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Micro Review

Applications of Catalysis in the Selective Conversion of Lignocellulosic Biomass by Pyrolysis

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Pyrolysis is one of the thermochemical methods to decompose lignocellulosic biomass that has a great potential for sustainable production of chemicals and fuels. This microreview focuses on catalytic reactions employed in the pyrolysis processes for the selective conversion of the biomass. The catalytic reactions are categorized into two groups according to the objective of the use of catalysis, and recent advances in each group are briefly reviewed. Our recent works on the pyrolysis of biomass with catalysis are summarized as well, and their originality, advantages over the other methods and challenges for the future were discussed.

1. Introduction

Lignocellulosic biomass is the most abundant, inexpensive and sustainable source of carbon, which includes various naturally derived materials such as woody and herbaceous species, bagasse, agricultural and industrial residues, sawdust, waste paper, etc. The conversion into renewable fuels and commodity/value-added chemicals have attracted a strong political and technical attention over the past few decades due to declining petroleum resources, combined with increased demand for fossil fuels by emerging economies. With the contributions of countless researches devoted to this field, many technologies have been developed to convert biomass resources into gas, char (solid residue), and liquid product. Thermochemical conversion methods, apart from biochemical methods that convert the biomass into alcohols or oxygenated products by biological activity, generally involve the gasification, pyrolysis, liquefaction and sub/super-critical fluid extraction¹⁾. The gasification produces a gas product called syngas or producer gas that contains CO/H₂/CO₂/CH₄ in various proportions, while the other methods are generally used for the purpose of producing liquid products.

Pyrolysis has several advantages over other methods to produce the liquid product: a simple reactor configuration resulting in low capital cost, a short reaction time, concentrated liquid products (less energy-intensive for product separation), and an adaptability to a wide range of feedstocks²⁾. It is difficult or almost impossible to selectively convert the biomass into monomer units by the pyrolysis only due to the complex and recalcitrant nature of biomass, while the liquid product from the pyrolysis, which is a multi-component mixture of organics, has received increasing attention as a fuel alternative to petroleum derived fuels, so-called bio-oil. Fast pyrolysis, an effective conversion with high heating rate over 10² °C/s, achieves the yield of bio-oil as much as 70–80%³⁾ and is regarded as the most reasonable and promising technology. It is, however, still required to upgrade

the bio-oil with respect to the heating value, moisture content, stability, corrosiveness, and incomparability with standard petroleum fuels^{4,5)}. On the other hand, if the feedstock is not biomass but cellulose, the production of monomer units is feasible because it is composed of units of glucose. The conversion of cellulose is worth given priority also in the context of processing lignocellulosic biomass because nearly half of the organic carbon in the biosphere is present in the form of cellulose. The recent report from US department of energy identified twelve chemicals that can be produced from biomass and converted to a number of high-value chemicals or materials⁶⁾. The proposed scheme planned to produce those chemicals from sugars as an intermediate platform. Hydrolysis with liquid or solid acid catalysts would be a candidate for the selective conversion of cellulose to sugars among the thermochemical methods⁷⁾. Pyrolysis of cellulose, however, produces a multi-component mixture of dehydrated sugars, furans, etc., with only a trace amount of sugars.

While the pyrolysis thus seems like not suitable for the production of fuels and chemicals, an employment of catalyst causes the liquid product to undergo a drastic change in the composition. Although the use of catalytic reactions in the pyrolysis processes is not yet well-studied as compared to plenty of researches in catalytic hydrolysis, solvolysis, liquefaction, hydrogenolysis, and hydrogenation, it does offer tremendous potential for future development of a route to produce chemicals or to modify fuel properties⁸⁾. Studies on catalysis in biomass pyrolysis can be categorized into two groups depending on the purpose: 1) *in-situ* reforming of volatiles evolved from the pyrolysis, 2) changing the mechanism of thermal decomposition, *i.e.*, pyrolysis. These are generally called with the same name, catalytic pyrolysis, but the roles of catalyst in the biomass conversion processes are clearly different by the group.

In the present work, the catalytic reactions are distinguished as *in-situ* catalytic reforming of volatiles

and catalyzed pyrolysis, respectively (Fig. 1), and recent advances in each group are briefly reviewed. The focus is on the works that exploited the complex chemistry of pyrolysis for the catalysis to selectively produce the target product. Along with the current research trends, our recent contribution is presented with the originality of the research concept.

