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Plenary Lectures

Hydrothermal Conversion of Biomass to Fuels and Chemicals

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The ability to convert biomass economically and sustainably to fuels and chemicals would allow society to transition from being hunter-gatherers for our fuels and fuel precursors to becoming cultivators of our fuels and chemicals feedstocks. All biomass has a high moisture content and drying the biomass requires significant energy input. Direct conversion of wet biomass in hot, compressed water is a process concept that could be more economical and more sustainable than competing process concepts.

This presentation will outline research done to develop hydrothermal processes for the conversion of aquatic biomass (i.e., microalgae) and to elucidate the reaction networks and kinetics. More specifically, we will discuss hydrothermal carbonization, hydrothermal, liquefaction, and hydrothermal gasification [1-5]. Carbonization provides a path toward recovery of lipids and valuable fatty acids while simultaneously producing a fuel precursor with an energy density that exceeds that of the biomass feedstock. Hydrothermal liquefaction uses the combined action of thermal and hydrolytic reactions to decompose the biomacromolecules in biomass into smaller molecules approaching those useful for fuels. Catalytic upgrading of the raw biocrude can then lead to a largely hydrocarbon mixture that could potentially be blended with petroleum and processed in existing refineries. Hydrothermal gasification converts biomass feedstocks or organics-laden aqueous streams into fuel gases such as methane or hydrogen.

In addition to work done with whole biomass, this presentation will provide results from experiments and modeling with simpler model systems, which provide opportunities to better understand the chemical reaction pathways.

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Optimal conversion of biomass to useful chemicals

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The current and projected increase in demand of commodities, chemicals, water and energy caused by the growing world population drives innovation in process synthesis-design towards more sustainable processes. This is achieved by using alternative (renewable) raw materials, such as biomass, incorporating new process technologies and satisfying new design objectives and constraints, including sustainability factors. A 3-stage approach to sustainable process design has been developed[1]. This approach breaks down the design process into three stages: [1]synthesis of processing routes, [2]detailed design and analysis of selected alternatives and innovation for more sustainable processes.

A computer-aided framework for synthesis of processing networks, stage 1, has been developed[2] and recently extended[1]to account for the location dependency of the solution of biomass conversion to useful chemical products. Recently, the framework has been further extended, to include the allocation of various processing sections, feedstocks and products in different geographical locations and to account for the cost of transportation of materials between them. A set of methods and tools have been developed alongside the framework, which include a comprehensive database with data from various geographical locations, including biomass feedstocks, chemicals, reaction paths, technologies, prices, and more. Moreover, a software implementation of the framework, named Super-O, has been built.

This work describes the extended framework and tools along with the development, modeling and optimization of a comprehensive biorefinery superstructure with multiple products and feedstocks with the capability to consider scenarios involving multi-stage, multi-location enterprise-wide networks. Over 100 processing alternatives for converting the mentioned feedstocks into the various chemical products are included, leading to over a hundred trillion theoretical alternative solutions.

Various applications of this framework are shown in this contribution using problems derived from the biorefinery superstructure, under different scenarios with a focus on the multi-location solutions, biomass-product connection and the effect of transportation costs.

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Can algae-based technology is a green approach for biofuel production and wastewater remediation?

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Algae is a well-known organism which has been chosen as the most prominent candidate for biofuel production and wastewater remediation. This critical review study aims to present the applicability of algae with in-depth discussion regarding three key aspects: (i) characterization of algae for its applications; (ii) the technical approaches and their strengths and drawbacks; and (iii) future applications of algae. The review showed that algae biomass was firstly applied for methane production in the early 1950s and during that time the remediation of wastewater by algae was also proposed. Since then, the application of algae in these sectors has improved significantly. The process optimization and combination with other chemical, biological, advanced oxidation processes has generated efficient. Nutrients are being removed in appreciable amounts while heavy, organic and micro-contaminants removal is potential and promising results have been obtained. Thus, the algae-based technology can reasonably be considered as a green approach. However, this technology does have its constraints in terms of commercialization and industrial scale applications. The high energy and capital cost demands limit the projected profits. More research and development work are therefore necessary to minimize the production costs whilst maximizing revenue toward delivering a more efficient algae-based application in the coming decades.

Biological and Chemical Pretreatment Methods for Lignocellulosic Ethanol Production

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The process of converting lignocellulosic biomass to ethanol involves pretreatment to disrupt the complex lignin, cellulose, and hemicellulose, freeing cellulose and hemicellulose for enzymatic saccharification and fermentation. Determining optimal pretreatment techniques for fermentation is essential for the success of lignocellulosic energy production process. The purpose of this study was to evaluate energy cane for lignocellulosic ethanol production. Various pretreatment processes for energy cane variety L 79-1002 (type II) were evaluated including different concentrations of dilute acid hydrolysis and solid-state fungal pretreatment process using brown and white rot fungi. Pretreated biomass was enzymatically saccharified and fermented using a recombinant *E.coli*. The results revealed that all pretreatment processes that were subjected to enzymatic saccharification and fermentation produced ethanol. However, the best result was observed in dilute acid hydrolysis of 3% sulfuric acid. Combination of fungal pretreatment with dilute acid hydrolysis reduced the acid requirement from 3% to 1% and this combined process could be more economical in a large-scale production system.

Keynote Lectures

Process Control Towards the Production of Chemicals with High Selectivity from Actual Biomass

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Raw biomass, as alternative to replace the exhausting fossil resource, can be used as feedstock to produce chemicals.[1] However, its complex composition and structure with great biodiversity from molecular to macroscopic levels make its conversion difficult. In addition, its solid state and indissolubility in most solvents greatly hinder the mass and heat transfer as well as the action of catalyst.[2] Thus, the direct conversion of actual biomass usually obtained chemicals with low productivity and poor selectivity, inhibiting their wide application in industry. These challenges appeal the development of process control to produce chemicals with high selectivity.

By using optimized solvent with controlled reaction conditions (temperature, pressure, and catalyst), the solid biomass can be transformed to fluid with oligomers and monomers dissolved, thereby promoting the mass and heat transfer. Additionally, the action of catalyst to fluid conversion is much easier to be exerted, improving the productivity and selectivity of the target chemicals. Process control may include the following aspects: (1) one-step simultaneous dissolution and conversion of one/two main components directly to target chemical; (2) the dissolution of one/two components in the first step and then further conversion of the fluid obtained. Thus the development of processes with efficient solvents, catalysts, and other reaction conditions for both the selective dissolution of one/two component and the selective conversion of the resultants species is crucially important for effective utilization of biomass.

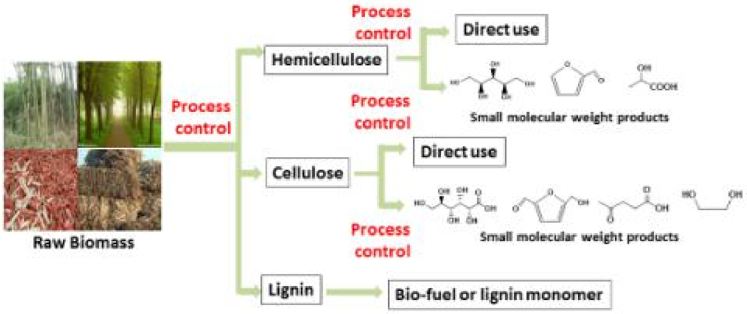

Fig. 1 Process control towards the conversion of raw biomass.

dAs for one-step strategy, more than 90% of lignin in birch sawdust was directly converted to lignin oil containing above 50% of phenolic monomers and about 20% of phenolic dimmers in the presence of Ru/C in methanol system.[3] By adjusting the percentage of GVL in H_2O-GVL co-solvent and the concentration of H_2SO_4, the hemicellulose and cellulosic fraction could be simultaneously converted to levulinic acids (61%) and furfural (56%), respectively.[4] As for step-wise strategy, a high yield of 20.0 wt % γ-valerolactone (GVL) with high selectivity of 90.5% was achieved without addition of external hydrogen from the hemicellulose fraction of Pubescens.[5] By the catalysis of MgO, high yield (79.6 wt%) and selectivity (90%) of lactic acid was also obtained directly from constover.[6]

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Catalytic Transformation of Cellulose into Organic Acid

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The transformation of cellulose into chemicals and fuels under mild conditions is important for establishing green and sustainable chemical processes. Organic acids. The conversion of cellulose into organic acids, which are important fine chemicals or monomers for important polymers, with no or less H_2 consumption is an attractive route for biomass utilization. Here, I will present our recent studies on the conversion of cellulose or its derived carbohydrates into organic acids, including gluconic acid, 2,5-furandicarboxylic acid (FDCA) via 5-hydroxymethyl-fufural (HMF), adipic acid and lactic acid.

The bifunctional catalysts containing Au nanoparticles on Keggin-type insoluble polyoxometalates are efficient catalysts for the conversion of cellulose into gluconic acid. Functionalized CNT is a superior support of Au-Pd alloy or Pt nanoparticles for the selective oxidation of HMF to FDCA under base-free conditions. We developed a new route for the conversion of cellulose to adipic acid via glucose and glucaric acid (Fig. 1).

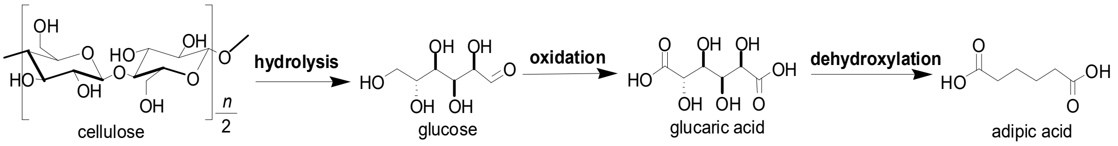

Fig. 1. Novel route for the synthesis of adipic acid from cellulose.

We discovered that simple metal cations, in particular Pb^{II}, could catalyze the selective conversion of cellulose into lactic acid in water under anaerobic conditions. Mechanistic studies clarified that Pb^{II} in water possesses the abilities of both isomerization and retro-aldol fragmentation, thus providing high yield of lactic acid (Fig. 2). An efficient dual-functional catalytic system composed of Al^{III} and Sn^{II} cations for lactic acid formation has also been designed.

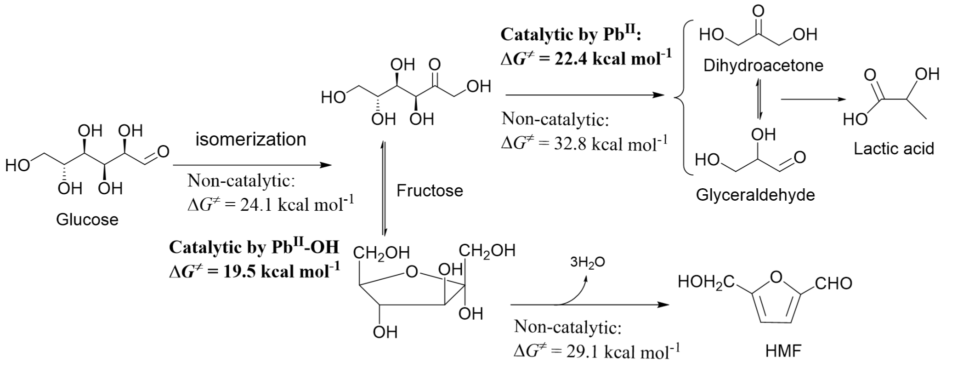

Fig. 2. Mechanism for the formation of lactic acid and the catalytic functions of Pb^{II} cation.

Cleavage of C-C bond: A Key Step in the Biomass Conversion to Chemicals

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Biomass, in particular lignocellulosic materials, is a kind of renewable yet abundant organic carbon source in nature. The efficient utilization of biomass for production of liquid fuels and chemicals will be envisioned as a promising way towards a low-carbon and sustainable society. So far a variety of transformation strategies of biomass have been proposed and established. Among them, the transformation of biomass into low-molecular chemicals and fuel additives (ethylene glycol, ethanol, ethanol amine, etc.) has attracted intensive attentions, and also present grand challenges in the selectivity control. As biomass is composed of three-dimensional macromolecules, the cleavage of C-C bond becomes a key step in the transformation of biomass to low-molecular chemicals and fuel additives.

In this presentation, I will give three examples to show the selective cleavage of C-C bond of cellulose in the presence of tungsten-based catalysts. First, the direct conversion of cellulose to ethylene glycol will be discussed in terms of catalyst design and reaction kinetics. Then, cellulose conversion to ethanol via methyl glycolate is presented. Finally, a two-step process for the conversion of cellulose to ethanol amine is developed. In the above three transformation processes, a common intermediate, glycolaldehyde is involved, which is produced through retro-aldol condensation of cellulose-derived glucose under the presence of W-based catalysts. To rapidly convert the unstable glycolaldehyde to stable final chemicals (ethylene glycol, methyl glycolate, ethanolamine), bifunctional catalysts which can best match the rate-determining C-C cleaving step and the rapid successive step (hydrogenation or oxidative esterification or reductive amination) is required.

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Catalytic Conversion of Biomass to Chemicals and Fuels

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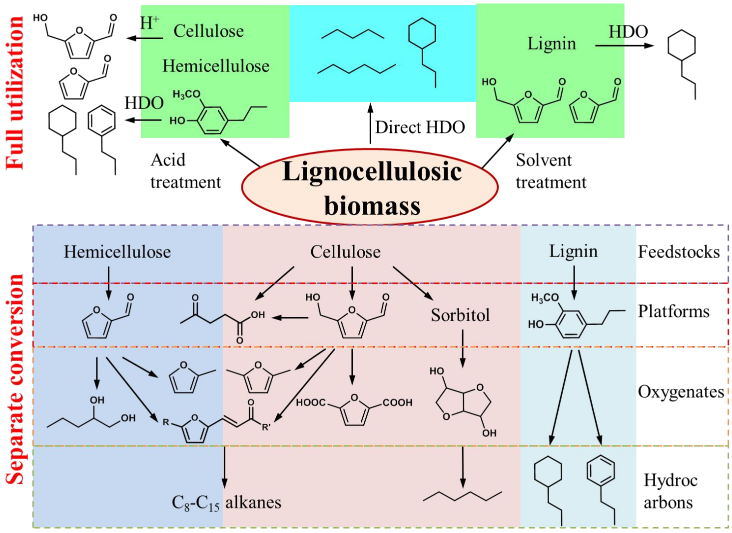
Being the only sustainable source of organic carbon, biomass is playing an ever-increasingly important role in our energy landscape. Plant-derived lignocellulosic biomass is considered as an important alternative source to fossil reserves for the production of chemicals and fuels, but the inertness and complexity of lignocellulose makes its depolymerization and usage difficult. Cellulose, as the main component of lignocellulose, can be converted to 5-hydroxymethylfurfural (HMF), one of the most versatile and important building blocks, because it can be upgraded into a large number of chemicals and fuels, such as 2,5-furandicarboxylic acid (FDCA), 2,5-dimethylfuran (DMF) and long-chain alkanes, while its selective conversion to HMF is still a challenge. Lignin, as the most energy-dense fraction of biomass and containing valuable aromatic functionalities, is the only one large-volume renewable source of aromatic chemicals, but its depolymerization and following hydrodeoxygenation to aromatics hydrocarbons is also challenging. To solve these problems, we designed various catalysts to convert cellulose into HMF, lignin to aromatic hydrocarbons and even raw woody biomass to alkanes separately or in full utilization. The following scheme shows the works in our laboratory.



Scheme. Reaction network of lignocellusic biomass conversion in our laboratory.

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Hydrogenolysis of Glycerol over Cu-based Catalysts

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Biodiesel is an advanced biofuel, it is a renewable, clean-burning diesel replacement which can reduce the dependence on crude oil, creating green jobs and improving our environment. It is made from an increasingly diverse mix of resources including agricultural oils, recycled cooking oil and animal fats. The productivity of biodiesel in America reached 2890 millions of gallon in 2016. Glycerol is a by-product during the production of biodiesel, and the rapidly rising production of biodiesel has led to a serious surplus of glycerol, which makes it one of the most attractive platform chemicals[1-4]. In the past years, catalytic hydrogenolysis of glycerol to valuable products (including propanediols, propanols, ethanol, and/or methanol) has become a hot research topic[5,6]. Mechanism investigation showed that the hydrogenolysis of glycerol proceeded in a series of tandem reactions[6], and efficient catalyst for this process must have appropriate dehydrogenation, dehydration, and hydrogenation active sites[7].

In the past ten years, a series of Cu-based catalysts were prepared via the impregnation[8], coprecipitation[9], solid combustion[10], reduction of layered double hydroxides[7,11-14], and decomposition of metal-organic frameworks[15] in our laboratory. The structure and surface properties of these catalysts were characterized in detail, and all these catalysts were tried in the hydrogenolysis of glycerol to valuable products in batch or continuous reaction condition. And the main conclusions of these researches were:

1. In a batch gas liquid solid hydrogenolysis reaction process, the activity of these catalysts depended strongly on the particle sizes of both Cu and MgO. Catalysts that have smaller sized Cu and MgO particles were more active for glycerol hydrogenolysis (Bioresource Technol. 2010, 101, 7088). Further experiments indicated that the activity of Cu-based catalyst increased with its alkalinity (Appl. Clay Sci. 2015, 118, 68). And these catalysts were more active and stable in a bio-ethanol solution than that in aqueous solution (Bioresource Technol. 2012, 104, 814).
2. Homogenously dispersed copper on layered solid base (with 80.1% dispersion of copper) could be synthesized via thermal decomposition of the as-synthesized layered double hydroxides. This bi-functional highly dispersed Cu-solid base catalyst was extremely effective for hydrogenolysis of aqueous glycerol. The detected conversion of glycerol reached 80.0% with a 98.2% selectivity of 1,2-propanediol at 180 °C, 3.0 MPa H_2 and 20 h (Appl. Catal. B. 2011, 101, 431). The activity of surface Cu atoms in $Cu_{0.4}/Zn_{0.6}Mg_{5.0}Al_2O_{8.6}$ reached 26.6 h^{-1} at 200 °C (J. Catal. 2012, 296, 1). Small amount of MWCNTs can further enhance the activity of $Cu_{0.4}/Zn_{0.6}Mg_{5.0}Al_2O_{8.6}$ catalyst (J. Mater. Chem. A 2013, 1, 11548), magnetic Fe_2O_3 can improve the thermal stability of catalyst (Catal. Sci. Technol. 2014, 4, 912).
3. A novel Cu/ZnO catalyst with nano sized ZnO particles dotted on Cu was synthesized via Cu(Zn)-HKUST-1 precursor. And the performance of final Cu/ZnO catalysts for continuous hydrogenolysis of glycerol was tested in a fixed-bed reactor. It was found that $Cu_{1.1}/ZnO$ catalyst derived from $Cu_{1.1}Zn_{1.9}(BTC)_2 \cdot 9.4(H_2O)$ was more active and stable than Cu/ZnO that prepared via solvent-free grinding and co-precipitation. Characterizations results inferred that the interface between Cu and ZnO played a crucial role on its catalytic performance, and ZnO dotted Cu was more stable than ZnO plate supported Cu particles (Appl. Catal. B. 2017, 203, 146).

4. More recently, it was found that Ni-substituted stichtite derived Ni/$MgCr_2O_4$ catalysts and Co(Zn)-HKUST-1 precursor derived (CoZn)-ZnO catalysts were capable for the further hydrogenolysis of glycerol to ethanol and methanol in continuous fixed-bed reactor. The best yield of ethanol reached 0.73 g-ethanol/g-cat/h at 250 °C over $Ni_{2.4}/Mg_{3.7}Cr_{2.0}O_{6.7}$

All these progresses will be presented during the congress and discussed with these participates. And we think that these works would be helpful to those researchers in the area of catalytic upgrading of glycerol and other platform chemicals.

