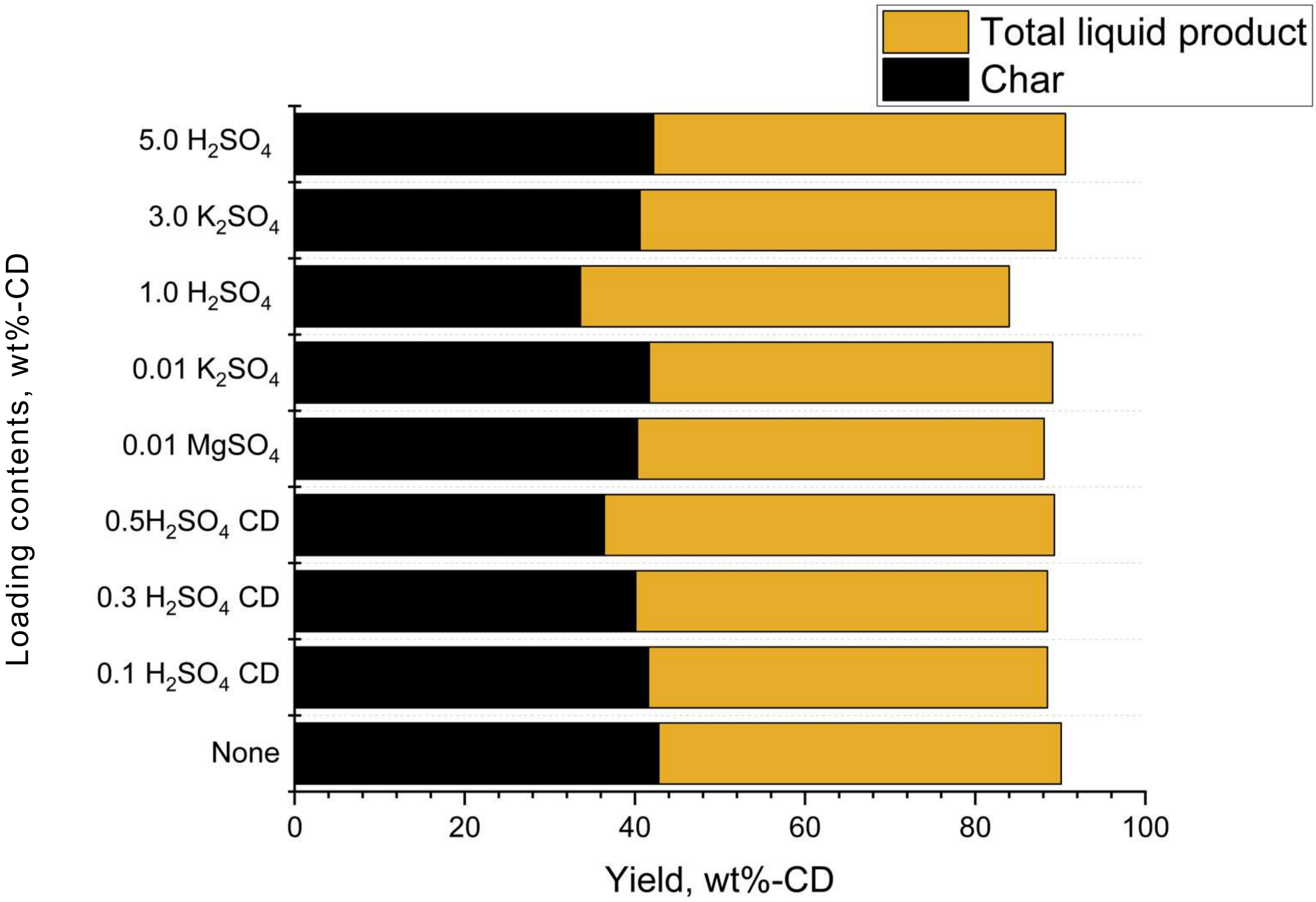


Fig. 40. Effects on yields of char and total liquid product from pyrolysis of AW-CD.

Table. 6. Yields solid and liquid products from pyrolysis of CD.