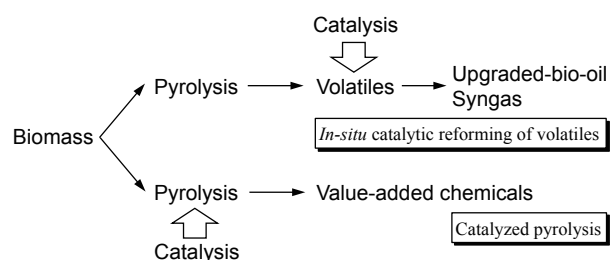


Fig. 1 Pyrolysis processes with catalytic reaction and typical products.

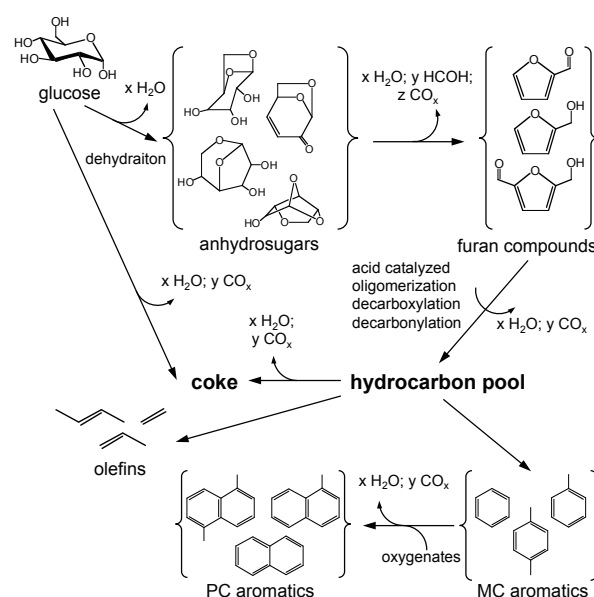
2. In-situ catalytic reforming of volatiles

2.1 Catalytic fast pyrolysis

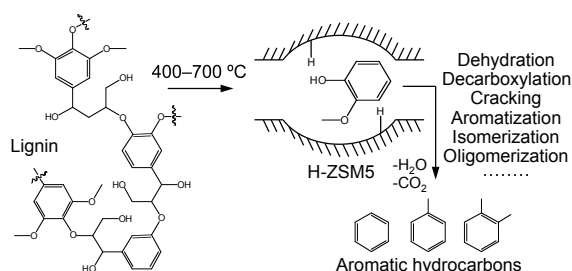
One of the emerging technologies for biomass processing is fast pyrolysis that produces high yields of a liquid product, called bio-oil, which contains up to 70% of the energy of the biomass feed⁹, but aforementioned problematic properties restrict its application. The compounds found in bio-oil have been classified into the following six broad categories: hydroxyaldehydes, hydroxyketones, sugars, dehydrated sugars, carboxylic acids, and phenolic compounds with molecular weights ranging up to 5000 or more depending on operating variables of the pyrolysis process⁸. The as-prepared bio-oils require upgrading at least to remove oxygen functional groups before they are compatible with existing fuel infrastructure.

By pyrolyzing biomass in the presence of a catalyst, it is possible to convert the volatiles evolved from the pyrolysis into aromatic hydrocarbons such as benzene, toluene, and xylenes². This approach to upgrade bio-oils is generally called catalytic fast pyrolysis (CFP), although the name is likely not describing phenomena occurring in the process because the catalysis is not aimed at thermal decomposition (pyrolysis) of biomass, but to change the composition of volatiles. The research on the catalytic production of hydrocarbons from biomass had already started since the late 1970s¹⁰, but become diminished with scattered researches until renewed attention by considerable works on CFP of Huber's research group^{2,11–14}. They investigated the overall reaction pathway in CFP using glucose as a model compound (Fig. 2 (a))¹¹. This reaction involves chemistry occurring in three phases: within the solid biomass, in the gas phase, and within the catalyst. Glucose first thermally decomposes into anhydrosugars, which are converted by dehydration reactions into furans. The dehydrated

products then enter the catalyst where they are converted into aromatics, CO, CO₂ and water through a series of various reactions. Coke formation is the major competing reaction with aromatic production. A maximum carbon yield of 32% aromatics was obtained at 600 °C using a ZSM-5 catalyst and a pyroprobe reactor. CFP of glucose can simulate an essential reaction pathway of cellulose and hemicellulose, while some reports demonstrated the potential of lignin as a source of aromatic hydrocarbons^{15,16}. Ma *et al.*¹⁷ reported 40 wt% yield of aromatic hydrocarbons from lignin using H-USY zeolite that has high number of acid sites and relatively large pores (Fig. 2 (b)).