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Biphasic Tandem Catalytic Process for Renewable Biofuel Production

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The market demand for renewable fuels has surged in the transportation sector in the past decades. However, today the cost of liquid hydrocarbon fuels from biomass is still too high to compete with petroleum derived transportation fuels. One of the grand challenges in biofuels production is the low carbon atom efficiency to the fuel products. Herein we have developed a novel “one-pot” biphasic tandem catalytic process (biTCP) that was used to convert plant biocrudes to hydrocarbons at an extraordinarily high carbon efficiency. Unlike the conventional monophasic catalytic processes, the biTCP is a new approach of tandem catalysis in water / organic biphasic solvent media with spatially separated different catalysts, which catalyze distinct reactions in water and non-polar organic solvents, respectively. For demonstration, the mono- and diterpenoids, e.g., the biocrudes of eucalyptus and grindelia squarrosa, have been converted into cycloalkanes, which are high-density jet fuel components, with the hybrid catalysts in aqueous and cyclohexane solvents, respectively, in the biTCP. This same process was also able to efficiently convert fatty acids and triglycerides extracted from oilseed crops to renewable diesel. The reaction mechanism was investigated to gain a fundamental understanding of the effects of catalyst properties and process conditions on the conversion of the two different types of biomass feedstock.

Anti-Stress Gene Circuits Boost Fermentation Process for Low Energy Consumption and Emission

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The growth and production of microorganisms in bioconversion are often hampered by heat stress and product feed-back repression. In this study, the intelligent microbial heat regulating engines (IMHeRE) which are novel gene circuits were developed and customised to improve the thermo-robustness of Escherichia coli and Saccharomyces cerevisiae via the integration of a thermotolerant system and a quorum regulating system. At the cell level, the thermotolerant system composed of different heat shock proteins and RNA thermometers hierarchically expands the optimum temperature by sensing heat changes in both strains. At the community level, the quorum regulating system dynamically programs the altruistic sacrifice of individuals to reduce metabolic heat release by sensing the temperature and cell density in Escherichia coli. Using this hierarchical, dynamical and multilevel regulation, the IMHeRE are able to significantly improve cell growth and production. In real applications, the production of lysine was increased five-fold at 40°C using the IMHeRE. Additionally, both tolerant to thermo stress and high concentration of ethanol in Saccharomyces cerevisiae has recently become much useful as the industry moves toward the use of simultaneous sacchrification and fermentation (SSF). So double-tolerance gene circuits were rationally designed and successfully obtained through one-pot parts random assembly via Golden Gate Shuffling. The cooling water and energy consumption are all significantly reduced of 31% and 24% as well as ethanol production and productivity enhanced by 5% and 12% by engineered Saccharomyces cerevisiae, respectively, in 35-37°C fermentation. Our work provides new potential for the development of bioconversion by conserving energy and increasing productivity.

pH control in fermentation and cell culture is also a worldwide concern because the fluctuation of pH level tremendously influences the performance of microorganism and cells. In this study, intelligent pH regulation genetic circuits including acid regulation circuit (ARC) and base regulation circuit (BRC) were proposed and designed in E.coli to achieve self-responsive pH adjustment and alleviate pH stresses. Results showed that both ARC and BRC could successfully enhance the ability of strains to regulate the external pH without adding acid and base.

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ARTP Mutagenesis as a Useful Tool for Integrative Engineering of Cell Factories

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Development of rapid and powerful mutagenesis tools is always of importance for effective evolution of strains or germplasms for integrative biotechnology research and bioindustry development. ARTP (atmospheric and room temperature plasma) mutagenesis system developed by our group can directly cause complex genome mutation including chain break and bases mutation via a unique mechanism. By quantification of the DNA damage strength and the subsequent mutation rate of living cells, ARTP has exhibited the strongest DNA damage, and the highest mutation rate among the physical and chemical mutagenesis methods. Further, genome sequencing of E. coli mutated by ARTP indicated that diverse breakages of DNA occurred. By omic analysis of the representative mutants of such as bacteria, yeast, fungi and microalgae generated by ARTP or followed by combination with adaptive evolution, global changes in the metabolic network pertaining to different phenotypes of growth rate, tolerance and productivity, was discovered, which enabled the new genetic functions to be explored. The ARTP mutagenesis has been validated to be efficient for reverse metabolic engineering of microbial cell factories. More than 100 types of microbial strains and plants as well as animals have been successfully improved by ARTP mutagenesis so far. Taken together, ARTP can be a useful mutagenesis platform for integrative engineering of cell factories by combining with different high throughput screening methods and rational design.

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Design and Use of Whole-cell Biocatalysts for Green Synthesis of High-value Chemicals

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Ursodeoxycholic acid (UDCA) is the active ingredient of natural bear bile powder with multiple pharmacological functions. 7β-Hydroxysteroid dehydrogenase (HSDH) is a key biocatalyst for the synthesis of UDCA. However, all the 7β-HSDHs reported commonly suffer from poor activity and thermostability, resulting in limited productivity of UDCA. In this study, a multiobjective directed evolution (MODE) strategy was proposed and applied to improve the activity, thermostability, and pH optimum of a 7β-HSDH. The best variant (V_{3-1}) showed a specific activity 5.5-fold higher than and a half-life 3-fold longer than those of the wild type. In addition, the pH optimum of the variant was shifted to a weakly alkaline value. In the cascade reaction, the productivity of UDCA with V_{3-1} increased to 942 g L^{-1} day^{-1}, in contrast to 141 g L^{-1} day^{-1} with the wild type. Therefore, this study provides a useful strategy for improving the catalytic efficiency of a key enzyme that significantly facilitated the bioproduction of UDCA.

Imine reductases (IRs), a rapidly emerging class of useful biocatalysts, catalyze the asymmetric reduction of cyclic imines to form chiral amines. In this study, new imine reductases were discovered for asymmetric reduction of sterically hindered cyclic imines, including two enantiocomplementary imine reductses from Paenibacillus lactis (PlSIR and PlRIR) for reduction of 3H-indoles and an (S)-selective imine reductase from Stackebrandtia nassauensis (SnIR) for reduction of dihydroisoquinolines. PlSIR showed a high activity of 15.1 U/mg protein toward 2,3,3-trimethylindolenine at 30°C and pH 6.0 and good thermal stability with a half-life of 49.5 h at 50°C. An enzymatic process was developed for the first time for efficient asymmetric reduction of 3H-indoles as well as 3H-indole iodides. Using this (S)-selective PlSIR, various N-unprotected indolines and N-alkylindolines were facilely synthesized in good yields and excellent enantiopurities (up to >99% ee). Compared to PlSIR, the enantiocomplementary PlRIR exhibited a relatively lower catalytic efficiency ($k_{cat}/K_m = 1.58\ s^{-1}\ mM^{-1}$) towards 2,3,3-trimethylindolenine. In addition, SnIR displayed 25-1400 fold greater catalytic efficiency for 1-methyl-3,4-dihydroisoquinoline (up to 15 g L^{-1}), as compared to other imine reductases reported.

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Establishing a Platform Escherichia Coli Strain to Generate Xylose-derived Value-added Products

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Xylose is the most abundant C5 sugar in lignocellulosic biomass and also represents a source of carbon from non-edible feedstocks. Here, we report the construction of a platform Escherichia coli strain for the production of high value compounds via the nonphosphorylative xylose metabolism. Firstly, we constructed a novel biosynthetic pathway for the production of 3,4-dihydroxybutyric acid, the hydrolyzed form of 3-Hydroxy-γ-butyrolactone (3HBL), which is one of the top value-added building block for synthesis of various drugs and nutraceuticals. Efficient enzymes screening, host strain engineering and highly active 3,4-dihydroxybutanal dehydrogenases identification enabled production of 1.27 g/L 3,4-DHBA in shake flasks, which is the highest titer reported so far. Then, the application of this platform was further demonstrated by building an artificial pathway for biosynthesis of 1,4-butanediol (1,4-BDO). The Klebsiella oxytoca diol dehydratase was engineered to achieve non-native catalysis of 1,2,4-BTO into 1,4-BDO by a series of rational protein engineering strategies. Those efforts enabled 209 mg/L 1,4-BDO produced via a novel metabolic route from xylose, which sets an example to build novel biosynthetic pathways via rational protein engineering. Finally, we investigated and illustrated the synergetic effect between xylose isomerase pathway and Weimberg pathway for the synthesis of chemicals derived from 2-ketoglutarate and acetyl-CoA. When using glutaric acid as the target product, employment of such synergetic pathways in combination resulted in an increased glutaric acid titer (602 mg/L) compared with using each pathway alone (104 or 209 mg/L). This work validates a novel and powerful strategy for xylose metabolic utilization to overcome the inefficiency of using single xylose metabolic pathway for the synthesis of TCA cycle derived chemicals.

Lignocellulosic Biomass for the Production of Industrially Important Platform Chemicals

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The chemical industries are primarily dependent on fossil based chemicals and there are significant steps are being taken around the world to move from fossil based economy to a more sustainable and environmental friendly methods based on bioprocesses. With the increasing demands on reducing the green house gas emission and carbon foot print attributed to fossil based production, the industries are looking for alternative renewable cleaner resources for the production of certain chemicals. The present study describes the development of a bioprocess for the production of two industrially important diols, 1,3-propanediol and 2,3-butanediol from lignocellulosic biomass.

1,3-propanediol (1,3-PDO) is a specialty chemical monomer gained an economic importance from being a fine chemical to commodity bulk chemical. This chemical has wide range of applications as monomer in the production of polymers like polyurethane, polyether etc. and also used in cosmetic, food, pharmaceutical and textile industries. The aim of the study was to evaluate a novel onsite enrichment approach to isolate a crude glycerol utilizing facultative anaerobic bacteria. An onsite enrichment in natural conditions resulted an isolate, Lactobacillus brevis N1E9.3.3, that can utilize glycerol and produce 1,3-propanediol with a yield of 0.89 $g_{1,3\text{-PDO}}/g_{\text{glycerol}}$ and productivity of 0.78 $g_{1,3\text{-PDO}}/l/h$ at alkaline pH-8.5 under anaerobic conditions. Batch fermentation experiments with glycerol-glucose co-fermentation strategy was carried out to evaluate the production of 1,3 propanediol and other byproducts using rice straw. The effect of other carbon sources as co-substrate was also evaluated.

Batch fermentation trials for the production of 2,3-butanediol were carried out using an isolated strain Enterobacter cloacae SG-1. The study resulted 14.67g/l of 2,3-butanediol using glucose as the carbon source. In order to replace the expensive glucose in the production media, oil palm frond hydrolysate was used as the carbon source. The ability of the strain, Enterobacter cloacae SG-1, for utilization various pentoses and hexoses were evaluated and found that the strain can utilize both arabinose and glucose with a comparable 2,3-butanediol yield.

Metabolic Construction of High Efficient Biocatalytic Systems Characterized by "Lignocelluloses Utilization" and "Non-photosynthetic CO2 Fixation"

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Lignocellulose instead of starchy based materials as the substrate for biorefinery systems can potentially provide the quantity needed to make a significant impact, improve the net carbon and energy balances, lower production cost, and avoid food competition. Hence, an anaerobic bio-transformation system characterized with "simultaneous utilization of component sugars in lignocellulose" and "non-photosynthetic CO_2 fixation" was successfully established. 1) To realize the utilization of xylose by recombinant E. coli BA002, the ATP supply between Actinobacillus succinogenes and E. coli was compared and it was found that insufficient ATP supply resulted in eliminated cell growth and xylose utilization in the recombinant E. coli. Through introduction of ATP-forming phsophoenolpyruvate carboxykinase from Bacillus subtilis 168, the recombinant E. coli regained the capability of using xylose for succinic acid production. Moreover, by deleting ptsG gene to relieve carbon catabolite repression effect, the simultaneous utilization of glucose and xylose was achieved and the fermentation period shortened. 2) To increase the cell growth and metabolic capability, intracellular NAD(H) system was modified. By regulating the total NAD(H) pool and NADH/NAD^+ ratio, succinic acid productivity was increased 30.7-fold. Additionally, through co-regulating NAD(H) and ATP system, the recombinant E. coli was obtained with obvious enhanced succinic acid productivity. 3) ATP is the driving force participating not only intracellular metabolism but also stress-adaption. By improving intracellular ATP supply, the resistance of recombinant E. coli to low pH, osmotic stress, and high temperature, the cell growth and succinic acid production were all significantly improved.

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Converting Biomass into Biofuels and High-value Chemicals via Selective Catalytic deoxygenation

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Biomass is the only renewable carbon resources in nature and it is considered as an ideal substitute for nonrenewable fossil resources. Since the oxygen content of biomass is relatively high, a series of catalytic deoxygenation processes become necessary for the conversion of biomass and its derived molecules to biofuels and high-value chemicals. Selective catalytic deoxygenation of biomass could be achieved through dehydration, hydrogenolysis, decarbonylation, and so on. With the catalytic hydrolysis of novel solid acids, such as magnetic solid acids and heteropoly acids, biomass derived sugars would be directly converted to formic acid, levulinic acid, furfural and 5-hydroxymethylfurfural, etc. Those sugar derived molecules could be transferred to biofuels and high-value chemicals, e.g. γ-valerolactone, cyclopentanone, hydroxymethyl-cyclopentanone, methylfuran and dimethylfuran via catalytic hydrogenolysis over different metal based catalysts. The formed γ-valerolactone would be further deoxygenated to valeric acid and esters under mild conditions with the adding of strong Lewis acids. Except the catalytic hydrogenolysis, decarbonylation has also been confirmed in the deoxygenation process of furfural to furan. Besides, phenols and fatty acid methyl esters, as two other kinds of biomass-derived molecules which are respectively obtained from lignin and grease, are also used for the production of biofuels and high-value chemicals. Phenols could be transferred into cycloalkanes and aromatic hydrocarbon via selective catalytic hydrogenolysis. However, fatty acid methyl esters are mainly employed for the production of bio-diesel.

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Rapidly and Highly Effective Conversion of Biomass and CO_2 into Chemicals and Fuels by Mimicking Nature

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The Earth’s environment is threatened by a serious global energy crisis and the increase in atmospheric carbon dioxide linked to global warming, which can be attributed to the rapid consumption of fossil fuels caused by human development and the slow absorption and conversion of CO_2 by nature. To diminish the imbalance, an efficient method should involve the rapidly and highly effective conversion of biomass and CO_2 into fuels and chemicals. For this, we can learn from the geologic formation of fossil fuels. Geochemists have found that hydrothermal reactions have played an important role in the formation of fossil fuel from organic wastes. Thus, if humans could simulate the natural phenomena of the formation of fossils, then, it should quickly turn biomass and also carbon dioxide into fuels and chemicals and then improving the Earth's carbon cycle.

This presentation gives an overview of some recent studies of hydrothermal conversion of biomass and also carbon dioxide into value-added chemicals and fuels (1-2). Biomass conversion mainly involves the conversion of cellulosic and lignocellulosic biomasses as well as food waste into carboxylic acids. Some discussions on hydrothermal reaction mechanisms, as well as some of new catalysts and solid oxidants in the conversion of biomass are also presented. For the reduction of CO_2, it is presented that a novel strategy of the reduction of CO_2 with renewable biomass.

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Utilization of CO_2-Derived Microalgal Biomass as Cofiring Fuel with Coal and the Future Prospects

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The soaring CO_2 levels caused by the anthropogenic emissions and the resulting climate changes are the most serious problems facing humanity. To reduce the CO_2 emissions, various CO_2 capture, utilization and storage technologies have been suggested for now. Among them, photosynthetic CO_2 conversion processes as exemplified by microalgae cultivation system have garnered considerable attention due to their advantages over other candidates, including: 1) The biological system is able to convert CO_2 into a diversity of feedstocks for bioenergy, such as biodiesel and bioalcohol using solar energy as a sole energy source, thereby avoiding the requirement of the auxiliary CO_2-emitting energy sources; and 2) the average productivity of the microorganisms dominates that of the other conventional biomass resources which strengthens the practicability of the biomass. For these reasons, microalgal biomass was considered and studied as a promising source for biodiesel to date. For the preparation of the liquid fuel, however, various energy-intensive downstream processes are required and thus several disputes on the CO_2 neutrality of the bio-derived liquid fuel system has been raised recently. In this context, direct combustion of biomass is receiving popularity since the utilization strategy can exploit the biomass energy with relatively simple downstream processes. Herein, we highlight the holistic potential of microalgae as solid fuel for the practical energy production in terms of the energy density, productivity and CO_2 mitigation ability. For the quantitative analysis, biomass productivities, calorific values and cellular compositions of various microalgal species were estimated. Consequently, we found that there are advantages of microalgae as solid fuel over as feedstock for the biodiesel considering the life-cycle (from production to consumption) and energy yields of the fuels. In this presentation, the potential of microalgae-based bioenergy with carbon capture and storage (BECCS) technology in negative CO_2 emissions is also discussed for the future prospects of the energy system.

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Conversion of Biomass to Microbial Lipids for Biofuels

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Microbial lipids, especially produced by oleaginous yeasts, consist mainly of triacylglycerols with fatty acid compositional profiles similar to those of commercial vegetable oils. Thus, microbial lipids are potential renewable resources for biofuels and oleochemicals. Over the years, we have been working on many aspects of microbial lipid technology in order to advance this area and reduce production costs. Specifically, different types of integrated processes were devised to explore low-value feedstock, such as raw glycerol, biomass hydrolysates, corn stalk, and cellular wastes of fermentation industry. In terms of lignocellulosic biomass, both cellulose and hemicellulose were converted into lipids. Processes were established to recover lipid and even make fatty acid esters directly from the culture broth without the isolation of "fatty" cells. Together, our efforts have been considerably advancing yeast lipid technology and should provide intriguing insights for biorefinery in general. We believe that yeast lipids will be further developed in near future for sustainable biodiesel production.

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Electrical Discharges for Fuel Gas Cleaning

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This paper discusses the state of art of electrical discharges for fuel gas cleaning, namely particle collection and tar cracking for pyrolysis and/or gasification. Traditional technique is based on negative corona discharge for particle and/or ash collection inside electrostatic precipitators (ESP) [1]. In order to simultaneously collect ash and remove tar, streamer corona based non-thermal plasma techniques (NTP) have been tested in both laboratory and industrial site [2]. Heavy tars can be cracked to light ones together with ash collection. Moreover, the NTP can be easily integrated with chemical catalysis by producing streamer corona on the catalyst surface for reducing NTP energy consumption. Our recent laboratory tests have also demonstrated that it is possible to integrate the NTP with ceramic bag catalyst filter to remove ash, SO2, NOx and tar simultaneously.

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Microfluidics Technique in Transformation of Biomass into Chemicals

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Microfluidics, also known as continuous flow or microflow, has been widely used in process intensification during past decade, since better mass and heat transfer could be achieved in a microreactor due to scale effect. In terms of chemistry, transformation of biomass always involves harsh reaction conditions, such as high pressure, high temperature, strong acidic condition, biphasic reaction. Therefore, microfluidics technique was introduced into transformation of biomass to accelerate the reaction process and reduce side reactions.

In this presentation, biobased polyurethane and biobased plasticizers prepared in continuous flow system were demonstrated. Various polyols were designed and produced by continuous process, which increased quality of the product and safety of the process. Eventually, a novel oil-based polyurethane with benefits of lower cost and better thermal insulation properties was developed. Plant oil and citrate acid were employed to prepare biobased plasticizers in microfulidics system. Safety of the epoxidation of oil was improved by microflow technique due to better heat transfer. Meanwhile, the epoxide number of the product was increased from 6.0 to 6.5, while the consumption of hydrogen peroxide was reduced by over 30%, which made the whole process be green and safe.