Loading contents/wt%	Char	Total liquid products
None	42.8	47.3
0.1 H_2SO_4	41.6	46.9
0.3 H_2SO_4	40.1	48.4
0.5 H_2SO_4	36.4	52.9
0.01 $MgSO_4$	40.3	47.8
0.01 K_2SO_4	41.7	47.4
1.0 H_2SO_4	33.6	50.4
3.0 H_2SO_4	40.6	48.9
5.0 H_2SO_4	42.2	48.4

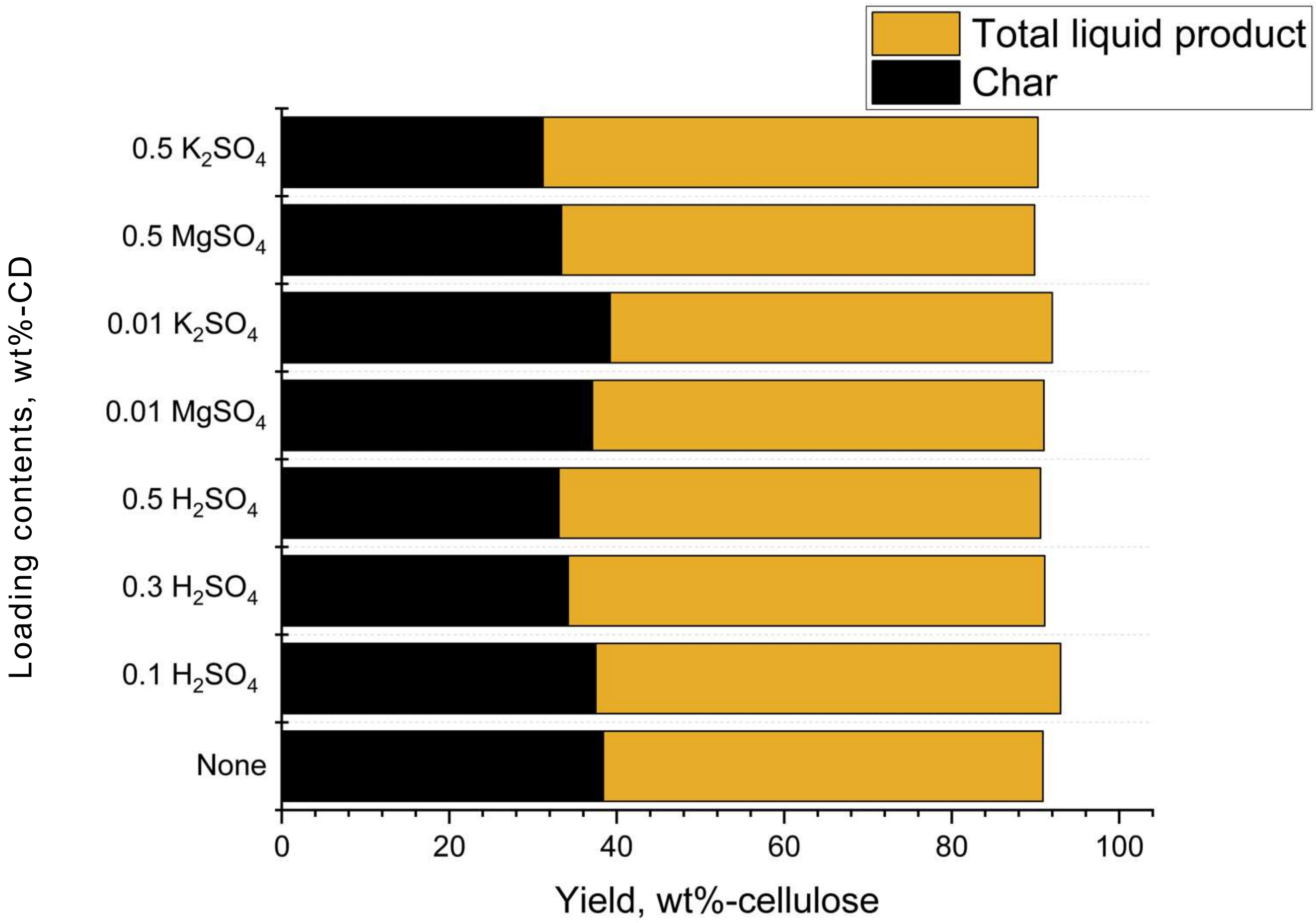


Fig. 41. Effects on yields of catalysts on char and total liquid product from pyrolysis of cellulose.