(a) Reaction pathway of glucose CFP proposed by Carlson *et al.*¹¹



(b) Reaction pathway of lignin CFP proposed by Ma *et al.*¹⁷

Fig. 2 Reaction pathways in CFP.

Zeolite ZSM-5 is a catalytic cracking catalyst commonly used in petroleum industry for upgrading low-octane components¹⁸. A wide range of catalyst has been tested for CFP of biomass including zeolites, mesoporous materials (such as Al-MCM-41), Co-Mo catalyst, and Ni/Al catalyst^{8,12}. The majority of studies on zeolites concluded that ZSM-5 was the catalyst that gave the highest yield of aromatics. Jae *et al.*¹² investigated the influence of zeolite having variety of

pore sizes and shapes (ZK-5, SAPO-34, Ferrierite, ZSM-23, MCM-22, SSZ-20, ZSM-11, ZSM-5, IM-5, TNU-9, SSZ-55, Beta zeolite, and Y zeolite) on the conversion of glucose to aromatics, and found medium pore zeolites with moderate internal pore space and steric hindrance (ZSM-5 and ZSM-11) had the highest aromatic yield and the least amount of coke.

Pyroprobe is a convenient semi-batch type reactor to test the catalytic activity for reforming of the volatiles evolved from biomass. Fixed catalyst bed reactors are also often used for *in-situ* reforming or gasification of volatiles^{10,19}. Those reactors, however, cannot practically and economically be scaled up toward commercial production. Recently, Carlson *et al.*¹³ demonstrated that CFP can be done efficiently in a fluidized bed reactor with an appropriate reactor configuration and optimized operating conditions. Fluidized bed reactors have been proven in a vast number of processes across industry due to their excellent mass and heat transfer properties, scalability and simplicity of operation. The highest yield of aromatics from sawdust was 14% on carbon basis using ZSM-5 catalyst at 600 °C. After ten reaction-regeneration (by combustion) cycles of the catalyst, they found impurities (alkali and alkaline metal species) deposited on the catalyst surface and broken pieces of catalyst, however, the acid sites on the zeolite were not affected.

Significant advantages of CFP would include: 1) all the desired chemistry occurs in a single reactor and 2) main products, aromatics and olefins, are already fit into existing infrastructure¹⁴. In fact, CFP can produce five of the six primary petrochemicals, including benzene, toluene, xylene, ethylene and propylene¹³. If the objective is to use the aromatics as a gasoline additive, toluene and xylene would be the best aromatics to produce as they are higher in octane number than benzene and naphthalene²⁰. However, benzene is more valuable than toluene due to its use in the chemical industry. One of the critical challenges with CFP is to increase the yield of these chemicals by reducing the formation of coke. The recovery of product chemicals on an energy basis is still low as compared with other technologies such as fermentation and gasification. Co-feeding of other hydrocarbons, such as alcohols^{14,21} and olefins¹³, is one of the options on this issue.

2.2 Utilization of coke formation potential of volatiles

The formation of coke on/in porous materials proceeds through the entrance and adsorption of volatiles into micropores and the succeeding coking as illustrated in Fig. 2. In CFP, the coke formation is the major competing reaction to the formation of aromatics, resulting in the significant loss of aromatics yield. Hosokai *et al.*^{22,23} also demonstrated the coke formation over charcoal and mesoporous alumina.

We have recently proposed three methods fully

utilizing coke-forming potential of volatiles to produce light oil²⁴ and syngas free from heavy tar^{25,26}. Fig. 3 illustrates conceptual process diagrams. They employed a raw biomass (process (a)), potassium-loaded biomass char (process (b)), and low-grade iron ore (process (c)) as materials for capturing volatiles, especially heavy tar, and the succeeding reactions.