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Product Selectivity Controlled by Zeolite Crystals in Biomass Hydrogenation over Metal Catalysts

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This work delineates first example for controlling product selectivity in metal-catalyzed hydrogenation of biomass by zeolite crystals. The key to this success is to combine the advantages of both Pd nanoparticles (highly active sites) and zeolite micropores (controllable diffusion of reactants and products), which was achieved from encapsulation of the Pd nanoparticles inside of Silicalite-I zeolite crystals as a core-shell structure (Pd@S-1).[1-4] In the hydrogenation of biomass-derived furfural,[5] the furan selectivity over the Pd@S-1 is as high as 98.7%, outperforming the furan selectivity (5.6%) over conventional Pd nanoparticles impregnated with S-1 zeolite crystals (Pd/S-1). The extraordinary furan selectivity in the hydrogenation over the Pd@S-1 is reasonably attributed to the distinguishable mass transfer of the hydrogenated products in the zeolite micropores.

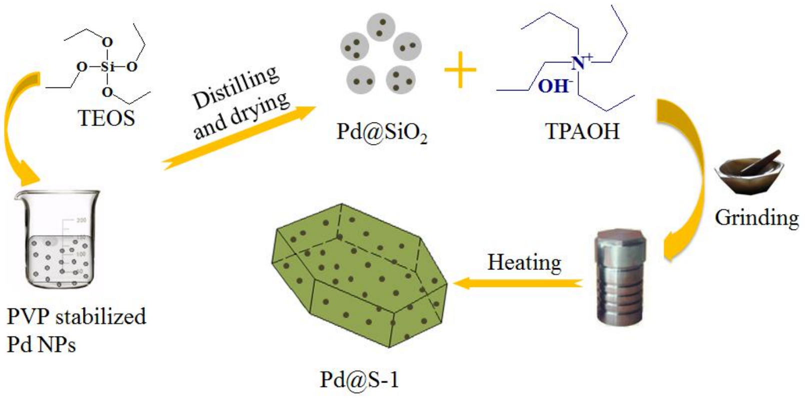

Figure 1. Synthesis of Pd@zeolite S-1 catalyst.

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Biomass Utilization in High Efficient Nitrogen Removal Process

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Biomass valorisation for biofuels and production of any platform molecules from vegetal wastes are generally focussed and evaluated from their carbon recycling performances. However, nitrogenous by-products produced in these processes are more seldom considered, though nitrogen fraction generally represents 5 - 15 % of biomass dry mass. Biomass revalorisation processes generally produce soluble nitrogen as ammonium form (NH_4^+) or gaseous nitrogenous compounds as NO_x. Those compounds must be removed from environment, preventing soluble nitrite production and eliminating NO_x that are toxic and pollutant. Therefore efficient ammonium removal process is mandatory for improving global sustainability of any biomass valorisation processes. A valuable option consists in complete oxidation of ammonium to nitrate, instead of a nitrification / denitrification process, leading to fertilizers production and a join recycling of minerals and nitrogen.

A nitrification fixed-bed bioreactor has been conceived in order to intensify a nitrogen recycling system that is used to improve biomass valorisation processes. Two pure bacteria strains have been grown on polystyrene beads: Nitrosomonas europaea ATCC® 19718™ which oxidizes ammonia into nitrite and Nitrobacter winogradskyi ATCC® 25391™ which produces nitrate from nitrite. A mineral media with ammonium as the sole nitrogen source is used as effluent. After a characterization of the bacterial strains and of the hydrodynamics of the bioreactor, the packed-bed column has been run for more than one year. During this long-term experiment, various operating conditions were: (i) residence time (2 - 50 h), (ii) nitrogen concentration (0.29 - 0.8 $kgN \cdot m^{-3}$), (iii) nitrogen load (0.45 - 4.5 $kgN \cdot m^{-3} \cdot d^{-1}$), (iv) robustness tests of system failure, such as gas supply and electric power shutdown. The maximum nitrogen load that allowed a total nitrification in the column was 2.5 $kgN \cdot m^{-3} \cdot d^{-1}$. The biomass has been transitory exposed at high nitrogen loads (up to 4.5 $kgN \cdot m^{-3} \cdot d^{-1}$) to observe the response to a stress and the level of nitrification at the outlet of the bioreactor.

The nitrate produced during this kind of continuous experiment can be used as the nitrogen source for plant growth and / or cyanobacteria cultures. This process is an economic and robust solution to remove nitrogen from effluents. Ammonia removal can then be coupled to other economically valorisation processes, achieving both carbon and nitrogen recycling.

NHC-Based Coordination Polymers as Solid Molecular Catalysts toward Biomass Transformations

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A class of robust solid molecular NHC-based catalysts was readily fabricated via self-assembly from diverse bis-benzimidazolium salts with selected metal precursors. Among them, the NHC-Ru and NHC-Ir polymer have demonstrated high catalytic activity and excellent stability as a solid molecular catalyst for the solvent-free reductive amination of biomass levulinic acid and oxidative dehydrogenation of glycerol with dihydrogen liberation, respectively, at very low catalyst loadings. All solid catalysts were readily recovered by simple filtration and reused for dozens of runs without obvious loss of activity. Probably owing to the effective suppression of inactive binuclear metal species in a homogeneously catalyzed reaction, the catalysts assembled via self-supported strategy exhibited high selectivity and productivity for corresponding products, with the highest turnover numbers (TON) achieved so far in large-scale reactions The high catalytic activity, recyclability, and scalability of the robust solid molecular catalysts highlight their potential toward the development of practical technologies for transformation of biomasses to value-added chemicals.

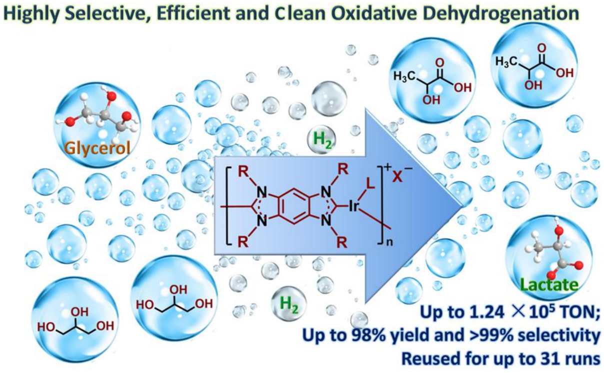

Fig. 1. NHC-Ir catalyzed oxidative dehydrogenation of glycerol to lactate with hydrogen liberation.

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Designing Integrated Electrocatalyst/Semiconductor Photoelectrodes for Efficient Photoelectrochemical Hydrogen Production

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Water splitting by solar-driven photoelectrochemical (PEC) reactions has been broadly recognized as one of the most promising chemical method for sustainable energy conversion and storage systems. Effective integration of semiconductor and electrocatalyst is critical for fabricating efficient PEC devices. However, this is a big challenge, because the introduction of interfacial recombination centers on the electrocatalyst/semiconductor junction result in charge recombination. Moreover, considering the advantages of electrocatalysts with ultrathin morphology, the rational design of electrocatalyst/semiconductor architecture to improve the hydrogen evolution reaction (HER) or oxygen evolution reaction (OER) kinetics without sacrificing light harvesting is of significance to achieve efficient PEC system.

Recently, we found that amorphous materials synthesized by a facile electrodeposition method can serve as highly efficient electrocatalysts for efficient photoelectrochemical water splitting. We realized the rational design of a novel 3D p-Si/NiCoSe$_x$ core/shell nanopillar (NP) array photocathode by uniform photo-assisted electrodeposition of NiCoSex electrocatalyst on bamboo shoots-like Si NP array backbones. We demonstrate its enhanced PEC performance with a photocurrent density of -37.5 mA/cm^2 at 0 V (vs. RHE) under simulated 100 mW/cm^2 (1 Sun) with an AM 1.5 G filter, which is the highest value reported for p-type Si photocathodes. The synergic effects of the excellent light harvesting of Si NP array core and the good optical transparency, as well as excellent electrocatalytic activity of NiCoSe$_x$ shell boost the production and utilization of photo-generated electrons. Furthermore, amorphous cobalt-iron hydroxide (CoFe-H) nanosheets by the electrodeposition can be simply integrated with $BiVO_4$ semiconductor to construct CoFe-H/$BiVO_4$ photoanodes that exhibit a significantly enhanced photocurrent density of 2.48 mA/cm^2 (at 1.23 V vs. RHE) and a much lower onset potential of 0.23 V (vs. RHE) for PEC-OER. Careful electrochemical and optical studies reveal that the improved OER kinetics and high-quality interface at the CoFe-H/$BiVO_4$ junction, as well as the excellent optical transparency of CoFe-H nanosheets, contribute to the high PEC performance.

Our work proves that the electrodepositon is a promising approach for rationally designing integrated electrocatalyst/semiconductor photoelectrodes for high performance solar-driven photoelectrochemical water splitting. We think high-quality electrocatalyst/semiconductor interface and excellent optical transparency of electrocatalysts result in the high PEC performance.

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Invited & Oral Lectures

Hydrothermal Liquefaction of Algae and Upgrading of Algae Based Bio-oil

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Microalgae are considered as a third generation biofuel, and have a notable advantage over other biomass in that they do not compete with food or cropland resources. The conversion of algal biomass into liquid fuels provides a long-term sustainable option for fuels production, which can be achieved in an environmentally compatible manner. Among the microalgal conversion methods, hydrothermal liquefaction, which can make full use of all components in the algae and avoid feedstock drying process, is viewed as one of the best conversion methods, especially for low-lipid microalgae.

Bio-oil derived from algae via the hydrothermal liquefaction processes has a higher oxygen content, lower stability and lower HHV than petroleum, Moreover, compared to bio-oil derived from lignocellulosic biomass, microalgal bio-oil contains significant amounts of nitrogen rooted from protein in microalgae, which is undesirable in the final product. Therefore, it requires further upgrading for subsequent practical application as transportation fuel. Because of the high diversity of compounds in the bio-oil, the upgrading of bio-oil is a complex reaction network; reprehensive reactions include cracking, decarbonylation, DCO, hydrocracking, hydrodeoxygenation (HDO), and hydrogenation. The new kind of non-noble, non-sulfide catalyst with low cost, simple preparation, high thermal stability and high deoxygenation activity would be a potential candidate for the upgrading process of algal bio-oil.

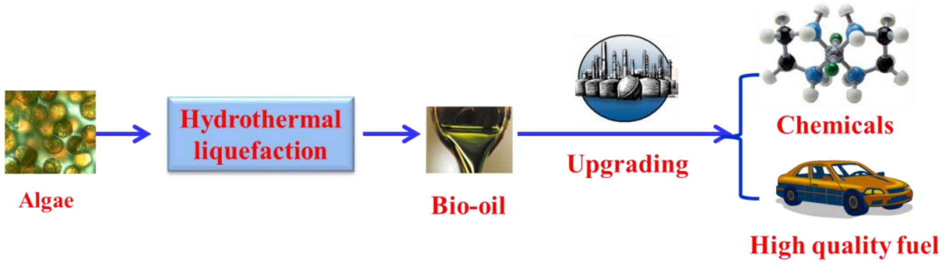

Fig 1 Hydrothermal liquefaction of algae and upgrading of algae based bio-oil

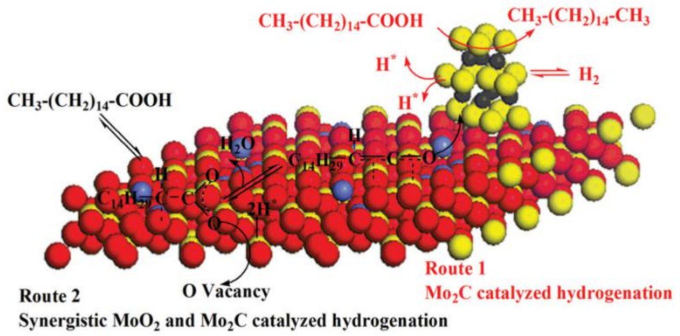

Fig 2. Scheme for bio-oil model compound HDO on the surface of the catalyst

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Synthesis of High-Density Jet Fuels Using Biomass-Derived Feedstocks

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High-density jet fuels, generally with density higher than 0.85 g/ml, can significantly improve the flight distance, flight speed and loading capacity of air vehicles. Catalytic conversion of inedible and renewable biomass to high quality jet fuel has attracted great attention as response to the concerns to sustainable development of energy sources and environmental protection. But current biomass-derived jet fuels composed by linear hydrocarbons have relative low density. Our group have synthesized several branched mono-cyclic, multi-cyclic and spiro hydrocarbons as potential candidate of high-density biofuel, using biomass-derived materials like turpentine, cyclic ketons, aromatic oxygenates and furfuryl alcohol as the feedstock [1-5]. Alkylation and condensation reactions were studied to construct cyclic structure to get high density and low freezing point, in which highly active and selective catalysts like hydrophobic mesoporous acidic resin and MOF encapsulating phosphotungstic acid have been developed. The hydrodeoxygenation of synthesized precursor was also studied to get final hydrocarbons, and an unexpected hydrogenated intramolecular cyclization was realized by tuning the composition of deoxygenation-hydrogenaiton bi-function catalyst, which provides a new way to further increase the density of biofuel. Moreover, spiro-fuels are synthesized from lignocellulose-derived cyclic ketones for the first time, which show not only higher density but also higher neat heat of combustion and lower freezing point compared with other biofuels synthesized using the same feedstock, and thus represent a new type of renewable high-density fuel attractive for practical applications.

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Design of Cu-Ni Alloy Catalyst for the In-situ Hydrogenation and Deoxygenation of Furfural and Unsaturated Fatty Acids without Hydrogen Used

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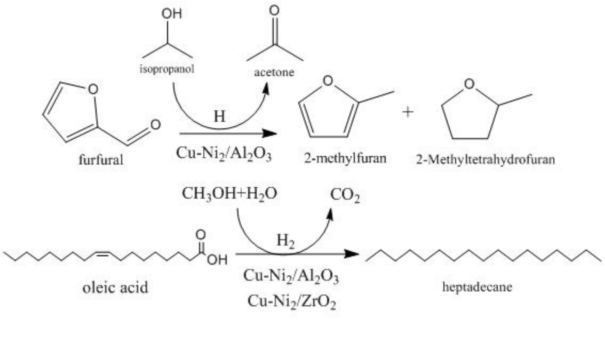
Biomass possess remarkable potential for solving energy problems such as the depletion of non-renewable sources and the greenhouse effect.[1] Furthermore, the upgrading of C=C and C=O bonds in the biomass is an important step for the synthesis of high value-added chemicals and bio-fuels.[2] In this work, supported bimetallic Cu-Ni catalysts were synthesized and studied for the in-situ hydrogenation and deoxygenation of furfural and oleic acid. In the two reaction systems, the supported bimetallic Cu-Ni catalysts exhibited a significant improvement in both activity and selectivity towards to the production of 2-methylfuran and heptadecane respectively in comparison to corresponding monometallic catalysts. The formation of Cu-Ni alloy are demonstrated by high-angle annular dark-field scanning transmission electron microscopy (HADDF-STEM), energy dispersive X-ray spectroscopy (EDS-mapping), X-ray diffraction (XRD) and temperature programmed reduction (TPR). A partially oxidized Cu in Cu-Ni alloy is revealed by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) following CO adsorption and X-ray photoelectron spectroscopy (XPS). Temperature programmed desorption of ethylene and propane (ethylene/propane-TPD) suggests that the addition of Cu to form Cu-Ni alloy greatly reduces the adsorption ability of C-C and C=C bonds. For the catalytic transfer hydrogenation of furfural, the highest yield of 2-methylfuran were achieved over Cu-Ni$_2$/Al$_2$O$_3$ with isopropanol as a hydrogen donor at 230 °C. For the conversion of oleic acid, supported Cu-Ni alloy exhibited a significant improvement in both activity and selectivity towards to the production of heptadecane in comparison to monometallic Cu and Ni based catalysts. In addition, supported Cu-Ni catalysts showed good reusability for the two reaction systems. These results indicated that the formation of the Cu-Ni alloy and a partially oxidized Cu leads to an enhanced activity.



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Selective Catalytic Transfer Hydrodeoxygenation of Oleic Acid over Bimetallic PdCu and Pdni Alloy Supported Catalysts for the Production of Diesel Like Hydrocarbons

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Fixed bed autoclave catalytic hydrodeoxygenation of a model monosaturated fatty acid to diesel range hydrocarbons over monometallic catalysts (Pd/C, Ni/C, Cu/C) and a wide compositional range of bimetallic $Pd_xNi_{(1-x)}/C$ and $Pd_xCu_{(1-x)}/C$ catalysts is reported. The surface and bulk properties of both monometallic and bimetallic catalysts are determined by an array of techniques including XPS, BET, ICP-OES, PXRD, CO Pulse Titration, TGA and HRTEM. The synthesized materials are used for catalytic hydrodeoxygenation of oleic acid using 1,2,3,4 – tetrahydronapthalene as a hydrogen donor molecule at 603 K with autogenous pressure. The results demonstrated that bimetallic $Pd_{75}Cu_{25}$ catalyst outperforms monometallic catalysts in terms of both activity and selectivity to diesel range (C_{17}+C_{18}) hydrocarbons. The promoting effect is understood by the capacity of Pd to dehydrogenate 1,2,3,4 – tetrahydronapthalene to naphthalene, leading to a much higher availability of molecular hydrogen for the catalytic reaction as compared to monometallic Ni and Cu catalysts. In short, alloying Pd with Cu and Ni lead to very active catalysts in terms of oleic acid conversion with substantial alteration in selectivity towards diesel products as compared to monometallic catalysts.

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One-pot Catalytic Conversion of Bagasse to Furfural Using Solid Acid Catalyst in Heterogeneous System

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A feasible approach was developed to produce furfural from bagasse via the new solid catalyst (tin-loaded and sulfonate ions-impregnated montmorillonite, Sn-MMT/SO_4^{2-}) in the DMC/water-NaCl biphasic system. This new catalysts were prepared by ion exchange and impregnation methods, which were characterized by XRD, SEM, TG-DTA, BET, Py-FTIR and NH_3-TPD. Sn-MMT/SO_4^{2-} was employed for the catalysis of bagasse into fufural in biphasic systems. The influences of the reaction time, temperature and catalyst amount on furfural yield were optimized by the Response surface methodology (RSM). Results showed that the Sn-MMT/SO_4^{2-} contained double acid sties of Lewis acids and Brosted acids, and exhibited the excellent catalytic performance for the conversion of bagasse into furfural. Under the optimum reaction conditions, 97.2% furfural was directly obtained from bagasse by a one-step process. The recyclability of the Sn-MMT/SO_4^{2-} catalyst was also discussed, and it was found that this catalyst was reused for 5 times without the loss of furfural yields.

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Gasification and Hydrogenation of Phenol in High-Temperature Water System

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Phenols are the major byproducts from non-catalytic gasification or liquefaction process. Studies of phenol gasification and hydrogenation provide a better understanding of tar elimination and waste energy utilization [1, 2]. Effects of supports on supercritical water gasification of phenol were investigated firstly. At an operating temperature of 500 °C and with a water density of 0.0867 $g \cdot cm^{-3}$, the carbon efficiencies of Ru supported by CeO_2, La_2O_3, Pr_4O_7, Y_2O_3, ZrO_2, Y_2O_3-ZrO_2 and MgO were obtained to be 83.1%, 79.4%, 78.5%, 78.3%, 76.2%, 73.3% and 65% respectively. Rare-earth oxide series showed the best activity [3]. Noble-metal-free NiCo/AC bimetal also shows high performance for gasification in supercritical water, the carbon efficiency can reach about 90% [4].

Meanwhile the Pd/W-Ce-AlO_x catalyst showed a high activity for the phenol hydrogenation and high selectivity at a moderate temperature (180 ^{o}C) in HTW. Nearly complete conversion of phenol was achieved within a short reaction time 60 min at 260 and 300 ^{o}C. At higher temperatures in HTW system, the changes of transport properties increase the dissociation of cyclohexanone from acidic sites, which future reacts with hydrogen to form cyclohexanol then to cyclohexane [5]. UiO-66, a kind of Metal-organic framework materials (MOFs) was also used as a support for nano-palladium particles (i.e., Pd-UiO-66), which was used in the catalytic hydrogenation of phenol in aqueous media. Pd-UiO-66 has high activity for aqueous phenol hydrogenation, with 100% conversion of phenol being achieved within 2 h at 120 ^{o}C, which is much higher than with the Pd-UiO-66-NH_2 catalyst [6]. The kinetic model of detail pathways to give the insight views was proposed.