Table. 7. Yields solid and liquid products from pyrolysis of cellulose.

Loading contents/wt%	Char	Total liquid products
None	38.4	52.5
0.1 H_2SO_4	37.5	55.5
0.3 H_2SO_4	34.2	56.9
0.5 H_2SO_4	33.1	57.5
0.01 $MgSO_4$	37.1	53.9
0.01 K_2SO_4	39.2	52.8
0.5 $MgSO_4$	33.4	56.5
0.5 K_2SO_4	31.2	59.1

3.2.3. Acid Catalysts effects on the CD (AW) and cellulose

Fig. 42 and **43** depict the effects of acid catalysts on the yield of AHSs of CD (AW) and cellulose. As shown clearly in the graphs, acid catalysts can even boost the yield of LGA of CD (AW) with over 10 times than that wasn't load any acid. Similarly, the yield of that from cellulose increase to 8 times than pure cellulose. The figurations characterize not only the trends of LGA but also the yields of LGO also multiplied. Such facts can be explained by the mechanism mentioned on the introduction chapter. Overall, the maximal amplification of total AHSs were found at 0.5 wt% of H_2SO_4 loading of CD (AW) and 0.3 wt% of H_2SO_4 loading of cellulose recorded as around 14% and 43 percent respectively. The result of maximum LGA+LGO yield, 43.1 wt%, was slightly lower than that reported by Cao *et al* and Wang *et al* (48 wt% and 51 wt%),[10, 18] but the LGO yield of 21.6 wt% was greater than their reported, 14 wt% and 17.6%. This was explained by an advantage of the fixed bed that allowed progress of the catalytic dehydration of LGA into LGO during the diffusion of LGO through the bed as well as within particles. The change trend is also clearly described in **Fig. 44**. Finally, if the loading acid catalyst is too much, the yields of LGA and LGO may decline which suggests too much loading induce the charring and cleavage of the monomer units. The optimum loading range can be inferred from 0.1~0.3 wt%.