In the production of light oil, feedstock biomass was firstly loaded in the sorber to capture heavy oil from the pyrolysis by condensation, adsorption, and/or absorption. Because the temperature of the sorber was maintained at 110–180 °C, the captured heavy oil was not converted to coke, while light oil was allowed to escape from the sorber. The feedstock biomass loaded with heavy oil was subjected to the pyrolysis to simulate recycling of heavy oil and a continuous operation of this process. The cycle of capturing and pyrolysis of heavy oil was repeated 10 times. Recycled heavy oil was successfully converted into light oil and char by self-pyrolysis and with some contribution of a type of catalysis by biomass. The proposed process, a recycling of heavy oil, was thus effective for the selective production of light oil. The produced bio-oil was highly volatile that 99.8% of its portion was evaporated in heating to 250 °C, in other words, nearly free from coke precursors. This property is beneficial in the applications of the bio-oil, such as catalytic steam reforming for syngas production, that are intolerant of coke/carbon formation.

The processes (b) and (c) aimed at simultaneous steam reforming of volatiles and steam gasification of char from the pyrolysis of biomass with materials loaded in the reformer. Potassium (K)-loaded char was produced from the pyrolysis of K-loaded biomass and loaded in the reformer. Volatiles from the pyrolysis were reformed over the char in a sequence of carbon deposition onto the pore surface and steam gasification of the deposit. Even at the low temperature of 600–700 °C, the catalysis of K simultaneously realized the concentration of heavy tar in the product gas as low as 20 mg/Nm³-dry and progress of the char gasification as fast as that of char formation from the pyrolysis, at the steam/carbon molar ratio of 0.55–1.10, wherein the steam was supplied as a moisture in the feedstock biomass and from water produced by the pyrolysis. Furthermore, it was suggested a major portion of K retained by the spent K-loaded char could be recycled to the process by the extraction with water at the ambient temperature.

The process with the natural iron ore was also effective to produce clean syngas. With the reformer loaded with the iron ore, the yield of heavy tar from the pyrolysis-reforming process was less than 0.01% by its oxidation with the ore and coking into/onto the ore. The ore was reduced from hematite to magnetite/wustite after the reaction, but it was possible to further reduce to iron/wustite upon reheating up to 800 °C in the absence of volatiles. It was suggested that the coke formed in/on the ore played a role of an agent for its further reduction.