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Lignin Depolymerization in Cooperative Ionic Liquid Pairs

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Lignin is the second abundant renewable carbon resource on the globe. It contains lots of useful functional groups such as phenolic hydroxyl, benzene ring, aldehyde and ester groups, which indicates that it has a great potential to be an excellent starting material for high quality biochemical and biofuel production [1-3]. In this study, we propose a novel and efficient process for lignin depolymerization in the presence of cooperative ionic liquid pairs (Figure 1), due to its tunable structure, excellent catalytic activity and char inhibition capability [4]. Under the optimized condition of 250 ˚C for 15 min, 66.7% of lignin is converted, giving 14.5 wt% of the volatile phenolic monomer yield and negligible char formation. The weakening of the ester bond and hydrogen bonds in the lignin molecular is considered to the main reason for the high conversion and phenolic monomer yield. At the same time, the in situ elimination of the carbocation and free radical by the ionic liquid additive, which would decrease the recondensation of the phenolic oligomer, is responsible for the no char formation. Furthermore, the volatile products were identified by GC-MS. The structure evolution of sugarcane lignin was also intensively investigated via the comparative characterization of the original and regenerated lignin using HSQC, ^{1}H-NMR, FT-IR, GPC and elemental analysis. It shows that all three structure units of lignin are effectively degraded in this process, whereas, H-lignin is found to be the most active. In additional, the cooperative IL shows good reusability, and a satisfactory lignin depolymerization performance was demonstrated even after the fifth run. And thus, the present work would be a good reference for further high-value utilization of lignin, the most abundant natural aromatic polymer on the globe.

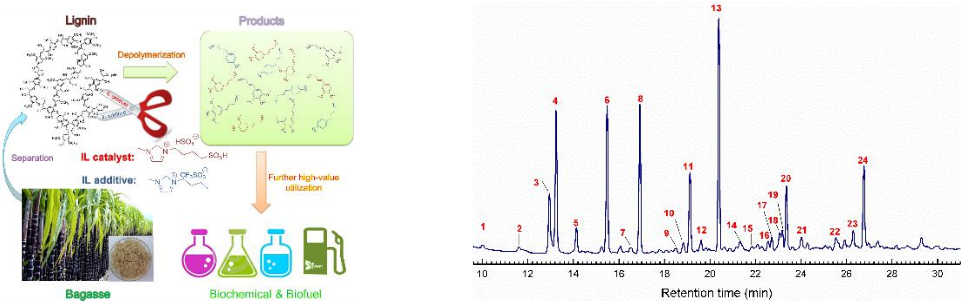

Figure 1 lignin depolymerization in cooperative IL pairs

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One-pot Conversion of Fructose to 5-Ethoxymethylfurfural by a Novel Sulfonated Nitrogen-containing Polymer Catalyst

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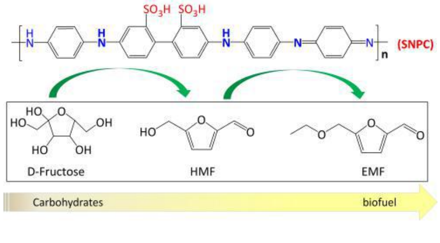
The production of liquid fuels from renewable biomass-based feedstock has attracted much attention because of the declining fossil resource and increasing energy demand.[1] Among others, 5-ethoxymethylfurfural (EMF) has been regarded as a promising biofuel alternative with high energy density (30.3 MJ· L^{-1}). Herein, we report an effective approach for the one-pot synthesis of EMF directly from fructose by a novel sulfonated nitrogen-containing polymer catalyst (SNPC).

The organocatalysts (poly(aniline-co-2,2'-benzidinedisulfonic acid)) were preparaed by oxidative copolymerization of aniline (AN) and 2,2'-benzidinedisulfonic acid (BDSA, n_{BDSA}/n_{AN} = 1/9~1/1) in aqueous ammonium persulfate (APS, $n_{APS}/n_{monomers}$ = 3/3~15/3) solution at 5 ^{o}C for 24 h, followed by heated in a dihydroxy acetone (DHA)-ethanol mixture at 140 ^{o}C for 2 h. The catalysts were deliberately characterized by means of SEM, elemental analysis, FITR, XPS, EPR, NH_3-TPD, and $^{1}H/^{31}P$ MAS NMR.[2] Their catalytic performance for EMF production from fructose were tested in ethanol-THF co-solvent (V/V = 3/1) under an autogenous pressure with continuous stirring. The as-prepared SNPC catalysts were highly active for the one-pot production of EMF from fructose via 5-hydroxymethylfurfural (HMF) intermediate, giving out a highest EMF yield of 70% over SNPC-0.25-11/3 catalyst. Ethyl levulinate (12%), formic acid (8%), and HMF (4%) were detected as the main by-products. The SNPC-0.25-11/3 catalyst showed stable catalytic activity for EMF formation for at least four runs without obvious loss of activity. We demonstrate that hydrogen bonds form between the ring-attached $–SO_3H$ group and the quinoid imine nitrogen (–N=) in the polymer chain, which confine the Brönsted acidity of the polymer catalysts. The H-bonded $–SO_3H$ species was the main active species for cascade reactions of dehydration and etherification from fructose and the suppression of side-reactions possibly promoted by strong Brönsted acids. This work represents a new strategy of oriented production of biofuel candidate with high product selectivity.



Scheme 1. Diagram illustrating the one-pot synthesis of EMF directly from fructose over SNPC catalyst

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Alcoholysis of Wheat Straw for Methyl Levulinate Production Catalysed by Copper Sulfate in a Biorefinery Concept

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The present study investigated the alcoholysis of wheat straw for methyl levulinate (ML) production in a biorefinery concept. The optimization of ML production from raw wheat straw was performed by using the response surface methodology, and a ML yield of 53.1mol% was obtained at 182 °C and 3.3 h with 0.64 g of copper sulfate as solid catalyst. To utilize the whole components of wheat straw, sodium hydroxide pretreatment and decanal pretreatment were conducted individually and in combination, and the mass balances of different processes of ML production were compared. Results showed that the molar yield of ML from pretreated wheat straw was not increased as expected. However, the byproducts including biosurfactant and lignin converted from hemicellulose and lignin components of wheat straw may increase the economics of the whole process. Moreover, copper sulfate showed higher catalytic activity on ML production from wheat straw, and the fresh and recycled copper sulfate were characterized by powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS), respectively. The results indicated that copper sulfate was a stable catalyst and can be reused more than five times.

Catalytic Conversion of Bio-based Levulinic Acid

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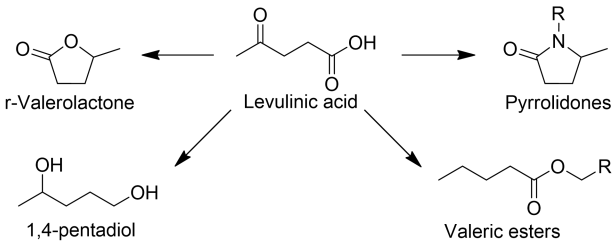
Unlike petroleum based raw materials, biomass feedstocks are highly functionalized and thermally unstable, thus making them very difficult to be refined in the gas phase.[1] So the upgrading is normally carried out in liquid phase reactions, wherein the heterogeneous metal catalysts are usually suffering from the irreversible deactivation problem caused by the leaching of active metal species into the solution. At the same time, the deactivation greatly impedes the utilization of a catalyst in industrial processes, in this sense, the catalyst stability is crucial to the economic and environmental sustainability of catalytic processes.

Catalytic conversion of LA into valued chemicals plays a key role in low carbon and sustainable biomass conversion, meanwhile, poses more challenge on the catalyst stability, due to the high activity or affinity of acid group toward the supported metal species under hydrothermal condition. To address this challenge, as shown in scheme 1, we fabricated chitosan derived Ru-Ni bimetallics catalyst in order mesoporous carbon, which gave high TOF valure (>2000 h-1) in the hydrogenation of LA intoγ-valerolactone within at least 15 runs.[2] Further, a tandem transformation of LA into valeric biofuel could be achieved over an encapsulated Co@HZSM-5.[3] The 1,4-pentanediol could be efficiently synthesized from LA in high selectivity over a copper based catalyst featuring strong metal-support interaction.[4a] We also interestingly found an alternative route to prepare pyrrolidone enabled by a carbon nanofilm coated Ni catalyst.[4b]



Scheme 1. Conversion of LA to chemicals and fuel additives.

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One-Pot Conversion of Jatropha Oil to Jet-Fuel over NiMo/MCM-41 Catalysts

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The rising concern about the energy and environmental problems effectively prompted research on renewable resources derived from biomass. Jatropha oil was served as one of promising plant-based feed stocks for future aviation biofuels, which had a unique research prospect.[1] In numerous studies, NiMo(S) catalysts have received a lot of attention on the conversion of bio-oil. However, most of these studies reported that C15~C18 were the main products, which had a poor freezing point and could not be used as jet fuel directly.[2] Here, we report Ni and Mo supported on Al/MCM-41, which have the multifunctions of deoxygenation, cracking and isomerization to transform Jatropha oil into aviation range hydrocarbons through a single process. The results suggested that Jatropha oil could been completely transformed on Ni/A, Mo/A, and NiMo/A catalysts. The yield of aviation range hydrocarbons could reach 63wt.% over 10%NiMo/A catalyst with appropriate molecular weight range (150~180), which was consistent with the 3# aviation fuel molecular weight of China. Bimetallic NiMo/A catalyst not only displayed significant improvement in the yield of jet fuel than monometallic Ni/A and Mo/A catalysts but also improved the ability of the catalyst to resist carbon deposition. Combined with RAMAN, XPS, H_2-TPR, TEM-MAPPING results, we concluded that there were a synergies effect between Ni and Mo. Furthermore, geometric features from bimetallic NiMo/A catalyst would lead to high jet fuel yield.

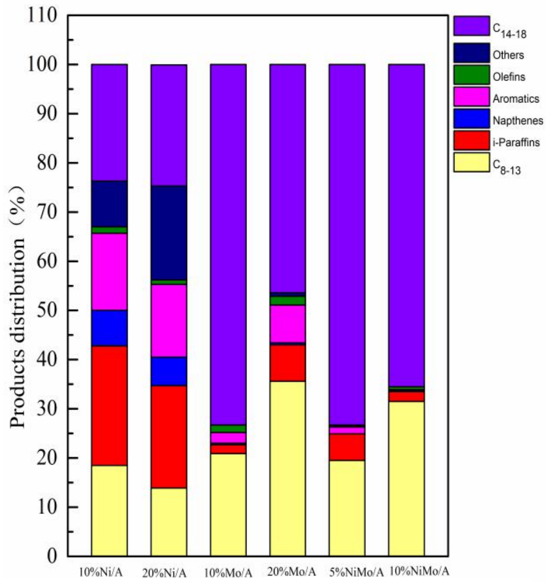

Fig.1 Product component distribution for different catalysts after reduction of 600°C

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Efficient Degradation of Lignin in Raw Wood via Pretreatment with Heteropoly Acids in γ-Valerolactone/Water

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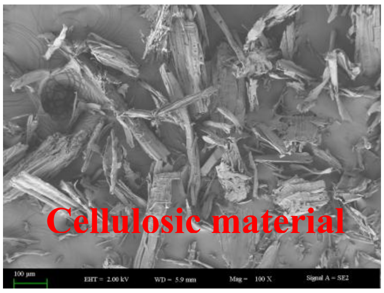
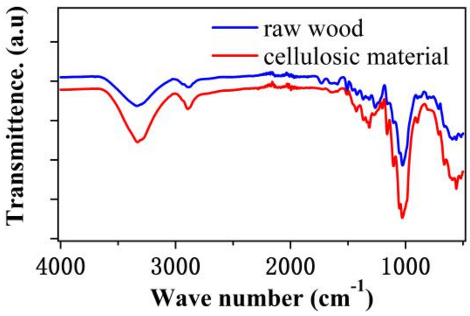
The degradation of lignin in raw wood is an important pretreatment process to liberate fibers or obtain cellulose-enriched materials. In previous studies, sulfuric acid (H_2SO_4) has been adopted as catalyst to degrade lignin in a mixture of γ-valerolactone (GVL) and water as green solvent. However, the polluting and corrosive nature of H_2SO_4, along with its negative effects on process equipment, make it unattractive for industrial applications. To overcome these disadvantages, we utilized heteropoly acids (HPAs) as substitutes for H_2SO_4. By optimizing catalyst concentration, reaction time and temperature, we obtained optimal lignin degradation conditions. SEM and FTIR measurements demonstrated the efficient lignin degradation ability of HPAs in the GVL/H_2O solvent, with negligible damage to cellulose and hemicelluloses. Furthermore, a detailed enzymatic hydrolysis study of the thus obtained cellulosic feedstock revealed its suitability for enzymatic digestion, with great potential as starting material for the production of sugar from biomass in future biorefinery applications.





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Continuous Catalytic Upgrading of Ethanol to N-Butanol over Cu-CeO2/AC Catalysts

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Bio-butanol has been considered as one of the most promising bio-fuels in future due to its similar properties as gasoline. In the present work,[1] Cu-CeO_2/AC (AC: activated carbon) catalysts with different molar ratios of Cu/Ce were prepared and evaluated in the continuous catalytic upgrading of ethanol to n-butanol under mild reaction conditions. As shown in Figure 1, the Cu–CeO_2/AC catalysts exhibited an average 45% ethanol conversion and up to 20% n-butanol yield that is the highest ever reported under the similar reaction conditions, which outperformed all other heterogeneous catalysts, such as Mg–Al mixed oxides, hydroxyapatites, Ni/Al_2O_3 and Cu/CeO_2 catalysts. This superior catalytic performance can be ascribed to the synergy of Cu, CeO_2 and the activated carbon support, in which the high dispersion of Cu metals (~7nm) was favourable for high ethanol conversion, while the presence of highly dispersive Ce species (~2nm) as basic sites was beneficial for the aldol condensation of acetaldehyde and drove the reaction equilibrium towards n-butanol production. Moreover, the good stability of these catalysts is attributed to the formation of a special structure of Cu metals and Ce species, in which Ce species partially covering Cu metals (in the case of low Ce loading) and further isolating Cu metals (in the case of high Ce loading). Therefore, the Cu–CeO_2/AC catalysts possess a great potential in future industrial n-butanol production.

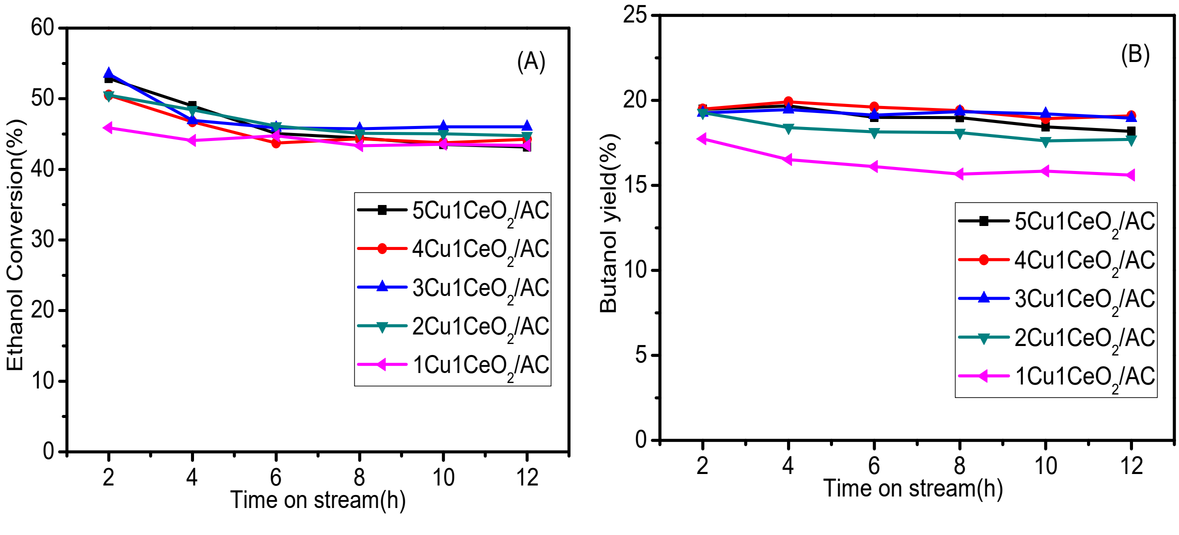

Figure 1. Ethanol conversion (A) and n-butanol yield (B) over Cu-CeO_2/AC catalysts with different Cu/Ce molar ratios. Reaction conditions: mass of catalyst, 1.0 g; T = 523 K, P =2 MPa (N_2), LHSV =4 ml/(h·gcat), N_2/ethanol(v/v) = 500:1.

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Selective CO_2 Adsorption on Oil-tea Shell Derived Porous Carbons

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CO_2 emissions will bring about global environmental problems[1]. Porous carbons derived from natural biomass have the potential to become industrial adsorbents for CO_2 adsorption in biogas and flue gas because of its low cost, availability in large quantity, and environment-friendly nature[2-3]. Our carbon precursor derived from agricultural waste oil-tea shell in Jiangxi province, The objective of the study is to develop efficient adsorbent for the selective separation of gas mixture pairs of CO_2/CH_4 CO_2/N_2 and CH_4/N_2, by optimizing the specific surface area and micropore volume of the carbons through adjusting the activation conditions including the ratio of oil-tea shell/KOH and carbonized temperature. The porous carbon adsorbents were characterized with several analytical instruments for their pore textural and physical properties. The adsorption properties of the carbons were studies by measuring the adsorption isotherms of CO_2, CH_4 and N_2, and calculating the ideal adsorbed solution theory (IAST) selectivity of the binary systems (CO_2/CH_4, CO_2/N_2 and CH_4/N_2). The porous carbon prepared from oil-tea shell exhibits a high CO_2 adsorption capacity up to 6.15 mmol/g at 273 K and 3.96 mmol/g at 298 K and 1 bar. The IAST selectivities at 298 K, 1 atm for equimolar mixture pairs of CO_2/CH_4, CO_2/N_2, CH_4/N_2 are 7.6, 62.7 and 5.7, respectively, which are much higher than that of many other sorbents [4-6]. This project has developed an efficient way for making cost effective adsorbents for CO_2 capture in flue gas and natural gas.

Table 1. Adsorption Properties of Oiltea Shell Porous Carbons

	CO_2 adsorption (@1bar, mmol/g)		CO_2/N_2	CO_2/CH_4	CH_4/N_2
			IAST selectivity		
Sample	273K	298K	(@1bar, 298k)		
OTS-1-550℃	4.13	2.8	62.7	7.6	5.7
OTS-2-550℃	4.64	3.19	44.6	6.2	5.3
OTS-1-650℃	5.33	3.62	26.4	4.3	5.5
OTS-2-650℃	6.15	3.96	23	3.9	5.1
OTS-2-750℃	5.88	3.56	14.7	2.8	4.9

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High Yield of Aromatic Alcohols from Catalytic Ethanolysis of kraft Lignin over Ni Supported La_2O_3/Al_2O_3

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This paper presents a single-step, environmentally friendly approach for efficient catalytic ethanolysis of kraft lignin, which was successfully conducted in ethanol system to give high-value aromatic alcohols over Ni supported La_2O_3/Al_2O_3 without external adding H_2. Different temperatures (250, 275 and 300 °C) and residence times (10-60 min) to investigate the effects of solvent and various reaction parameters on product distribution. GC–MS/FID, elemental analysis, GPC and ^1H-^{13}C HSQC NMR were employed for entire investigation the character of liquid products. It shows that low char yield and high lignin conversion was achieved. The results also indicate that the hydrocracking process was thermally controlled and catalysts showed significant influences condensation of ethanol and reduced the formation of oxygenic-chain compounds. Importantly, the yield of aromatic alcohols was more than 60 wt% and the undesired phenols or chars were undetected in products. Meanwhile, the whole catalytic processed out of external H_2 due to H_2 generation contributed to the hydrodeoxygenation of liquid components. Reusability tests of catalyst indicated that the phase transformation and agglomeration of support and carbon deposition were the reason for the loss of activity. Comparing with other common solvents, such as water, methanol and isopropanol, ethanol was the best effective solvent for this depolymerization process.