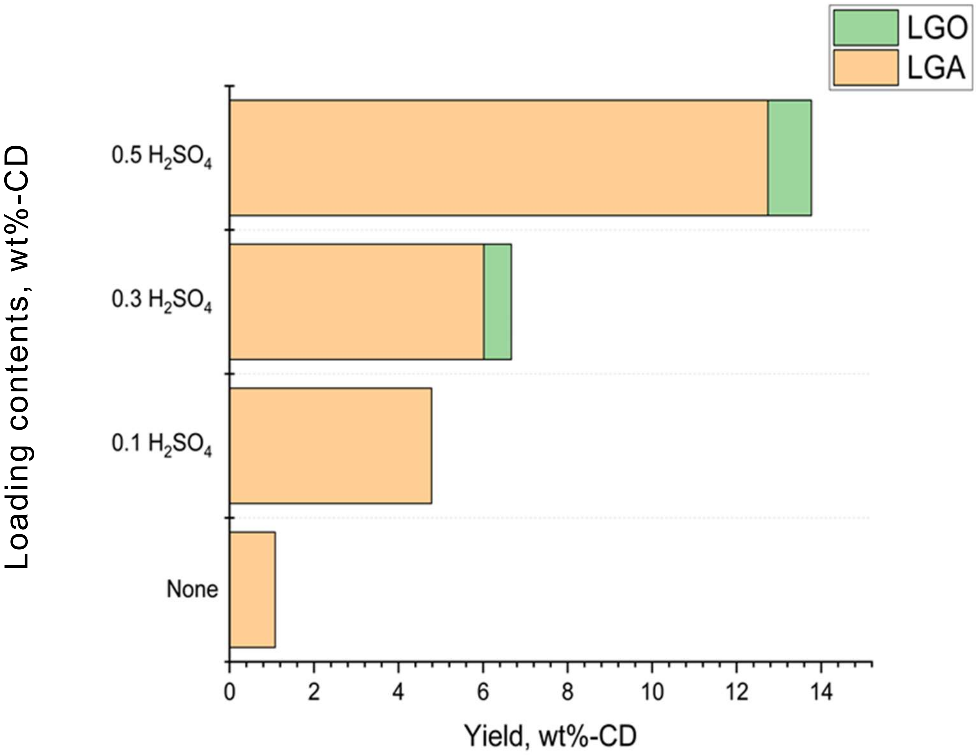


Fig. 42. Effects of acid catalysts on the yield of AHSs of CD (AW).

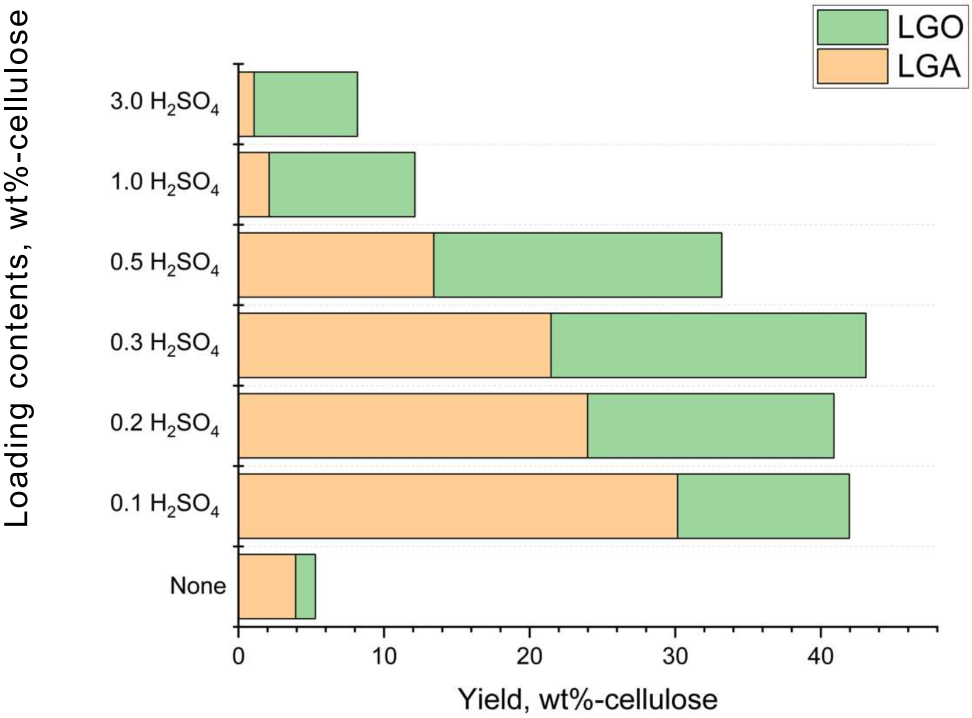


Fig. 43. Effects of acid catalysts on the yield of AHSs of cellulose.