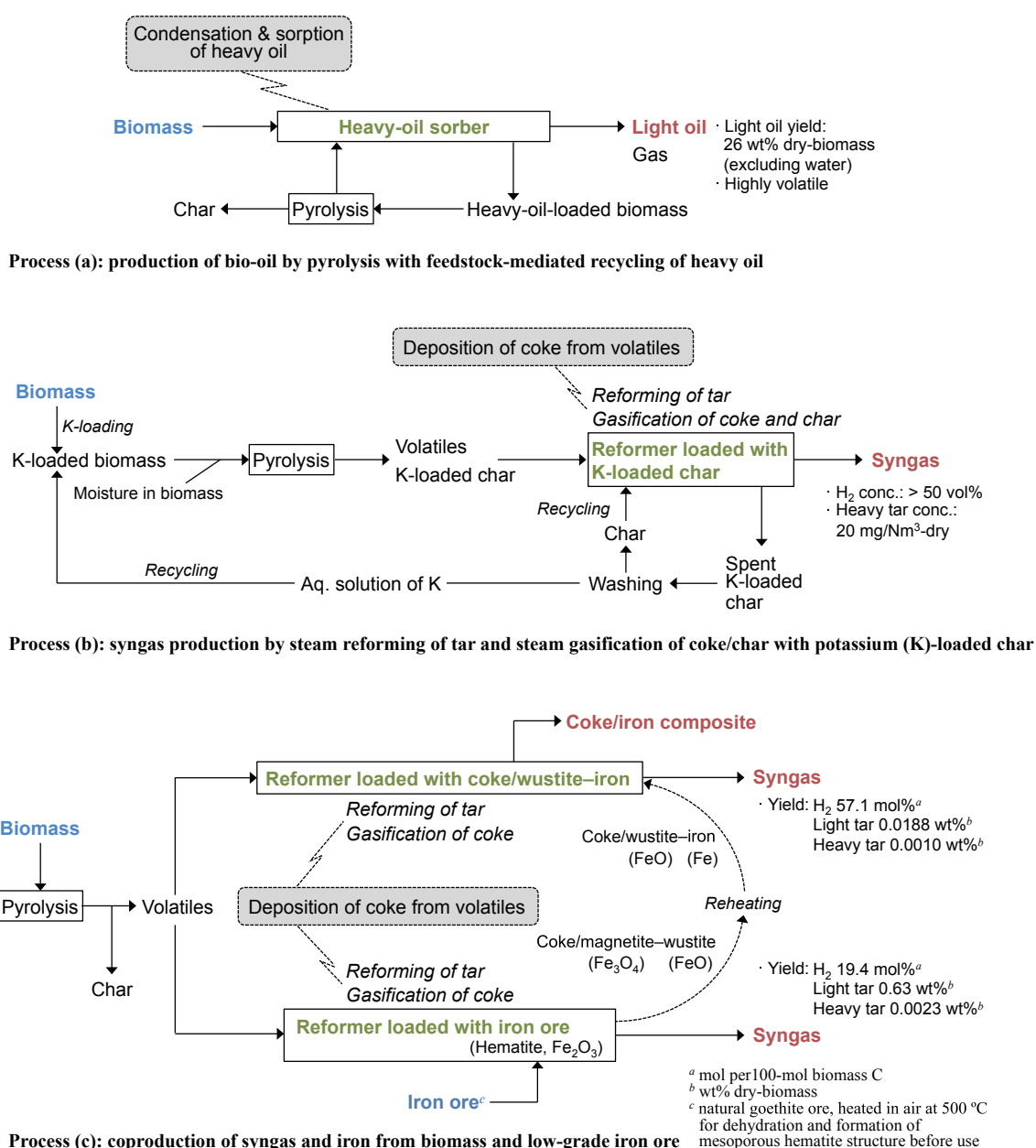


Fig. 3 Conceptual diagrams of biomass conversion processes proposed by our research group: process (a)²⁴, process (b)²⁵, and process (c)²⁶.

The reduced ore was more active as a catalyst for the reforming/gasification reactions, producing syngas with tar (including both light tar and heavy tar) concentration below 10 mg/Nm³-dry. Although not demonstrated in the work, the long time use of the ore would lead to its deactivation. The spent coke/iron composite, however, is a useful feedstock in steel production, in particular, that to be fed to electric arc furnaces.

Clean syngas produced from the processes (b) and (c) can be directly used as a fuel for internal combustion engines, which limits the residual concentration of tar to a level below 50–100 mg/Nm³-dry, and even in the application to Fischer-Tropsch synthesis^{26,27}. There

have been many reports on the catalytic gasification of volatiles from pyrolysis, however, most of them suffered from the loss of catalyst activity by coking and poisoning due to metallic species, chlorine, sulfur, and ash²⁸. The concept employed here, *i.e.*, acceleration of coking and the succeeding gasification of the coke with the catalyst-like materials (K-loaded char and iron ore), allowed us to overcome this problem.

These studies were conducted with a fixed bed of reformer or heavy oil sorber to simulate the proposed processes. In their practical application, the process would include a type of moving bed reactor, which continuously receives and drops the solid materials.

Challenges with this technology exist in maintenance of the product quality by adjusting the balance between the feeding and dropping rates. To cope with this issue, for example, one of our current researches focuses on kinetic analysis to simulate the reactions, which occur in the moving bed reactor, such as pyrolysis and gasification. The application to other feedstocks such as a low-grade coal is also in progress.

3. Catalyzed pyrolysis of biomass

To increase a content of the target compound in the product liquid, several methods have been proposed to catalytically-change the mechanism of pyrolysis, but the number is very limited. The presence of alkaline cations in biomass is known to affect the mechanism of thermal decomposition during the pyrolysis. These cations cause fragmentation of the monomers that comprise the natural polymer chains, rather than the predominant depolymerization that occurs in their absence⁸⁾. Liquid acids such as sulfuric acid, hydrochloric acid, phosphoric acid, and Lewis acids, if impregnated, also work as a catalyst for pyrolysis.

Typical products from the catalyzed pyrolysis of biomass are summarized in reports by Mohan *et al.*⁸⁾ and Zhou *et al.*⁷⁾. The products include levoglucosan, levoglucosenone and furans as a main product, all of which are cellulose derivatives (Fig. 4). The catalysis thus seems to be effective for the selective conversion of cellulose, but not for hemicellulose and lignin.