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1-Butyl-3-Methylimidazolium Hydrogen Sulfate Catalyzed In-Situ Transesterification of Nannochloropsis to Fatty Acid Methyl Esters

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1-Butyl-3-methylimidazolium hydrogen sulfate ([Bmim][HSO_4]) is used as a solvent and an acid catalyst for in-situ extractive transesterification of wet Nannochloropsis with methanol. The reaction is supposed to be a five-step process: (1) wet algae cell wall dissolves in ionic liquid at reaction temperatures; (2) hydrogen ions and sulfate ions release from the ionization of HSO_4^-. The hydrogen ions (H^+) act as catalysts for accelerating the reactive extraction of triglyceride from wet Nannochloropsis; (3) hydrogen ions and methanol molecules transfer from bulk to active site of cells without passing through cell wall that is dissolved by ionic liquid; (4) in-situ transesterification of lipid (mainly triglycerides) with methanol; and (5) products transfer from inside of algae cells to outside of cells. The crude biodiesel yield of [Bmim][HSO_4] catalyzed in-situ transesterification is about 95.28% at reaction temperature of 200 ^oC, reaction time of 30 min, mass ratio of [Bmim][HSO_4] to wet Nannochloropsis of 0.9:1, and a mass ratio of methanol to wet algae of 3:1. It decreases to 81.23% after [Bmim][HSO_4] is recycled for 4 times, which indicates that [Bmim][HSO_4] catalyzed in-situ transesterification is an economic approach for biodiesel production from wet algae.

Ethylenediamine Pretreatment Improves the Biomass Bioconversion

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Biomass is the largest renewable source on the earth, which can be converted to fuels, chemicals and biomaterials. Although the commercial utilization of biomass is a challenge due to the low oil price, the governments consider the bioconversion of biomass as important technical reserves and the Frontier exploration field. Our group are trying to promote the bioconversion of biomass on two aspects, development of the microbes catalyzing the conversion of biomass, and optimization of the conversion process. Here, a novel pretreatment method using ethylenediamine (EDA) was presented as a simple process to achieve high enzymatic digestibility of corn stover (CS) by heating the biomass–EDA mixture with high solid-to-liquid ratio at ambient pressure. EDA pretreatment improves the enzymatic digestibility of lignocellulosic biomass significantly, and the improvement was caused by the transformation of cellulose allomorph, lignin degradation and relocalization in EDA pretreatment. We evaluated the effect of the EDA pretreatment on the sugar release and fermentation. SF of EDA pretreated CS cause significant inhibition during enzymatic hydrolysis due to the solid-to-solid process. With low wash liquor concentrations, xylose consumption rate, cell viability and ethanol yield were maximally stimulated in fermentation without nutrient supplementary. Soluble lignins were found as the key composition for promoting sugars utilization and cell viability without nutrient supplementary. The dual effects of soluble materials on enzymatic hydrolysis and fermentation resulted in the reduction of ethanol yield as soluble materials increased in SSCF.

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A Novel Biofilm-Based Enzyme Mediator System Tailored in Escherichia Coli and Its Application in Producing Glucosamine from Chitin

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The process of food production has generated a large amount of by-products, most of which are still underuse. These food leftovers contain some useable substances of high value. Especially, if not treated properly, it can have a negative impact on the environment and create risks to human health. Among them, crustacean by-products are of great interest. Glucosamine (GlcN, 2-amino-2-deoxy-D-glucose) is one kind of hydrolyzed product from chitin, being widely used as herbal/dietary supplement, food preservative. It can also be used to treat osteoarthritis in humans. Chemical and enzymatic methods are widely used in producing GlcN, though limited by shortage of raw materials, high costs and bad influence on environments. In this paper, we used a novel metabolism of chitin from the Hyperthermophilic Archaeon Thermococcus kodakaraensis KOD1, which consists of three enzymes encoded as Tk-chiA, Tk-glmA and Tk-dac. We utilized Curli system and two pairs of peptides (SpyTag & SpyCatcher, SnoopTag & SnoopCatcher) to anchor three enzymes to the surface of biofilm one by one. The multi-enzyme system can catalyze chitin into GlcN with no additional add. Thus, we could achieve GlcN directly as an end product and reuse the enzyme system for several times, which can reduce the cost of production. The method provided us with a novel way to use chitin as raw materials and produce high-value product.

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Bioconversion of Methanol into Organic Acid by Model Microorganisms through Metabolic Engineering

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Methanol is increasingly becoming an attractive substrate for the production of different metabolites, due to the increment of annual production capacity and decrement of prices. However, there is a dearth of engineered microorganisms, which could convert methanol into value added chemicals. In this study, methanol metabolic module was introduced into prokaryotic Escherichia coli by employing the NAD-dependent methanol dehydrogenase from Bacillus methanolicus and ribulose monophosphate pathway from different donor organisms. The recombinant could simultaneously consume glucose and methanol during the anaerobic fermentation. Furthermore, the succinic acid yield can be increased from 0.90 g/g to 0.98 g/g. The level of NADH/NAD$^+$ ratio in vivo decreased from 0.67 to 0.45 in the recombinant, indicating that the efficiency of succinic acid synthesis further driven by methanol. However, methanol still cannot be used as the sole carbon source. Hence methylotrophic Saccharomyces cerevisiae was further investigated for achievement of direct methanol utilization. After successful integration of methanol oxidation pathway originated from Pichia pastoris into the chromosome of S. cerevisiae, the recombinant showed 1.04 g/L consumption of methanol and 3.13% increase of cell growth when using methanol as the sole carbon source. Moreover, 0.26 g/L of pyruvate was detected in the fermentation broth. This study offers a promising strategy for the achivement of chemicals production processes using methanol as an sole or auxiliary substrate.

Cells' Disruption and Directional Regulation of Hydrolysate of Microalgae During the Medium-Low Temperature Hydrothermal Hydrolysis Process

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Due to the complex structure of microalgae cells' wall, the wall disruption is a obstructive process for efficient energy utilization of microalgae biomass. To rapidly break the multi-layered three-dimensional structure of microalgae cell wall, the catalyst-free hydrothermal hydrolysis was studied. The microstructures of microalgae cells were analyzed by scanning electron microscopy and transmission electron microscopy. It was found that microalgae cell membrane was destroyed at 100 °C, while the cell wall loosed at 150 °C. The material inside the cells started to release after cell membrane destroyed but not the cell wall. With the reaction temperature and residence time increased, the particle size of microalgae cells decreased, the cells were destructed more severely, and the precipitation rate of internal organelles was increased. However, the ratio of substance that could be directly used for biogas fermentation in hydrolysate, such as reducing sugar, was limited due to side reactions that happened without catalyst. Therefore, formic acid was choosed to directional regulate the hydrolysate for the late fermentation. Under 3% diluted formic acid-assisted hydrothermal hydrolysis, the yield of reducing sugar in the hydrolysate was increased by 458% to 189.79 mg/g dry biomass compared to that in the hydrolysate without acid. Compared with the alkali-assisted hydrothermal hydrolysis, diluted formic could obviously inhibit the side reactions. And there was no HMF in hydrolysate. The hydrolysate obtained by low-content formic acid-assisted hydrothermal hydrolysis could match the need of the late biogas fermentation.

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High Cell Density Cultivation for Microbial Lipid Production from Various Low-Cost Biomass

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The current crisis of global warming is primarily attributed to CO2 production from excessive use of fossil fuels during recent decades, and has increased demand for renewable biofuels tremendously. Lipids are drawing considerable attention in relation to the production potential of biodiesel on the basis of their nontoxic, sustainable, and energy efficient proprieties. However, the high cost of microbial lipid produced by oleaginous microorganisms mainly stems from the high cost of glucose, which is estimated to be about 80% of the total medium cost. Therefore, considerable efforts have been directed toward minimizing the carbon source cost and finding new alternative carbon sources. In this report, several low-cost biomass including food-waste-based volatile fatty acids, lignocellulose-based hydrolysates, and methane derived from biogas were investigated for lipid production. After developing the culture modes and optimizing the culture conditions, both high lipid titer and productivity were achieved in high cell density cultures of different microorganisms using various carbon sources.

Catalytic Conversion of Biomass-Derived Polyols to Alkenes

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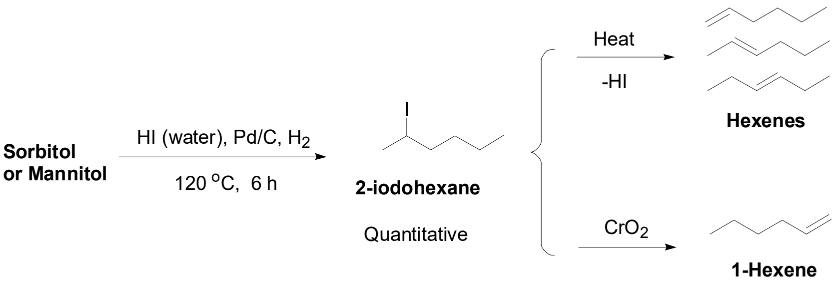
The depletion of fossil fuel reserves and detrimental environmental impacts associated with the use of fossil fuels have mandated the search for alternative, inexpensive, and renewable resources.[1] Biomass is a preferred candidate as an alternative source for both energy and chemicals due to its abundance and sustainability.[2] Polyols are readily available in large quantities derived from biomass resources, such as mannitol extracted from sea weed, sorbitol from cellulose hydrolysis, and glycerol as the side-product from biodiesel production. The selective conversion of polyols to value-added chemicals is an area of great importance. Their conversion typically requires a reduction step to remove the undesired hydroxyl groups. In this paper, we showed that with a multifunctional catalyst system mannitol and sorbitol can be quantitatively converted to 2-iodohexane, which can be further converted to hexenes. 1-hexene is a key co-monomer for the synthesis of linear low density polyethylene (LLDPE) and high density polyethylene (HDPE). The annual demand for 1-hexene is around 30 MT with an annual increase of 8% to 10%. Thus, a method to convert mannitol and sorbitol to 1-hexene with high selectivity under mild conditions would be highly desirable. To selectively obtain 1-hexene, a metal catalyst such as CrO2 can be used, which is still under investigation.[3] (Scheme 1)



Scheme 1. Sorbitol and Mannitol Conversion to Hexenes

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Pyrolysis of Pubescens Impregnated with $AlCl_3\cdot 6H_2O$ to Produce Phenols and Furfural

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Lignocellulosic biomass is increasingly and widely perceived as a renewable resource rather than an organic solid waste today, as it can be converted to various chemicals, biofuels, and solid biochar using modern process[1]. Pyrolysis, as a promising versatile route to convert biomass into valuable resources, has attracted growing interests[2]. $AlCl_3\cdot 6H_2O$, a Lewis acids, unlike $CrCl_2$ and $SnCl_4$, which is not environmentally and friendly, is cheap and nontoxic, and chosen as catalyst for pyrolysis of Pubescen.

We comparatively studied the Pyrolysis of Pubescens at 200°C with and without $AlCl_3\cdot 6H_2O$ impregnated. Products distribution in pyrolysis of raw stock and impregnated stocks were shown in Table 1. The conversion of impregnated stocks and the yields of liquid products at RT-200°C were much higher than those using raw stock, respectively.

In the pyrolysis from RT-200°C， in addition to carboxylic acids, furans and ketones, a variety of phenolics were obtained. With the increase amount of $AlCl_3\cdot 6H_2O$ added, the conversion of Pubecsens and the yield of liquid products increased monotonically. However, the constituents of bio-oil obtained from pyrolysis was still complex and there was no obvious main product. Besides the above monomers, oligomers with molecular weight less than 900 Da were obtained in all the above processes. The details of the variation of monomers and oligomers from breaking of the linkage of different kinds of chemical bonds will be discussed with the results of different characterizations of the liquid products and solid residues.

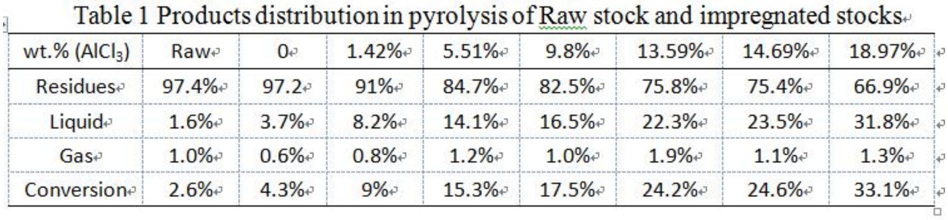

Table 1 Products distribution in pyrolysis of Raw stock and impregnated stocks

wt.% ($AlCl_3$)	Raw	0	1.42%	5.51%	9.8%	13.59%	14.69%	18.97%
Residues	97.4%	97.2	91%	84.7%	82.5%	75.8%	75.4%	66.9%
Liquid	1.6%	3.7%	8.2%	14.1%	16.5%	22.3%	23.5%	31.8%
Gas	1.0%	0.6%	0.8%	1.2%	1.0%	1.9%	1.1%	1.3%
Conversion	2.6%	4.3%	9%	15.3%	17.5%	24.2%	24.6%	33.1%

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Initial Cathode Potentials Determine Electron Transfer Pathway of Biocathodes Catalyzing CO_2 Reduction to CH_4

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Electromethanogensis (EM) is a promising energy conversion system for carbon dioxide reduction to methane. The key component of EM is the biocathode, on which microorganisms (mainly methanogens) can accept electrons and reduce carbon dioxide to methane. There are mainly two pathways for electron transfer between the cathode and microorganisms, i.e., direct electron transfer and indirect electron transfer via hydrogen [1]. To investigate the effects of applied potential on the electron transfer pathway of biocathodes, we started up two biocathodes under two different constant potentials of –0.7 V and –0.9 V vs Ag/AgCl, respectively. Carbon dioxide was used as the sole carbon source for all the biocathodes during the startup process. The results of cyclic voltammetry (CV) of the biocathodes cultivated at –0.7 V showed a typical sigmoidal shape with a midpoint potential of around –0.55 V, suggesting a direct electron transfer pathway, while no obvious sigmoidal shape of current was found in the CVs of the biocathodes cultivated at –0.9 V, suggesting different electron transfer pathways of the two biocathodes [2]. In addition, when the two biocathodes were operated at –0.5 V, the biocathodes started up at –0.7 V showed a current density of 186 mA/m^2, while the biocathodes started up at –0.9 V only generated a current density of 13 mA/m^2. Finally, microbial community analyses were conducted to investigate the difference of microbial communities on the biocathodes.

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Efficient Bioconversion of Lignocellulose into Biobutanol by Unique Solventogenic Clostridium Strains

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Butanol, a four-carbon primary alcohol, is not only an important intermediate chemical, but also considered as a promising next-generation liquid fuel. However, the high cost of traditional feedstocks restricts the development of industrial acetone-butanol-ethanol (ABE) fermentation. A lignocellulosic biomass-based route has been one of the thorough solutions for sustainable development of ABE fermentation. Solventogenic Clostridium species is one of the few microorganisms able to convert xylose and other pentoses to desirable products (ethanol, butanol and acetone), but on glucose/xylose mixtures, xylose is often left over at the end of the fermentation due to the low xylose utilization efficiency. Unless both glucose and xylose are completely utilized, the economics of converting lignocellulosic biomass into bio-based products are unfavorable. Moreover, direct butanol production from lignocellulose, known as consolidated bioprocessing (CBP), is widely recognized as the most attractive and potential strategy for converting cellulosic biomass to biofuel, since it offers outstanding potential for lower costs and higher efficiency. Therefore, unique solventogenic Clostridium strains with capabilities of efficient simultaneous utilization of glucose and xylose and even direct butanol production from lignocellulose through CBP are needed urgently.

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Production of 1,3-Propanediol: Co-Expression of Glycerol Dehydratase and 1,3-Propanediol Dehydrogenase Genes of Clostridium Perfringens and Biotransformation

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1,3-propanediol (1, 3-PD) is a promising versatile chemical compound which has a wide range of application in cosmetic, food, solvent, pharmaceutical industries. Especially, 1,3-PD is being used as a monomer for the synthesis of various polyesters and feedstock. With the increasing development of important applications of 1,3-PD, the demand for its production has been burgeoning around the world. 1,3-PD is usually produced by chemical method, and it also can be biosynthesized through two serialized glycerol's conversion by glycerol dehydratase (GDHt) and 1,3-propanediol dehydrogenase (PDOR). In view of various merits of biosynthesis of 1,3-PD, much focus has been attracted into the research of this area. In the present study, the dhaB gene encoding glycerol dehydratase and the dhaT gene encoding 1,3-propanediol dehydrogenase were cloned from an isolated strain of Clostridium perfringens, and then were co-expressed in E. coli BL21. The recombinant GDHt and PDOR were analyzed by bioinformatics methods based on the sequences of nucleotides and amino acids, respectively. Then, the recombinant enzymes were purified by nickel-chelate chromatography and characterized via pH and temperature optimization, substrate specificity assay and kinetic analysis. Subsequently, the biosynthesis conditions of 1,3-PD was optimized through biotransformation using the whole cell of BL21-dhaT-dhaB. Furthermore, based on the optimal conditions, the profile of 1,3-PD production was investigated via biotransformation. The bioconversion result showed that 1,3-PD production by whole cell of BL21-dhaT-dhaB was improved largely compared with the wild type strain of Clostridium perfringens. The result of this research may form a basis for the future work of 1,3-PD biologically synthesized.

Acknowledgement

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Integration of the First and Second Generation Bioethanol Technologies

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With growing concerns of environmental and social sustainability as well as energy security, conversion of biomass to biofuels, such as ethanol, has attracted much attention. The first generation bioethanol technology converts starch based (e.g. corn) or sugar based (e.g. sugar cane) biomass to ethanol through enzymatic saccharification and microbial fermentation, which has been fully developed and commercialized. However, the second generation bioethanol technology, which converts cellulosic biomass to ethanol via pretreatment followed by enzymatic hydrolysis and fermentation, has encountered problems, such as degradation products inhibition, low ethanol titer and low volumetric productivity.

This talk presents our research efforts in advancing the first and second generation bioethanol technologies. On most corn ethanol plants, only corn starch is converted to ethanol, while the corn kernel fiber, a cellulosic substrate, is unconverted. This cellulose stream accounts for around 4% of the total corn mass. Conversion of this stream to ethanol will not only result in cellulosic ethanol production but also improve bound starch conversion. We applied the second generation bioethanol technology to in situ convert corn cellulose in the dry-mill corn ethanol production process. Cellulases selection, cellulase dosage, pH, and process design etc. were optimized and 2%-3% lift in ethanol yield was seen. As for the corn stover conversion, degradation products inhibition and end-product inhibition impedes high solids loading process resulting in low sugar conversion at high solids loading. This talk will also presents our research work in converting corn stover to ethanol at high solid loadings and its economics.