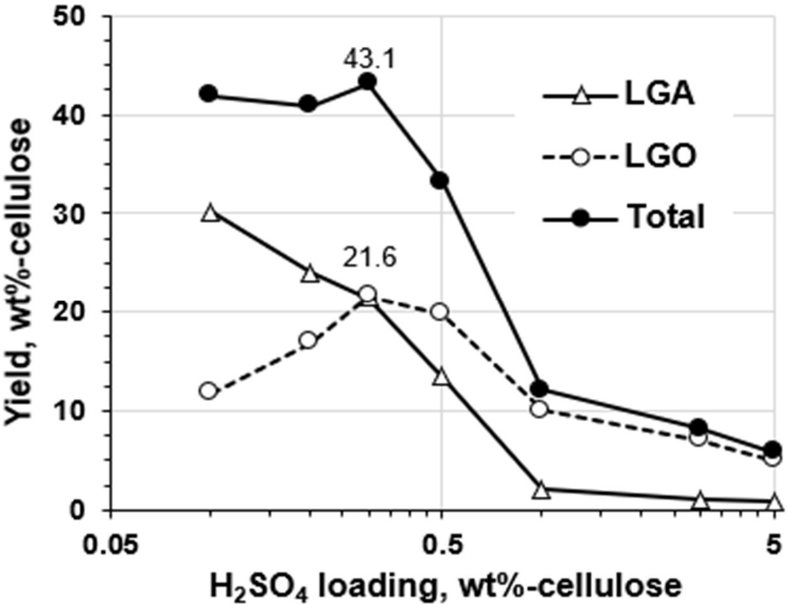


Fig. 44. Effects of acid loading on LGA and LGO yields from cellulose pyrolysis in FBR.

3.2.4. Sulfates Catalysts effects on the CD (AW) and cellulose

This chapter introduces the effects of sulfates on cedar or cellulose. It is widely accepted that a small amount of H_2SO_4 can increase the yields of LGA/LGO from the pyrolysis of lignocellulosic biomass which were explicated theory of acid catalysis and passivation of AAEMs as sulfates eliminating negative catalysis of AAEM species. However, **Fig. 45** and **46** highlight the new point differs from previous works. The K_2SO_4 and $MgSO_4$, unexpectedly, enhanced the LGA formation while suppressing the LGO formation recorded 2 times of the yield than that from AW-CD and 9 times than that from pure cellulose respectively. Not only that, but the datum also describes 0.5 wt% sulfate loading increased the LGA yield from the cellulose and AW-cedar up to 35–40 wt% on the cellulose bases which can even be compared with the sulfuric acid. Combined with the results of behavior of char and liquid product shown in chapter **3.2.2.**, it can be attributed to the sulfates or their derivatives which catalyze inter-monomer-unit linkages and thereby the LGA formation. Meanwhile, the other characteristic of inhibition of LGO can be speculated that only just sulfates cannot provide the high acidity required in the dehydration reaction of LGA. To sum up, we doubted and rejected the conclusion of passivation in this study.

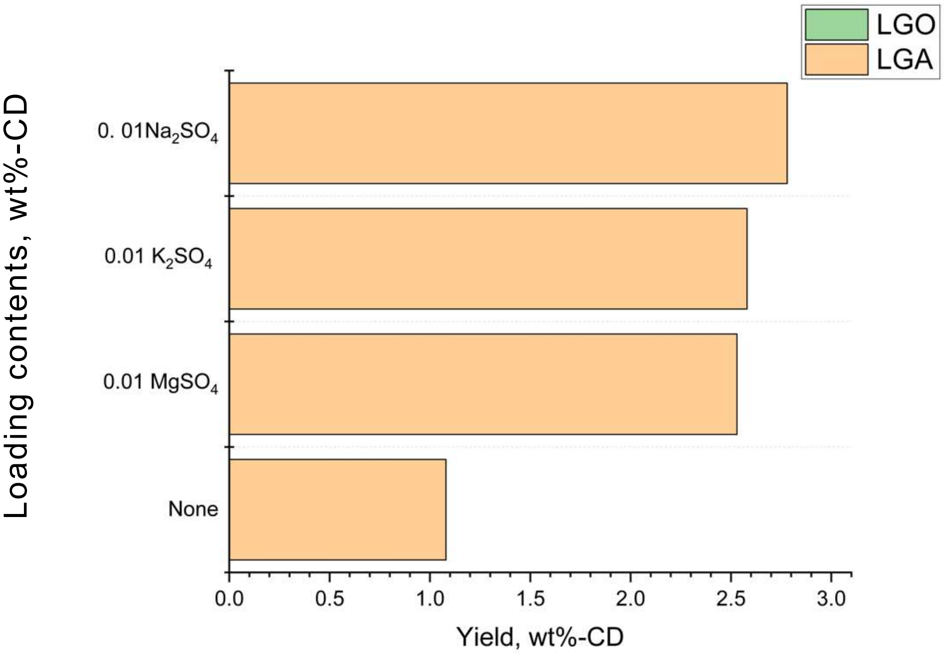


Fig. 45. Effects of sulfate loading on LGA/LGO yields from pyrolysis of CD in FBR.