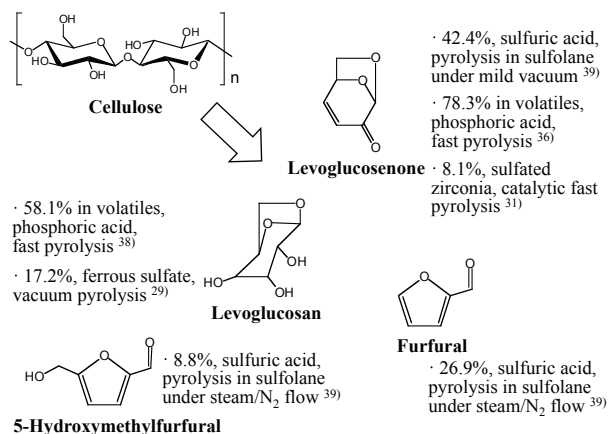


Fig. 4 Typical products from catalyzed pyrolysis of cellulose.

Richards and Zheng²⁹⁾ investigated the influence of incorporation of several different individual metal ions into cottonwood on the products from vacuum pyrolysis. They observed K, Li and Ca induced the formation of high char and low tar yields, while all of the other ions (Mg, Mn, Fe, Co, Ni, Cu, and Zn), especially transition metals, increased the yield of levoglucosan. Julien *et al.*³⁰⁾ examined vacuum pyrolysis of acid-impregnated

(H₂SO₄, HCl, HNO₃) cellulose. X-ray scattering showed SO₄²⁻ and Cl⁻ were incorporated into the cellulose structure by the impregnation. Those inorganic ions induced the formation of high yields of char and water and low yields of tar, and favored the formation of hydroxyacetaldehyde, acetic acid, and formic acid at the expense of levoglucosan. In contrast, no significant change in product yields was observed for cellulose pretreated with HNO₃.

Levoglucosenone (1,6-anhydro-3,4-dideoxy-β-D-glycero-hex-3-enopyranose-3-ulose) is one of the products from the pyrolysis of cellulose, having a multifunctional C₆ monomer structure. Due to its unique structure, levoglucosenone has been expected to serve as a feedstock for the synthesis of natural products (such as tetrodotoxin, multistriatin, rare sugars, Ras activation inhibitors) and chiral auxiliaries for application in other reactions³¹⁾. Other uses of levoglucosenone can be found elsewhere^{32,33)}. However, the synthetic exploitation of levoglucosenone has been limited and has not led to large-scale commercialized processes because levoglucosenone is not available directly from nature and its preparation from monosaccharide precursors requires several uneconomic steps³⁴⁾. In a series of studies, Dobeles *et al.*^{35–38)} reported that fast pyrolysis of cellulose pretreated with phosphoric acid or iron (III) sulfate selectively produced levoglucosenone. Maximum levoglucosenone content in the volatile product of 78% was reached by impregnation of phosphoric acid at 160 °C³⁶⁾. The result was attributed to the catalysis of the cellulose depolymerization and dehydration in the presence of acid from the pretreatment. Clearly, directly employing catalysts in the pyrolysis of cellulose can improve the selectivity to levoglucosenone. However, the yield of levoglucosenone, so far observed, with phosphoric acid impregnation method is less than 10% probably due to the accelerating effect of the acid for char formation^{31,34)}. In contrast, the catalyzed pyrolysis in sulfolane proposed by Kawamoto *et al.*³⁹⁾ produced less or no char of the cellulose. The yield of levoglucosenone reached up to 42.2% under mild vacuum condition. They experimentally clarified the degradation pathway of cellulose to levoglucosenone via levoglucosan, while suggested the partial existence of direct pathway to levoglucosenone. The drawbacks of this method are the low concentration of cellulose and difficulty in separating the products from the solvent. Recently, some new techniques utilizing a solid acid³¹⁾ catalyst and microwave⁴⁰⁾ have also been proposed to facilitate levoglucosenone production.