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Multiscale Intensification of Lignocellulose Bioconversion: from Nanoscale to System Scale

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Lignocellulosic biomass has attracted great interest as a renewable feedstock to produce biofuels, materials and chemicals in recent decades in a conception of biorefining. However, because of the hierarchy nano- and ultrastructure of lignocellulose cell wall, as well as the heterogeneity of conversion system, the bioconversion efficiency of lignocellulose to fuel such as ethanol is still not high enough. Here, we have analyzed the multiscale effects of lignocellulose bioconversion with regards to the substrate structure and the conversion system. We propose that the key issues related to cell wall structure limiting cellulose bioconversion majorly include the supramolecular structure of cellulose, ultrastructure of cell wall, as well as the inhomogeneity and diversity of the lignocellulosic biomass at the nano-, meso- and macro-scales, respectively. For the bioconversion system, the multiscale effects at least involve the molecular recognition of cellulose by cellulase, the interaction between cellulose surface and cellulase components, the permeation and diffusion of enzymes in the pores of cell wall, the rigorous kinetic modeling of biomass pretreatment and enzymatic saccharification, the high-solid effect of cellulose hydrolysis and the process integration to minimize energy consumption and production cost, from the nano to system scales. Our recent research progress on the understanding the multiscale effects of biomass structure and the corresponding process intensification strategies will be introduced. In more details, we have studied how hemicellulose and lignin limit the accessibility of cellulose, and found that strong interactive effects exited between hemicelluloses and lignin. To accurately determine cellulose accessibility, we have developed a novel visualizable fusion protein probe to measure cellulose accessible surface area under wet state. We also have proposed a novel kinetic model (potential degree of reaction model) to accurately describe the apparent kinetics of biomass pretreatment. At the system-scale, an economic evaluation based on process simulation indicates that multi-products coproduction greatly reduce the production costs of cellulosic ethanol with more revenues. These works can serve as a step for improving the efficiency of the lignocellulose bioconversion.

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Developing Bacteria-Imprinted Polymer for Fast Bacterial Recognition

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As classical bacterial recognition methods based on isolation, growth and biochemical tests are time-consuming or laborious[1]~[2],developing new methods for fast and accurate recognition of bacterial species is necessary for meeting the increasing needs in biomass fermentation and other biotechnology applications. Thus, the emergence of a new and rapid bacterial recognition technology is required.

A novel bacteria-imprinted polymer (BIP) was fabricated for bacterial recognition with bacteria-templated surface-initiated atomic transfer radical polymerization (SI-ATRP). Charge distribution on bacterial outer surfaces was encoded into charge heterogeneous polymeric interfaces on BIPs as chemical imprints. Four bacterial strains were used as templates for fabricating corresponding BIPs. Through integrating with a microfluidic chip, the synthesized BIPs exhibited excellent performance for fast bacterial recognition. The competitive bacterial binding assay demonstrated that the fabricated BIP could preferentially capture GFP-Escherichia coli in the presence of excess Staphylococcus aureus with an average selectivity factor of 3.7 and the S. aureus templated-BIP was able to selectively bind S. aureus with an average selectivity factor of 8.6.

The adhesion forces between a single bacterial cell and BIPs were quantified with single-cell force spectroscopy, which indicated that the target bacteria can be preferentially captured due to stronger specific electrostatic interactions. This fabrication strategy can graft BIPs from different materials in situ, which allows the fabricated BIPs to be integrated with various test platforms. The advantage of this fabrication strategy also resides in its versatility, since a variety of charged monomers could be exploited as building blocks in SI-ATRP. Also, this fabrication strategy can be extended to recognize biomacromolecules or other biologic entities associated with distinctive charge distribution. We envision that this fabrication strategy could be a versatile platform technique for developing novel biological recognition materials.

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Isolation, Identification and Characterization of Lignin-Degrading Bacteria from Qinling, China

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Lignin is an aromatic heteropolymer forming a physical barrier and is a big challenge in biomass utilization. This paper firstly investigated lignin-degradation bacteria from rotten wood in Qinling Mountain. 19 potential strains were selected and ligninolytic enzyme activities were determined during 84 h. The strains which had higher enzymes activities were selected. Further the biodegradation of wheat straw lignin and alkali lignin was evaluated, which indicated Burkholderia sp. H1 had highest capability. It was confirmed that alkali lignin was depolymerized into small fragments by GPC and FE-SEM. Further, the degraded products were analyzed by using GC-MS. The total ion chromatograph (TIC) of products treated for 7 d showed the formation of aromatic compounds and important intermediate from lignin degradation. Interestingly, they were disappeared in 15 d while the aldehyde and ester compounds increased. The results suggest that the lignin-degrading bacteria are abundant in the rotten wood and strain H1 has high potential to break down lignin.

Fed-Batch Simultaneous Saccharification and Fermentation of Moderately Pretreated Corncobs Using the Industrial Flocculating Yeast for Bioethanol Production

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Corncobs are abundant agricultural residues and have been pretreated by various methods previously. Severe conditions of pretreatment are associated with high energy consumption, as well as low efficiency of simultaneous saccharification and fermentation (SSF). These two are critical factors in large-scale application of fuel ethanol. In the present study, we used moderate pretreatment conditions for corncobs to produce ethanol through simultaneous saccharification and fermentation using the industrial flocculating Saccharomyces cerevisiae 6525 FLO1. The corncobs structure features were analyzed by fourier transform infrared spectrum (FTIR) and scanning electron microscope (SEM). Two-step pretreatment and ethanol fermentation were optimized. The results suggested that dilute acid pretreated biomass followed by 2% (v/v) sodium hydroxide pretreatment with a solid/liquid ratio of 1:10 (w/v) increased the cellulose content of corncobs by 102% when compared to un-pretreated corncobs. Lignin content was reduced by 0.77%. Therewith, after simultaneous saccharification and fermentation process, final ethanol concentration was increased to 35.46 g/L. Optimal conditions of SSF by the strain was confirmed: 15% substrate loading, 35 FPU/g cellulase dosage and fed-batch mode. 66 g/L ethanol concentration was obtained under the optimal condition, which was 84.9% higher when compared to control. Hence, moderate pretreatment combined with flocculating S. cerevisiae in optimized SSF process suggest a favorable strategy for efficient bioethanol production.

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Development of CRISPR/Cas9 Tools for Multiplex Genome Engineering of Laboratory and Industrial Yeast Strains for Lignocellulosic Biomass Utilization

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Yeast has been developed as one of the most popular cell factories to produce a wide range of fuels, chemicals, and pharmaceutics from lignocellulosic biomass. Designing an optimal microbial cell factory often requires overexpression, knock-down, and knock-out of multiple gene targets. Unfortunately, such rewiring of cellular metabolism is often carried out sequentially and with low throughput. To address these challenges, we developed a combinatorial metabolic engineering strategy based on an orthogonal tri-functional CRISPR system that combines transcriptional activation, transcriptional interference, and gene deletion (CRISPR-AID). This strategy enabled the perturbation of the metabolic and regulatory networks in a modular, parallel, and high throughput manner. Then we demonstrated the application of CRISPR-AID not only to increase the production of β-carotene by 3-fold in a single step, but also to achieve 2.5-fold improvement in the display of an endoglucanase on the yeast surface by optimizing multiple metabolic engineering targets in a combinatorial manner.

In addition, we adapted the CRISPR/Cas9 system for multiplex genome engineering in industrial yeast strains. Compared with laboratory yeast strains, industrial yeast strains have the advantages of higher productivity and robustness under harsh industrial conditions. However, the presence of multiple copies of chromosomes in industrial yeast strains makes their genome engineering rather challenging and less efficient. Although successful in the engineering of laboratory yeast strains, the application of the CRISPR/Cas9 system in polyploid industrial yeast strain engineering is less explored. We developed an efficient CRISPR/Cas9 system for industrial yeast strain engineering by introducing double strand breaks to all copies of the chromosome. The engineered CRISPR/Cas9 system enabled us to simultaneously knock out four genes in a diploid industrial yeast strain (Ethanol Red, 8 alleles in total) and in a triploid industrial yeast strain (ATCC 4124, 12 alleles in total) in a single step with 100% efficiency.

Facile Synthesis of Pd-Loaded Lignin Porous Carbons in Molten Salt Media by Hydrothermal Carbonization Method

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A facile strategy in the fabrication of Pd-loaded lignin porous carbon was reported. In the present work, lignin/Pd NP composites were first prepared under microwave irradiation. Then Pd NP-loaded porous carbon was constructed successfully from the mixture of lignin/Pd composites and porogen salt LiCl via hydrothermal carbonization method at 240 °C and subsequently served as catalysts in the reduction reaction of p-nitrophenol by sodium borohydride. The salt template can be easily removed by only washing with deionized water. Full characterization was performed using TEM, SEM, BET and UV-vis. The Pd-loaded lignin porous carbon using LiCl as porogen exhibited an orderly appearance and it displayed a mesoporous structure in microscale with higher specific surface area and pore volume, which provided more attachment sites for the immobilization of Pd NPs. The striation of the single Pd NP indicates its crystalline structure. In addition, it exhibited more effective catalytic performances in the reduction of 4-NP to 4-AP. In this research, lignin wastes were fully reused as not only reducing agents and stabilizing agents, but also as a precursor to construct porous carbons as catalyst support of Pd NPs. It provides a new idea for the high value utilization of agricultural and forestry biomass.

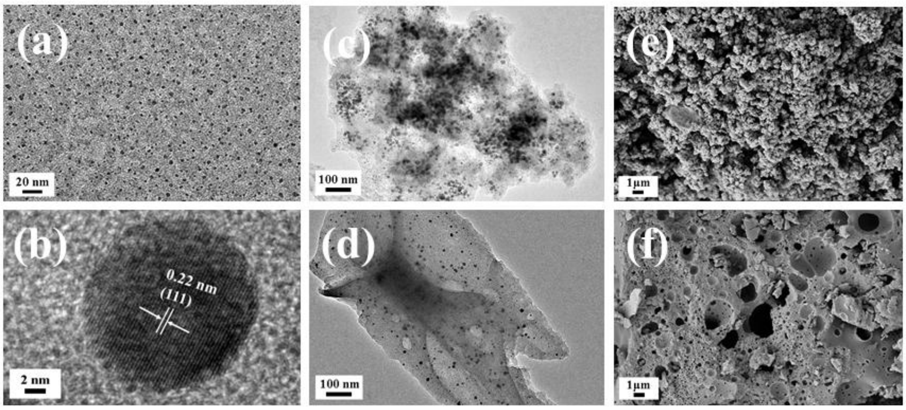

Fig. 1. TEM of (a) lignin/Pd NPs composites, (b) HRTEM result of a single Pd NP, (c) LigC-Pd and (d) LigC-Pd-LiCl. SEM of (e) LigC-Pd and (f) LigC-Pd-LiCl.

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Catalytic Hydrothermal Gasification of Microalgae over Ni/Zeolite: Influence of Support

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In this present study, Ni catalysts with different zeolite supports such as HY(Na_2O, 0.8%, 5%), Hβ, MCM-41(Si, 50%, 100%), SAPO-11, and HZSM-5(Si/Al, 50:1, 150:1, 170:1) were prepared by impregnation method. All these catalysts were screened for supercritical water gasification(SCWG) of a microalga-*Chlorella pyrenoidosa* under operating conditions of 430 °C, 60 min, ρ_{H_2O}= 0.162 g/cm^3, 200 wt.% Ni/zeolites in a batch reactor, to evaluate the influence of support on hydrogen gasification efficiency(HGE) and carbon gasification efficiency (CGE) and yield of each gaseous product fraction. Addition of Ni/zeolites can promote both CGE and HGE, and the higher the strong acid sites, the larger the CGE and HGE. With employing Ni/HY(Na_2O, 0.8%) which contains the highest amount of strong acid sites (0.132 mmol/g), the HGE and CGE are close to each other and can reach as high as 23.61 and 23.55%, respectively. This 23.61% CGE is even higher than those obtained with Ru/C, Pt/C, and Ir/C. Both the CGE and HGE increase with increasing the Si/Al molar ratio, particular as the Si/Al molar ratio increases from 150:1 to 170:1. The highest CGE and HGE of 19.24 and 25.53% was obtained at Si/Al molar ratio of 170:1, among which HGE is higher than those of obtained with HY(Na_2O, 0.8%). The main components in the gas-phase are typically of H_2, CH_4, CO, CO_2, C_2H_6, and C_3H_8. CO_2 was typically present in the highest amount. The yield of H_2 was increased about 4-5 times higher than that of produced without catalyst, among which Ni/HZSM-5(Si/Al=150:1) produced the highest H_2 yield of 3.61 mmol/g. CH_4 was the third largest fraction, which ranges from 0.63 to 1.16 mmol/g. The high total acid sites would accelerate the formation of coke deposition, resulting in catalyst deactivation.

Green Synthesis of Natural Benzaldehyde in Reactive Distillation with β-Cyclodextrin as Catalyst

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Nature benzaldehyde, the second largest flavor in the world, is a noteworthy flavour, because it can be widely used in food, beverages, cosmetics, and pharmaceutical industries etc. New technical process for nature benzaldehyde production has been presented with the alkaline hydrolysis reaction of cinnamaldehyde. The reason of choosing β-CD as the catalysts is break split-phase between two reactants. This technical process is the first to introduce reactive distillation to the production process of nature flavors, which can solve the defect of this process. In the present work, pilot plant experiments are completed to prove the feasibility of this new technical process. The results show that the high yield for nature benzaldehyde can be reached through the shorter residence time than the conventional process. The side reaction can be avoided effectively because the reaction product, acetaldehyde, is timely separated from the reaction zone. Meanwhile, the reactants ratio of water and cinnamaldehyde for the new technical process can be sharply reduced compared with the conventional process. ASPEN Plus v8.4 is used as the process simulation tool. A non-equilibrium-stage model of the reactive distillation for nature flavors is developed, which is validated using experimental data. Additionally, an analysis has been accomplished through computer simulation calculations to determine the effects of key design and operating variables on column performance.

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Pyrolysis Behaviours of Chemi-mechanical Pulping Spent Liquor and its Main Components

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Biomass thermochemical conversion technology is rapidly developing and updating, and is now considered to be an attractive way to produce liquid fuels and value-added chemicals in this century. Pulping spent liquor is a by-product from commercial pulping processes of papermaking industry. It is a complex mixture containing both inorganic chemicals (mainly soluble salt ions) and organic materials from fibrous plants (hemicelluloses, lignin and derivatives thereof). Pulping spent liquor pyrolysis or gasification technology has been suggested as a cheaper alternative for the traditional alkali recovery technology. The multiple components of the pulping waste make its pyrolysis process very complex. In-depth investigation of pulping spent pyrolysis based on its major components are urgently needed.

To this end, the three main organic components, i.e. alkali lignin (AL), lignin-carbohydrate complexes (LCC), and polysaccharide (PLS) form eucalyptus alkaline peroxide mechanical pulp (APMP) spent liquor were isolated and characterized. The pyrolysis characteristics of the three major components as well as the APMP spent liquor solid (ASLS) were then investigated and compared by TG-FTIR and amplifying experiments in a tubular furnace. The distributions of pyrolysis products, the effect of pyrolysis temperature, the impacts and contributions of each single component during pyrolysis were discussed in depth. It was found that the liquid product during ASLS pyrolysis was mainly attributed to AL, while the gases and char were mostly affected by PLS. The hydrocarbons released during ASLS pyrolysis at low temperature mainly came from AL and LCC. In addition, removing PLS from spent liquor resulting in the reduction of CO_2 in the pyrolysis of the waste solids. As for the organic chemicals in the liquid product, AL pyrolysis produced the largest amount of aromatics, and LCC and PLS mainly contributed to heterocyclic compounds, ketones, furans and acids etc.

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Potential Role of Biochar Amendment in Paddy Soil in Combating Climate Change

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Elevated global temperatures and increased concentrations of carbon dioxide (CO_2) in the atmosphere associated with climate change will exert profound effects on rice cropping systems, particularly on their greenhouse gas emitting potential. Incorporating biochar into paddy soil has been shown previously to reduce CH_4 and N_2O emission from paddy rice under ambient temperature and CO_2. We examined the effect of rice straw-derived biochar (RSB) on CH_4 and N_2O emission from paddy soil under elevated temperature and CO_2 concentrations expected in the future. Adding RSB to paddy soil reduced CH_4 emission under ambient conditions (BC) and significantly reduced emissions by 39.5% (ranging from 185.4 mg kg^{-1} dws $season^{-1}$ to 112.2 mg kg^{-1} dws $season^{-1}$) under simultaneously elevated temperature and CO_2. Reduced CH_4 release was mainly attributed to the decreased activity of methanogens along with the increased CH_4 oxidation activity and *pmoA* gene abundance of methanotrophs. However， elevated CO_2 and elevated temperature have antagonistic effects on N_2O emission from paddy soil. The amendment of RSB to paddy soil significantly increased N_2O emission under ambient CO_2 or ambient temperature or elevated CO_2 (ranging from -91 ~ -32 μg kg^{-1} dws $season^{-1}$ to 141 ~ 249 μg kg^{-1} dws $season^{-1}$). Increased N_2O emission was supposed to be resulted from the pathways of nitrification and dissimilatory nitrate reduction to ammonium enhancement by RSB amendment associated with increased soil C/N and pH in paddy soil. However, RSB amendment brought about 38.2% decline in global warming potential of CH_4 and N_2O under elevated CO_2 and temperature. Our findings highlight the valuable services of biochar amendment for potent greenhouse gas control from paddy soil in a future that will be shaped by climate change.

Microwave-Assisted Pyrolysis of Lignocellulosic Biomass Coupled with Reforming Enabled by Activated Carbon for the Production of Hydrogen-Rich Syngas

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In this study, microwave-assisted pyrolysis of biomass (MAPB) coupled with reforming enabled by activated carbon (REAC) was proposed for the production of hydrogen-rich syngas under mild operating conditions. The conventional biomass pyrolysis and the reforming of its bio-oil and gaseous fraction were also conducted. The bio-oil yield via microwave-assisted pyrolysis is lower than that of conventional pyrolysis. Through further reforming, the bio-oil yield dropped to below 3.0 wt.% and the yield of gas products increased accordingly. It was found that MAPB coupled with REAC showed high H_2 selectivity. The maximum H_2 fraction in gas product reached 55 vol.% for the microwave-assisted pyrolysis of bamboo coupled with reforming in the presence of activated carbon. It was found that activated carbon created a reducing environment favoring deoxidation reaction during the course of reforming; microwave irradiation enhanced the cracking reaction and subsequently resulted in the formation of H_2-rich syngas. The MAPB-REAC showed a high overall energy-conversion efficiency and enabled has been proved in this study as a potential approach for the conversion of biomass into hydrogen-rich syngas.

Catalytic Transfer Hydrogenation of Cinnamaldehyde into Cinnamyl Alcohol over Co-Re/TiO_2 Bimetallic Catalyst

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Selective hydrogenation of cinnamaldehyde (CAL) to cinnamyl alcohol (COL) has attracted much attention in recent years since COL is widely used in the synthesis of various fine chemicalsare and pharmaceuticals[1-4]. Compared with hydrogenation reactions involving molecular hydrogen (H_2), transfer hydrogenation is much safer and easier to handle since. In this study, we attempt to develop Co-Re/TiO_2 bimetallic catalyst for selective hydrogenation of CAL to COL using formic acid (FA) as hydrogen source.

As is shown in Figure 1, the Co-Re/TiO_2 catalyst with 1:1 molar ratio of Co/Re exhibited the highest yield of COL. The yield of COL decreased either increasing the Co/Re ratio to 1:0 or decreasing to 0:1. These results clearly demonstrate that Co and Re have synergistic effect, which causes electron density of carboxylic cardon atom in CAL to change, on COL yield. A number of cheap chemicals were used as hydrogen donors (Figure 2), FA being the most representative, which can not only provide high throughput of hydrogen atoms, but also avoid the contamination of products by releasing the CO_2 into gas phase. By further optimization of reaction conditions, a highest COL yield of 88% was obtained when using formic acid as hydrogen source and no obvious deactivation of the Co-Re/TiO2 catalyst was observed after using 5 times.