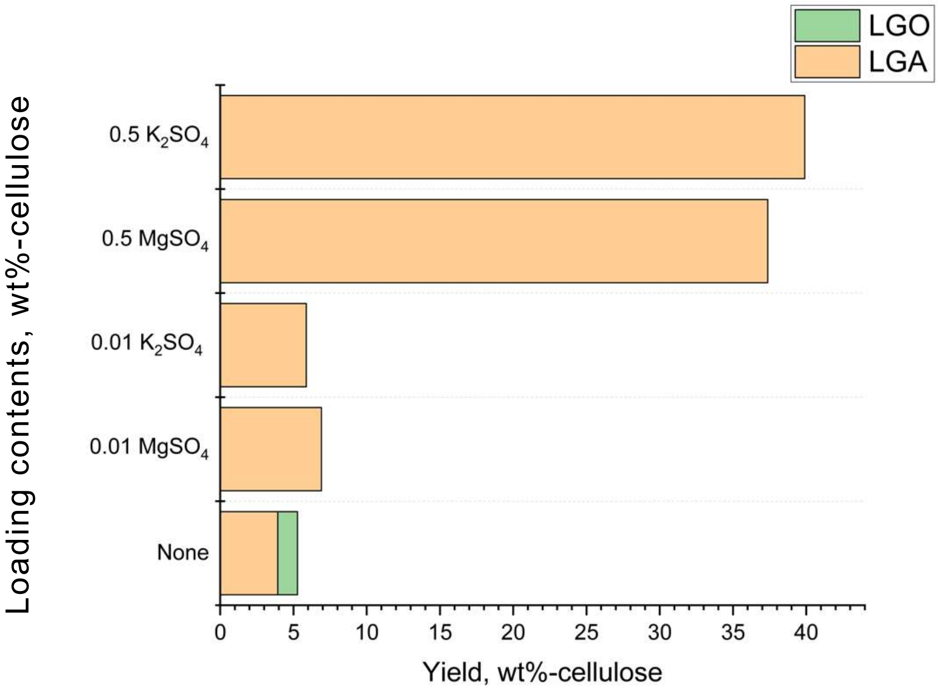


Fig. 46. Effects of sulfate loading on LGA/LGO yields from pyrolysis of cellulose in FBR.

Chapter 4: General Conclusions

In this study, the trends of changes of yields of AHSs from slow pyrolysis in FBR under different catalysts were demonstrated. Both sulfuric acid and sulfates have effects on augmenting the primary reaction as well as suppressing the secondary reaction. What's more, this study gave the facts of small amount of acid loading or appropriate quantity of sulfates can enhance the yields of monomers, the total output can exceed 40% at most in the PBR. Meanwhile, we disproved the viewpoint about "passivation", in other words sulfates can also be employed as catalyst. Although the amount of sample used in this study was still very small, about 1g, I think this is a meaningful step from analytical pyrolysis to practical pyrolysis. Last but not least, I hope this study could provide data support for the real realization of biomass conversion to platform chemicals with industrialization scale in the future.

Acknowledgment

Throughout the writing of this dissertation, I have received a great deal of support and assistance.

I would first like to thank my supervisor, Hayashi sensei, whose teaching was invaluable in formulating the research schemes and methodologies. His insightful feedback pushed me to sharpen my thinking and brought our work to a higher level.

I would particularly like to acknowledge Kudo sensei and Asano sensei, for their wonderful guidance at lab meeting and reminders out of meeting help me avoid detours in the process of experiment and prevent dangerous from chemical reagents and unsafe from experimental operation with patient support.

I would also like to thank technical staff, for their valuable assist throughout my studies. They provided me with the tools and methods that I needed in this study and successfully complete my dissertation eventually.

In addition, I would like to thank Japanese students in our lab for their wise counsel and sympathetic ear. They are always there for me.

Finally, I could not have completed this dissertation without the support of my Chinese students in our lab, who provided stimulating discussions They always help me when there is something unclear due to lack of language proficiency.

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