Our approach to efficient production of levoglucosenone is the use of ionic liquid (IL)⁴¹⁾. ILs possess a variety of special properties, including low vapor pressure, high thermal stability and especially solvent power for cellulose. Since the pioneering research by Rogers *et al.*⁴²⁾, ILs have been used as “green” solvents for liquid-phase catalytic conversion of cellulose into valuable

chemicals, *e.g.*, 5-hydroxymethylfurfural (5-HMF) and furfural^{43–45}). We used the IL as a reusable catalyst for pyrolysis of cellulose (Fig. 5). Catalyzed pyrolysis with liquid acids (such as phosphoric acid) proceeds with a partial consumption of the acids^{46,47}. It is therefore difficult to recover the acids from the char after the pyrolysis.

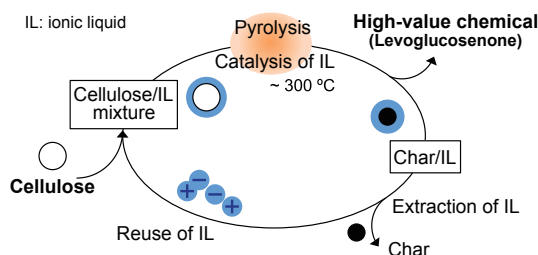


Fig. 5 Process flow of the proposed cellulose pyrolysis using IL as a reusable catalyst.

Several ILs (1-butyl-2,3-dimethylimidazolium [BMMIM] type) having different anion were mixed with cellulose in equal amount, and the mixture was tested for pyrolysis using a thermogravimetric analyzer (TGA). Mass change curves in Fig. 6 provide useful information concerning an applicability of IL to the proposed process. The mixtures with [BMMIM]BF₄, CF₃SO₃, and (CF₃SO₂)₂N lost their weight in two steps. The first mass loss (on the lower temperature side) was caused by the pyrolysis of cellulose, and the second one was primarily caused by decomposition of IL. Among them, the mass decrease by the pyrolysis of cellulose started at the lowest temperature when [BMMIM]CF₃SO₃ was used. The isolation of temperature range for cellulose pyrolysis and IL decomposition strongly supports the possibility of IL reutilization.

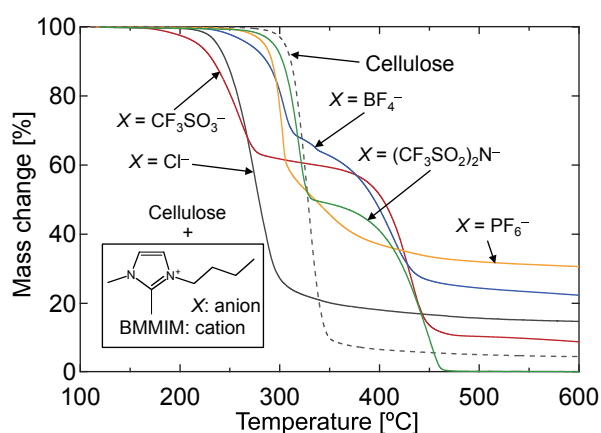


Fig. 6 Mass change curves of cellulose and cellulose mixed with [BMMIM] type ILs at 1:1 on a mass basis during pyrolysis: N₂ 200 mL/min, heating rate = 5 °C/min.

More importantly, the pyrolysis of cellulose at lower temperature than pure cellulose indicates the catalysis of IL toward the pyrolysis. Table 1 compares the yield of levoglucosenone and char from the pyrolysis of cellulose mixed with [BMMIM]CF₃SO₃ to that of pure cellulose and phosphoric acid impregnated cellulose. The highest yield of levoglucosenone, 27.6 mol%, was obtained by the proposed method, while the char yield was lower than that from phosphoric acid impregnated cellulose. This result demonstrated that the catalysis of [BMMIM]CF₃SO₃ selectively directed toward the dehydration and the splitting of the glycosidic bond of cellulose, not toward the formation of char. Furthermore, IL could be fully recovered from the residue of pyrolysis by extraction with ethanol, and the reused IL gave an identical product distribution as shown in Table 1.

Table 1 Yield of levoglucosenone and char from pyrolysis⁴¹⁾.

Sample	<i>T_p</i> ^a	Yield [wt% on a cellulose mass basis]	
		Levoglucosenone (in mol%)	Char
Cellulose	350	2.4 (3.1)	24.6
Cellulose/PA ^b	300	8.9 (11.5)	50.7
Cellulose/IL ^c	300	21.4 (27.6)	32.7
Cellulose/IL ^d	300	20.7 (26.6)	31.4

^a Final temperature for pyrolysis, °C. ^b Cellulose impregnated with 3 wt % of phosphoric acid. ^c IL = [BMMIM]CF₃SO₃. ^d Using [BMMIM]CF₃SO₃ recovered from pyrolysis.