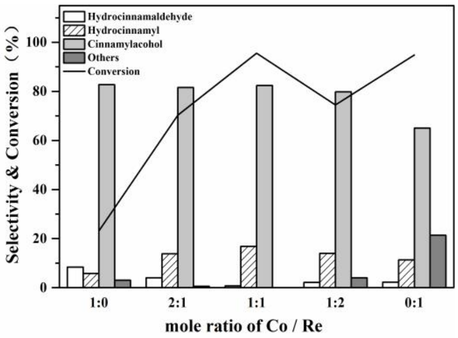

Figure 1. Effect of different molar ratio of Co/Re for cinnamaldehyde hydrogenation. Reaction conditions:80 mg cat, 160 ºC

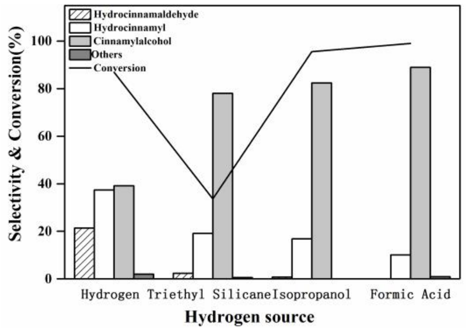

Figure 2. Effect of hydrogen source for cinnamaldehyde hydrogenation over Co-Re/TiO_2. Reaction conditions:80 mg cat.

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Genomic Analysis on the Galactose-Utilizing Clostridium Species Reveals Their Potential in Converting Marine Biomass into Biobutanol

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The sustainable biofuels, widely considered as an attractive alternative for the fossil fuels, can be generated by utilizing various biomass from the environment. Marine biomass, such as algal biomass, is regarded as another potential renewable source for biofuels conversion due to its abundant fermentable sugars (e.g., galactose). Previous studies focused on the biofuels production enhancement from different Clostridium species; however, there has been limited investigation on the metabolic pathway of utilizing galactose for biofuels production via the whole genomic comparison and evolutional analysis of various Clostridial strains.

Two galactose-utilizing Clostridial strains were achieved and identified to be Clostridium acetobutylicum strain WA and C. beijerinckii strain WB. During the batch fermentation, strain WA could generate up to 16.98 g/L butanol when using 60 g/L galactose as the sole carbon substrate, while strain WB was able to produce 12.47 g/L butanol but neglectable ethanol. Via the genomic sequencing of these two strains, the whole genome sequences together with the relevant protein prediction were compared with other 33 Clostridium species to reveal a clear genome profile based upon various genomic features. Among them, five representative strains, including C. beijerinckii NCIMB14988, C. diolis DSM 15410, C. pasteurianum BC1, strain WA and WB, were further discussed to demonstrate the main differences among their respective metabolic pathways, especially in the carbohydrate metabolism. Beside butanol, the metabolic pathway of other potential products, e.g., 1,3-propanediol and riboflavin, using marine biomass were also reconstructed.

The determination of biofuels production by both strains WA and WB as well as the genomic comparisons with other typical Clostridium species involved in various metabolic pathways further extend the current understanding of their potential capability of marine biomass utilization and also provide a systematic investigation on the relationship between this genus and bioenergy conversion.

Investigation of Char Under Different Heating Conditions of Stepwise Pyrolysis

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Stepwise pyrolysis with one pretreatment (torrefaction, carbonization) at low temperature and one main pyrolysis process at high temperature, is an important utilization of biomass. This study aims to investigate the effects of heating conditions on char production characteristics during two-stage stepwise pyrolysis. Schima wood, xylan, cellulose and milled wood lignin (MWL) were subjected to a tube furnace. The feedstocks were first pyrolyzed at 260 to 380°C for 60min and then pyrolyzed at 530 to 1028°C for 20min. Cumulated char yield and char reactivity were determined. The results showed that the existence of the first stage pyrolysis had significant effect on yield and reactivity of char produced from stepwise pyrolysis. Higher pretreatment temperature produced char with a higher yield in a fast stepwise pyrolysis while the pretreatment showed negligible effect on char yield in slow stepwise pyrolysis. It should be noted that this effect worked only when final temperature was higher than 530°C, and became more obvious as temperature raised. This proves char formation in pyrolysis is a complex joint effect of a number of parallel and competing reaction routes. By employing stepwise pyrolysis and different heating conditions, it is possible to achieve more desirable char production.

Molecular Representation Model of Petroleum Fractions:a Review

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Nowadays the refining industry is facing the decreasing of crude oil quality and the rising demand of light fuels, while the refining environmental problems are getting more and more concerns. To solve these problems and improve the oil processing efficiency, it is necessary to understand petroleum components, product properties and transformation process at the molecular level, and establish the process simulation and optimization model on the molecular scale. To fulfill this, molecular representation of petroleum fractions is the first step. However, conventional modelling methods using a pseudo-component (lumped components) cannot provide the detailed molecule information. It is necessary to develop a more detailed molecular representation model. In this review, the existing molecular representation models are classified according to the classification criteria of deterministic and stochastic methods. The modeling method and evolution of structure oriented lumping (SOL) approach[1-2], molecular type homologous series (MTHS) matrix method[3-5], stochastic reconstruction (SR) method[6-7], and stochastic reconstruction-entropy maximization (SR-EM) method[8-9] are introduced in detail, as well as several other referential approaches[10-11]. The advantages and disadvantages, wide scopes and limitations of these methods are discussed and compared, according to the range and characteristics of petroleum fractions required for representation. The opportunities and challenges for the future development of this field are also prospected.

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Selective Separation of Value-Added Bioactive Compounds Using Ionic Solution

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Natural bioactive compounds are very important resources of drugs and functional foods, but the coexistence of many structurally-related compounds makes the separation and production of specific value-added bioactive compounds very challenging. The extensively applied chromatography methods suffer from large solvent/energy consumption, low capacity and high cost, and the extractive separation has been strongly restricted by the trade-off between thermodynamic efficiency and kinetic performance. To address these problems, the authors developed diverse aqueous or non-aqueous ionic solutions as powerful medium for the selective separation of value-added bioactive compounds. These ionic solutions consist of common molecular solvent and a small amount of ionic liquids, and integrate strong H-bond basicity, tunable hydrophilicity/hydrophobicity, low viscosity, low cost, self-assembly microstructure, etc. Validated by the separation of different bioactive compounds such as tocopherols and ascorbic acids, liquid-liquid extraction processes using these ionic solutions achieved many desired characteristics including large selectivity, high capacity, good mass transfer efficiency, and inexpensive solvent. The trade-off between thermodynamics and kinetics were broke, along with more acceptable economy. Insights into the separation mechanism were given at a molecular level through both simulation and experimental approaches. As a result, the proposed ionic solution-mediated extractions provide promising opportunities for the selective separation of value-added bioactive compounds.

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Xylan Capped Au-Ag Nanoalloy for Surface-Enhanced Raman Scattering

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Au-Ag nanoalloys were green synthesized by using xylan as reducing, and then capped by xylan. Different conditions were engaged to prepare Au-Ag nanoalloys by tuning the mass ratios of nanometal precursors and their addition sequencing. UV-vis, XRD, XPS, particle size analysis, and TEM were used to characterize Au-Ag nanoalloys. UV-vis results reveal that surface plasmon resonance bands of Au-Ag nanoalloys shifted to low wavelength compared with Au nanoparticle. Particle size analysis and TEM results show that the major size of Au-Ag nanoalloys lied around 40 nm. Compared with Au nanoparticles and Ag nanoparticles, surface-enhanced raman scattering (SERS) activities of Au-Ag nanoalloys were higher efficiency for the sake of synergistic effect between Au and Ag. The Au-Ag nanoalloy could sensitively detected 4-mercaptobenzoic acid with linear detection range (2 μM- 0.2 μM) and low concentration of sudan I at 1 nM, which was stable to the corrosion of H_2O_2. This study provides a new way for high value utilization of biomass.

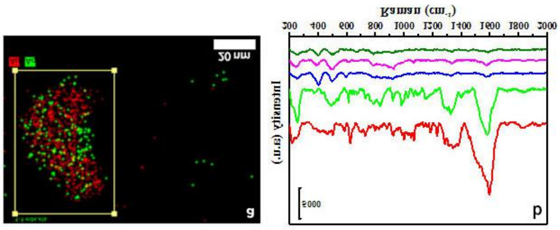

Fig.1. (a) HAADF images of Au-Ag nanoalloys, (b) Raman detection of different concentration of sudan I

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Preparation of Chemical Sunscreen/Lignosulfonate Capsules via One-Step Ultrasound Cavitation Method

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Uncomfortable physical sunscreens and unstable chemical sunscreens not only threaten skin health, but also burden the environmental problem. People are trying to find alternative natural sunscreens. Most of the plant extractives can only absorb ultraviolet radiation in UVB area. Small kinds of extractives such as chlorogetic acid are both effective in UVA and UVA areas and usually very expensive. In addition, these extractives are mostly small molecules and their photo stabilities are still poor. Lignin is the second most abundant component and unique aromatic polymer in the plants. Basic phenylpropanoid units, conjugated double bonds and carbonyl groups and introduced phenolic hydroxyl groups endow lignin excellent UV-blocking and antioxidant properties. Lignin is thus developed as natural macromolecular broad spectrum UV blocker.[1] However, the sunscreen performance of creams containing lignin cannot meet daily request. The deep color of industrial lignin is also the obstacle for its marketing.[2] Therefore, only hydrophilic industrial lignin, lignosulfonate, is used as surfactant in skin care products, and the addition is usually less than 0.3 wt%. In this work, chemical sunscreen/lignosulfonate capsules with light color, excellent UV-blocking property and good photo stability are prepared by one-step ultrasound cavitation method. The effects of ultrasound power and time on the structure and size of capsules are also investigated. By adjusting the ratio of chemical sunscreen and lignosulfonate, the synergistic effect between them is fully inspired. The UV absorbance of capsules is much better than that of lignosulfonate and free chemical sunscreens under same addition. The sun prefect factor (SPF) values of creams containing new prepared capsules can maintain 10 hours. Also, there is no obvious leakage during application and these capsules have good biocompatibility.

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Conversion of Glucose into 5-Hydroxymethylfurfural Catalyzed by Heteropolyacid-Based Ionic Hybrids

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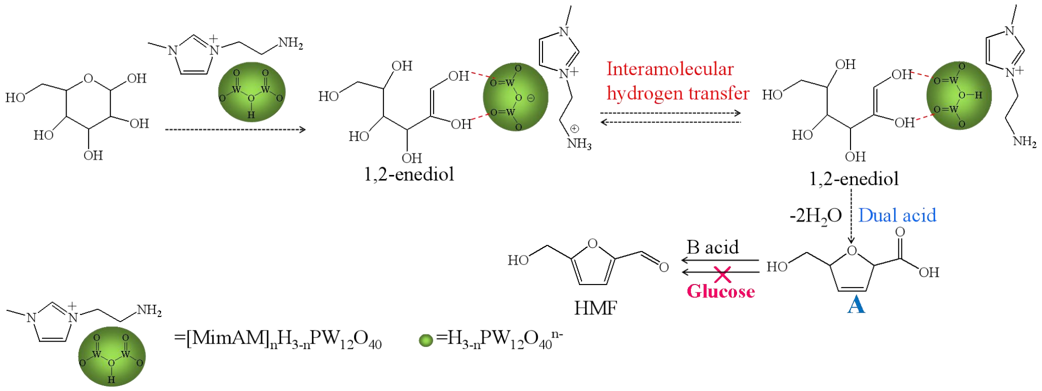
Design of stable acid-base bifunctional heterogeneous catalysts has become crucial for efficient catalytic conversion of renewable biomass to high value-added chemicals. Heteropolyacids (HPAs) and ionic liquids are of great interest in view of their unique tunable structures and suitable acidity. Recently HPA-based ionic hybrids were studied extensively as the catalysts for various heterogeneous reactions. [1,2] However, there are little reports on acid-base bifunctional HPA-based ionic hybrid catalysts for heterogeneous glucose dehydration to HMF.

In this work, we prepared a series of acid-base bifunctional ionic hybrid catalysts $[MimAM]_nH_{3-n}PW_{12}O_{40}$ (n = 1-3) by ion exchange method using amino-functionalized imidazolium ionic liquid and $H_3PW_{12}O_{40}$ as precursors. The introduction of ionic liquid resulted in a varied Lewis-Brønsted acidity for $[MimAM]_nH_{3-n}PW_{12}O_{40}$. The synergistic effect of dual acidic properties endowed $[MimAM]H_2PW_{12}O_{40}$ more efficiency for glucose dehydration in $THF/H_2O/NaCl$ with 53.9% HMF yield. The kinetic behavior suggested that the dehydration of glucose to HMF over $[MimAM]H_2PW$ might undergo a mechanism without fructose as a metastable intermediate. Thus, a unique interamolecular hydrogen transfer mechanism (Scheme 1) was proposed to understand the efficient heterogeneous catalytic performances. The heteropoly anion plays a dominant role for glucose dehydration and stabilization of the key intermediate 1,2-enediol in the reaction pathway, and the amine group plays an auxiliary role which facilitates the dehydration process through interamolecular hydrogen transfer.



The Scheme 1.   proposed intramolecular hydrogen transfer process for heterogeneous glucose dehydration to HMF over $[MimAM]_nH_{3-n}PW_{12}O_{40}$.

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Torrefaction Performance of Waste Biomass and Its Correlation with Torrefaction Indexes

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Weight loss has been considered as an important indicator of torrefaction severity in describing the performance of this thermal pretreatment process. The present study is intended to establish the correlation of torrefaction performance and severity. Three different biomass wastes, namely, coffee ground, Chinese medicine residue, and microalga residue, are torrefied in nitrogen at temperature ranges of 200-300 ºC for 15-60 min. By introducing a torrefaction severity index (TSI) in terms of the weight loss of biomass, the results indicate that TSI can correlate the properties of upgraded biomass well. However, for certain properties such as the enhancement factor of higher hearing value, decarbonization, and atomic O/C and H/C ratios, the difference between the two lignocellulosic wastes and the microalgal wastes is exhibited, stemming from the intrinsic difference of components between the wastes. Meanwhile, a new parameter termed upgrading performance is introduced to explore the energy efficiency or performance of biomass torrefaction where TSI is also considered. It is found that the upgrading performance has a trend to decrease when TSI increases, suggesting that biomass torrefied with higher severity has a higher energy efficiency in the reaction system.

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Enhancing Bioremediation of Cadmium With a Complex of Immobilized Chlorella sp. On Biochar Pellets

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Viable microalgae is widely used in the bioremediation of cadmium (Cd), however, it is difficult to harvest the biomass and to keep the viability of microalgae in the solution with high Cd concentration. To solve these problems, a complex of immobilized *Chlorella* sp. on biochar pellets was firstly proposed to be applied in the bioremediation of Cd. In order to optimize the immobilization efficiency as well as the Cd uptake efficiency, the materials of the pellet, the culture stage of *Chlorella* sp.(exponential growth, stationary and decline phase), and the light intensity (0-280 μmol m^{-2} s^{-1}) in the incorporation process were investigated with an initial Cd concentration of 10 mg L^{-1}. Water hyacinth leaf biochar pellet (WHLBP) was found to be the optimal carrier. Cells in exponential growth phase showed a maximum bioaccumulation capacity, 33.9% of the total Cd ions removed was taken in intracellularly under the illumination of 280 μmol m^{-2} s^{-1}, higher than most previous value reported on this species. The amount of loosely bound EPS was roughly negatively related to the immobilization efficiency. The maximum immobilization efficiency of 91.1% was achieved with algae in stationary phase without illumination. However, the highest total Cd uptake efficiency of 81.7% was obtained with immobilized algae in stationary phase under the illumination of 119 μmol m^{-2} s^{-1}, which indicates other related factors such as the soluble EPS composition should be taken into account in the remediation process. WHLBP kept good cell immobilization efficiency (≥80%) after third round of recovery, and the cells collected after biosorption can reproduce themselves in fresh media under favorable growth conditions.

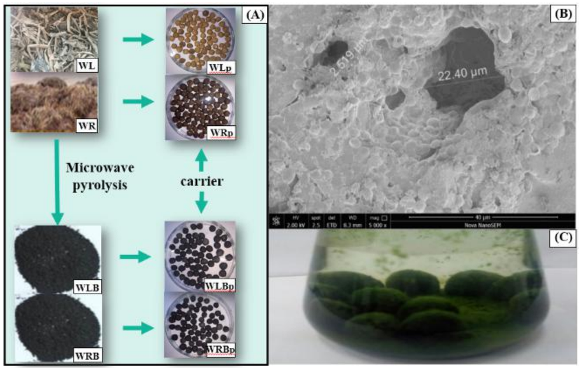

Fig.1 The characterization of the complex of the immobilized *Chlorella* sp. on biochar pellets

Hydrothermal Conversion of Biomass Wastes to Materials and Chemicals

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The main components of biomass wastes are cellulose, hemicellulose, and lignin. It could be converted to high-value added materials and chemicals by hydrothermal conversion under the controlling conditions. Here, we reviewed the recent progress of hydrothermal conversion of biomass wastes to materials and chemicals, especially the updated progress in Biomass Wastes Utilization Group, Fudan University, including: 1) Hydrothermal conversion of biomass wastes to xylose, lactic acid, phenolics, and so on, 2) Separation of bio-based chemicals (organic acid, phenolics, and sugar) by using membrane separation and column chromatography, 3) Anaerobic digestion of liquid part from hydrothermal conversion of biomass after separation of chemicals into methane, and 4) Controlled conversion of solid products of hydrothermal conversion of biomass wastes to functionalized carbon materials. The cellulose and hemicellulose components of rice straw were converted to lactic acid with NiO nanoparticle as catalyst. The lignin components were converted to phenolic compounds with CuZnAl as catalyst. The acetic acid, phenol, and sugar were efficiently separated by using cation and anion resin column chromatography and two step membrane separation. The solid products (i.e. hydrochar) was activated with chemical and physical activation methods into porous carbon materials with high surface area and magnetic properties, which were much efficient to remove the organic pollutants from water and convenient to recovery the carbon magnetic materials.

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Enhanced Cr(VI) Removal by Polyethylenimine-Functionalized Phosphorus Doped Hierarchical Porous Bbiochar

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The amino-functional phosphorus-containing biochar derived from oil-tea shell are facilely fabricated through a two-step strategy, phosphoric acid (H_3PO_4) activation and amino (polyethylenimine, PEI) modification. Herein, the as-synthesized biosorbents were prepared for the removal of Cr(VI) from aqueous solutions. Efforts were focused on establishing relationships between textural and physical-chemical properties of the precursor and the resulting materials, and their adsorption capacity toward Cr(VI). The influence of contact time, adsorbent dose, Cr(VI) concentration, pH and temperature were also investigated. The adsorption of Cr(VI) by the functionalized biochar followed the pseudo-second-order kinetic model and the Langmuir-Freundlich adsorption isotherm model. The maximum adsorption capacities of H_3PO_4 activated precursor and PEI modified biosorbent were 183.4 mg/g and 306.8 mg/g, respectively. The Thomas models fitted very well with the breakthrough curves obtained in a continuous column process. The biosorbents before and after amino functionalization, and the one after sorption of Cr(VI) were characterized by Fourier transformed infrared spectroscopy, X-ray photoelectron spectroscopy and other analytical instruments. The H_3PO_4 activated biochar exhibited a high specific surface area (1056 m^2/g) with abundant functional groups, which is in favor of PEI grafting. The excellent removal performance toward Cr(VI) is demonstrated to be a structure-dependent surface chemical process between Cr(VI) and heteroatoms (N and P), as well as the effect of high surface area and pore structure. This work may provide insights for designing other functional materials for high-efficiency removal of other heavy metals from polluted water. The results herein revealed that the PEI modified biochar had a good potential as a suitable material for sorption of Cr(VI) from aqueous solution.