Although the selectivity of levoglucosenone was 71.3 wt% for condensable matter (excluding water) in the study (reference 41)), recent study found that the selectivity could be further increased with the slower pyrolysis, *e.g.*, heating rate of 1 °C/min. In addition, condensation of volatiles from the pyrolyzer with a sequence of three condensers successfully separated the product compounds. In detail, the volatiles firstly entered cold traps (−30 and −70 °C), where the water and major part of furans were captured. Because dehydrated sugars tend to form aerosol particle, nearly half of them including levoglucosenone escaped from the cold trap and was finally captured by an aerosol filter trap. As shown in Fig. 7, the concentration of levoglucosenone in the filter trap exceeded 90 wt% (even including water) with the yield of 17.1 wt% of cellulose. Optimization of operating conditions, such as a flow rate of carrier nitrogen and volume of cold traps, might further enhance the purity of the product levoglucosenone.

The catalysis of ILs significantly depended on the type of counterpart anion. The selective production of levoglucosenone was observed only in the use of CF₃SO₃[−] among the anions investigated, while the change of cation from 1-butyl-2,3-dimethylimidazolium to 1-butyl-3-methylimidazolium had little influence on the product distribution. Further investigation of the effect of anion may lead to the selective production of other cellulose derivatives. A combined process with *in-situ* catalytic

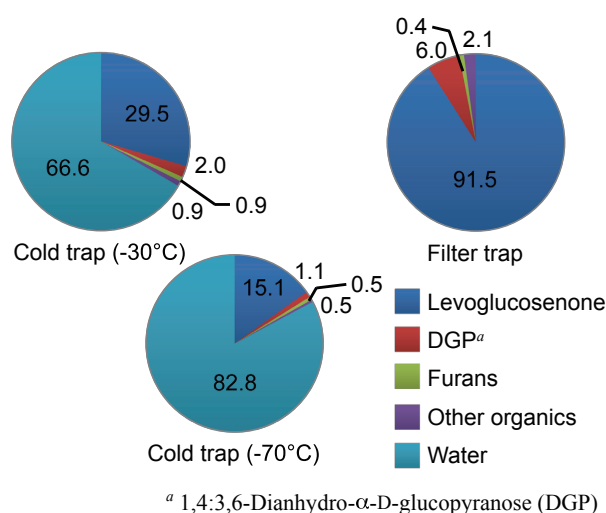


Fig. 7 Composition of liquid products in each condenser (wt%) from pyrolysis of cellulose/[BMMIM]CF₃SO₃ mixture.

reforming of volatiles will also give a wider variety of product chemicals. For example, because anhydrosugars including levoglucosenone are one of the precursors of furan compounds as shown in Fig. 2 (a), it might be possible to develop a pyrolysis method to selectively produce furans such as 5-HMF if levoglucosenone can be catalytically converted. 5-HMF is expected as a platform chemical that can be converted into a variety of useful acids, aldehydes, alcohols, and amines, as well as the promising fuel 2,5-dimethylfuran⁴³. The use of saccharides or polysaccharides other than cellulose for catalyzed pyrolysis would be an option.

4. Conclusions

Variety of the products, which can be selectively produced from the pyrolysis of biomass, is still limited. One of the reasons is that the pyrolysis decomposes biomass into too many compounds to be refined. This work presents two ways to cope with this problem by catalytic reaction: 1) catalytic reforming of a coherent group of compounds derived from volatiles, *e.g.*, hydrocarbon pool in Fig. 2 and coke in Fig. 3 process (b) and (c), and 2) controlling the pyrolysis mechanism with catalysis. Our approach to the reforming of volatiles resulted in high quality products by the utilization of coke formation potential of volatiles. The use of IL in the pyrolysis of cellulose gave new insight into not only the production of levoglucosenone, but also the utilization of ILs in the field of cellulose and/or biomass processing.

In technical and economic viewpoints, pyrolysis has clear advantages over other conversion methods. As described in this review, the application of catalysis has a great potential to put the pyrolysis of biomass into use, although this research area is still in its infancy.

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