Exploring Optimal Supplement Strategy of Medicinal Herbs and Tea Extracts for Bioelectricity Generation in Microbial Fuel Cells

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Augmentation of electron shuttles (ESs) to stimulate biodegradation via microbial fuel cells (MFCs) was evidently promising due to maximal electron transfer (ET) flux accelerating rate of pollutant attenuation[1][2]; however, supplement of artifically-synthesized ESs would still not be environmentally appropriate. Thus, this study disclosed optimal biostimulation strategy to supplement natural ESs (e.g., medicinal herbs and tea extracts[3][4][5]) to maximize efficiency of such electrochemically-steered bioremediation. As increasing ET capabilities would significantly control overall operation performance, determining optimal augmentation strategy of natural ESs to optimize power generation in MFCs is apparently crucial to this MFC-driven biodegradation. First, at moderate temperature and slightly alkali pHs for extraction, maximal contents of polyphenolics herbs and tea extracts to be ESs with maximal electrochemical activities were obtained. The most appropriate doses and timing of addition would then be quantitatively assessed. In addition, comparative analysis upon different modes of bioreactor operation with contacting patterns of reacting systems will be considered for system optimization[6]. Through optimal augmentation of polyphenolics-rich ESs for bioelectrochemically-directed biorefinery, this study provided the most sustainable strategy to trigger synergistic interactions[7] of natural ESs for maximal cost-effective extraction of bioenergy and biorefinery.

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Heavy Metals Removal by Magnetic Nanoscale Zero-Valent Iron Assisted Biochar: Mechanisms and Application Potential

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The heavy metals (HMs) contaminant recently imposes intense environmental risks. Although nanoscale zero valent iron (nZVI) assisted biochar (BC) owns excellent heavy metals removal ability, the feasibility of real water treatment is still unclear. The aim of this study was to provide valuable information with regard to the stabilization of nZVI-BC, effects of environmental factors, mechanisms of HMs removal, and actual HMs contaminated water treatment. nZVI-BC with 2:1 Fe/BC mass ratio was applied due to its higher HMs removal efficiency. Results revealed that various reaction conditions showed a significant impact on HMs removal performance resulting from existing HMs species, surface charged variance, and chemical conversion of Fe0 nanoparticles (NPs). By comparison with bare commercial nZVI and BC, nZVI-BC displayed an improvement of colloidal stabilization and positive surface charge attributed to enhancement of HMs removal performance. The pseudo-second-order kinetics along with Langmuir isotherm models was well fitted. Moreover, mechanisms of electrostatic force, complexes, electron donating, and Cr-O-Fe precipitates were included. Finally, the effect of coexisting anions, regeneration ability on real contaminated water were investigated. This study clearly suggests that nZVI-BC is considered as a superior and cost-effective candidate for HMs-containing wastewater treatment.

Separation and Value-Added Utilization of Distillers Dried Grains with Solubles (DDGS): the Coproduct of Corn Ethanol Process

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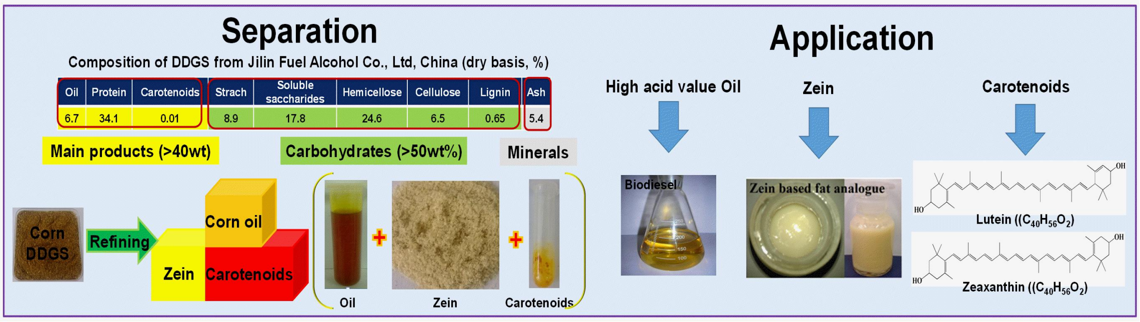
Distillers Dried Grains with Solubles (DDGS) is the by-product of corn fuel ethanol. Unfortunately, DDGS is often used as cheap animal feeds or exausted as wastes, but it contains considerable amount of high value-added substances such as corn oil, Zein and maize yellow pigments (mainly lutein and zeaxanthin). So extraction and utilization of the high value-added substances can effectively improve the profits of fuel ethanol industry and avoid the waste of corn resources. Therefore, in this article, on the basis of main chemical composition of DDGS, the intermittent, semi-continuous and continuous extraction methods are used to extract the oil, zein and carotenoids from DDGS, respectively. When compared with refined corn oil, the DDGS-extracted oil has a similar fatty acid composition but higher acid value (41.6 mg KOH/g) , so it can be used to produce biodiesel with excellent cold flow performance. The Zein is a great natural polymer material and can be used to prepare the fat analogue, which can substitute the oil in O/W food (e.g. mayonnaise) and reduce the caloric value of food. The maize yellow pigments are further separated into two main carotenoids: lutein and zeaxanthin, which are existed in macula retinae of human beings and can be used to produce eye health care product.



Composition of DDGS from Jilin Fuel Alcohol Co., Ltd, China (dry basis, %)

Oil	Protein	Carotenoids	Strach	Soluble saccharides	Hemicellose	Cellulose	Lignin	Ash
6.7	34.1	0.01	8.9	17.8	24.6	6.5	0.65	5.4

Separation and application of value added substances in DDGS

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Facile Synthesis of Pd-Loaded Lignin Porous Carbons in Molten Salt Media by Hydrothermal Carbonization Method

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A facile strategy in the fabrication of Pd-loaded lignin porous carbon was reported. In the present work, lignin/Pd NP composites were first prepared under microwave irradiation. Then Pd NP-loaded porous carbon was constructed successfully from the mixture of lignin/Pd composites and porogen salt LiCl via hydrothermal carbonization method at 240 °C and subsequently served as catalysts in the reduction reaction of p-nitrophenol by sodium borohydride. The salt template can be easily removed by only washing with deionized water. Full characterization was performed using TEM, SEM, BET and UV-vis. The Pd-loaded lignin porous carbon using LiCl as porogen exhibited an orderly appearance and it displayed a mesoporous structure in microscale with higher specific surface area and pore volume, which provided more attachment sites for the immobilization of Pd NPs. The striation of the single Pd NP indicates its crystalline structure. In addition, it exhibited more effective catalytic performances in the reduction of 4-NP to 4-AP. In this research, lignin wastes were fully reused as not only reducing agents and stabilizing agents, but also as a precursor to construct porous carbons as catalyst support of Pd NPs. It provides a new idea for the high value utilization of agricultural and forestry biomass.

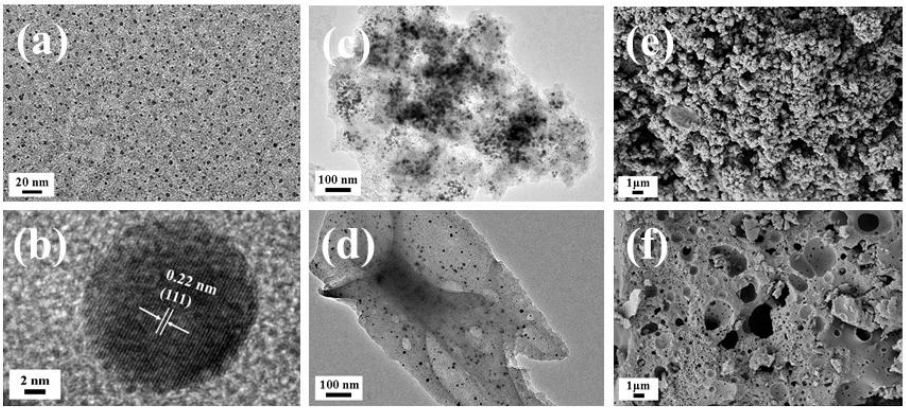

Fig. 1. TEM of (a) lignin/Pd NPs composites, (b) HRTEM result of a single Pd NP, (c) LigC-Pd and (d) LigC-Pd-LiCl. SEM of (e) LigC-Pd and (f) LigC-Pd-LiCl.

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Enhanced Methane Production of Cassava Pulp with Zero Valent Iron (Fe^0) in Batch Scale

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Starch and lignocellulose are main cassava pulp components. This lignocellulose affects decreasing biogas. Hydrolysis can break chemical bond of cassava pulp easily. It can convert cassava pulp to glucose or reducing sugar, and volatile fatty acid (VFAs). However, hydrolysis approaches to increasing biogas as well as methane (CH_4) proportion for cassava pulp have not been progressed. In this study, zero valent iron (Fe^0) was hypothesized to enhance biogas, methane production as well as accelerate the biogas processes. A number of 5 liter of anaerobic batch reactors, were used to investigate the effect of Fe^0. The biogas batch experiment controlled under room temperature. The quantity of Fe^0 affect the biogas production as shown in Figure 1. The highest biogas is 2.29 m^3/kg TVS when obtain Fe^0 60 g/kg VSS. This biogas production is 10.40 higher than control condition, which is without hydrolysis and adding Fe^0. Besides, it is 4.87

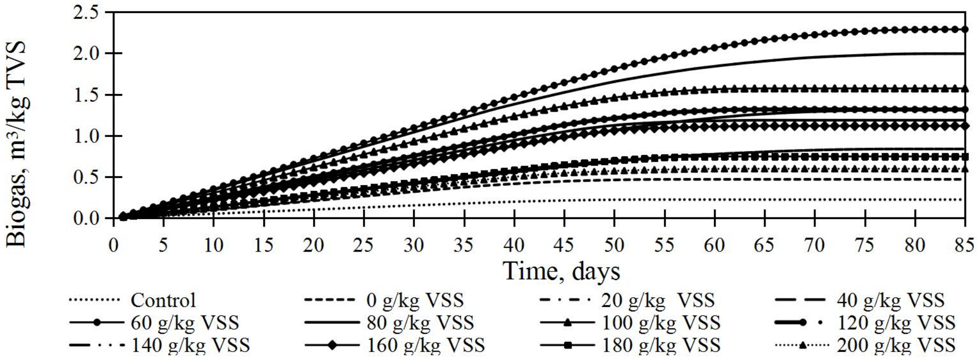

Figure 1. Biogas accumulation of cassava pulp in batch reactor, an effective volume 5 liter, for 85 days with various Fe^0 amounts adding after hydrolysis at pH 10, 100 °c for 30 minutes.

Table 1. Biogas proportion in anaerobic batch scale for three cases: (1) different pH between 8 and 12 for hydrolysis at 100 °C (2) Fe^0 during 40-120 g/kg VSS after hydrolysis at 100 °C and pH 10, (3) hydrolysis at 100 °C, pH 10 with various time reactions after that adding Fe^0.

First run				Second run				Third run			
pH	Biogas, %			Fe^0	Biogas, %			Reaction time	Biogas, %		
	CH_4	CO_2	O_2		CH_4	CO_2	O_2		CH_4	CO_2	O_2
Ctrl/pH 4.23	54.3	26.8	1.3	Ctrl/pH 4.23	54.3	26.8	1.3	Ctrl/pH 4.23	54.3	26.8	1.3
pH 8	63.9	26.3	0.9	40 g/kg VSS	80.3	18.5	0.7	15 min.	80.3	17.8	1.0
pH 9	76.4	20.1	1.1	60 g/kg VSS	83.2	16.5	0.9	20 min.	80.5	17.7	0.9
pH 10	77.5	19.2	1.0	80 g/kg VSS	81.3	17.8	0.6	25 min.	83.5	16.7	0.9
pH 11	74.5	20.7	0.9	100 g/kg VSS	79.5	17.9	0.7	30 min.	83.6	16.3	0.6
pH 12	75.3	19.6	1.0	120 g/kg VSS	79.3	18.0	0.7	35 min.	83.4	16.6	0.6

higher than under hydrolysis condition but without adding Fe^0. The proportion of CH_4 with Fe^0 60 g/kg VSS in Table 1., shown the highest value at 83.2% and less of CO_2 16.5%. This was hydrolyzed at 100 °C, 30 minutes and pH 10.

N-containing Chemicals from Renewable Biomass Recourses

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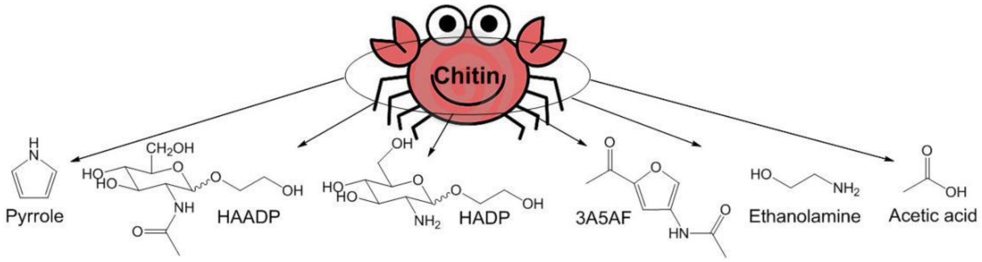
N-containing chemicals are crucial in the modern chemical industry. Their current production, unfortunately, are largely based on non-renewable resources. We present here alternative strategies to obtain some of these chemicals from renewable biomass resources. Our approaches include the valorisation of chitin, the most abundant, nitrogen containing biopolymer as the starting material, as well as starting with other biomass resources and introduce nitrogen at a later stage.

Chitin is the world second most abundant biopolymer widely existed in the exoskeleton of shellfish and insects containing 7 wt% of biologically fixed nitrogen. This sustainable biomass has an underestimated but remarkable potential for the production of industrially important chemicals especially nitrogen containing compounds. To date, the direct conversion of chitin into high value chemicals with high yield has yet to be demonstrated. [1-2] In this presentation, we will show case some of our efforts in the catalytic transformation of chitin into N-containing chemicals (Scheme 1). Several strategies, including dehydration, liquefaction, hydrogenolysis and hydrothermal treatment, will be described in detail [3-10]. This series of work demonstrated that chitin is indeed an attractive starting materials for the manufacturing of certain value added chemicals.

In the second part of the presentation, we will discuss our work on novel catalysts for the amination and reductive amination reactions, to transform alcohols, and sugars into a variety of N-containing compounds. The focus will be on the understanding of the active sites and reaction mechanisms.



Scheme 1. Chemicals that could be produced directly from chitin.

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Computational Fluid Dynamic Investigation of Bioreactors

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Bioenergy can be viewed as a renewable energy that uses biotechnology to convert biomass into biofuels and biobased products. The primary biomass sources are energy crops and organic wastes from industry and agriculture. Although bioenergy can be produced from a wide variety of processes employing a number of technologies, biochemical and thermochemical technologies are suggested to be two basic pathways for biomass conversion. This study focuses on the biochemical conversion that can be achieved by either anaerobes or photosynthetic microorganisms to produce gaseous and liquid fuels. First, the state-of-the-art of computational fluid dynamics (CFD) and its application to bioreactors are briefly reviewed. The bioreactors investigated are: (1) anaerobic lagoon, (2) plug-flow digester, (3) complete-mix digester, (4) anaerobic biohydrogen fermenter, (5) anaerobic biofilm reactor, and (6) photobioreactor. Second, several key issues of pre-processing and post-processing for the ANSYS-FLUENT commercial CFD software are addressed. Third, general modeling heat and mass transfer, turbulence, and multiphase flow is presented. Particular emphasis is given to Euler-Euler approach, sliding mesh method, and large eddy simulation. Predictions are made for bioreactors mixed by pumped circulation, gas sparging, and mechanical agitation. Finally, a comprehensive model that integrates physical and biological processes in anaerobic methane fermentation is developed to highlight the importance of CFD in the study of renewable energy.

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Selective Oxidation of Biomass-Derived 5-Hydroxymethylfurfural

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Renewable biomass is the is the most promising renewable source of available organic carbon.[1-6] Catalytic conversion of biomass can produce not only secure energy but also petrochemical-derived chemical supplies. 5-hydroxymethylfurfural (HMF) is an important platform molecule. It can be easily produced from the dehydration of xylose and fructose and oxidation of HMF can generate fuel and value-added chemicals.

As shown in figure 1, there are carbonyl and hydroxyl groups in HMF. The catalytic oxidation of HMF can produce many important furanic compounds and maleic anhydride (MA). Moreover, 2,5-furandicarboxylicacid (FDCA) can also be obtained by oxidation of carbonyl and hydroxyl group in HMF. FDCA is a promising alternative for terephthalic acid and the Coca-Cola company has used bio-based polyethylene furanoate (PEF) produced from FDCA for bottles in replace of traditional petrochemical-derived polyethylene terephthalate (PET) produced from terephthalic acid. Our group has successfully achieved the selective oxidation of HMF to 2,5-diformylfuran (DFF), 5-hydroxymethyl-2-furancarboxylic acid (HFCA), and FDCA by thermal-process. [7-12] Recently, we designed a novel photocatalyst of cobalt thioporphyrazine (CoPz) dispersed on g-C_3N_4 (abbreviated as CoPz/g-C_3N_4), which exhibits excellent catalytic activity towards the selective oxidation of HMF into FDCA under simulated sunlight using oxygen molecules in air as a benign oxidant.

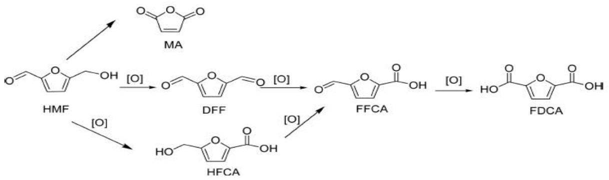

Figure 1 Catalytic oxidation of HMF

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One-pot Production of Gluconic Acid from levoglucosan over Polyoxometalate Supported Gold Catalyst

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Gluconic acid is widely used in many fields, including food additives and pharmaceutical raw materials. Nowadays, it is mainly manufactured through fermentation of glucose, which is obtained by hydrolysis of starches. It's highly desired to develop new process from the nonfood renewable resources. Fractionation of biomass through staged pyrolysis or condensation can produce relatively simple cut of concentrated products like levoglucosan and other oxygenates, which can then be selectively converted to value added chemicals.[1] Santhanaraj et al. reported a two-steps strategy to convert levoglucosan to glucose via hydrolysis with Amberlyst-15, followed by subsequent oxidation to gluconic acid with Pd/C catalyst in alkaline conditions.[2] In this work, we use Au/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst for one-pot oxidation of levoglucosan to gluconic acid without base. Table 1 shows the catalytic performances of typical solid acid supported gold catalyst. It's clear that Au/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst exhibited the highest gluconic acid selectivity (90.5%) with 93.4% levoglucosan conversion. Moreover, the reaction pathway, gluconic acid as co-catalyst and relevant kinetics are also studied in detail.

Table 1. Catalytic performances of Au loaded on typical solid acid catalysts.

Catalyst	Conversion (%)	Selectivity (%)		Gluconic acid yield (%)
		glucose	gluconic acid	
Au/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	93.4	0	90.5	84.6
Au/nano ZrO_2-SO_4^{2-}	93.5	9.6	31.9	29.8
Au/TiO_2-PO_4^{3-}	99.4	12.6	47.3	47.0
Au/HZSM-5 (20)	41.3	70.7	24.7	10.1
Au/CNT	77.8	14.7	69.7	54.2

Reaction conditions: 77 mM levoglucosan, 0.15 g catalyst, 145 ℃, 3 h, 0.5 MPa O_2, 20 ml H_2O, 1% Au loading.

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Geometric and Electronic Effects of Bimetallic Ni-Re Catalysts for Selective Deoxygenation of M-Cresol to Toluene

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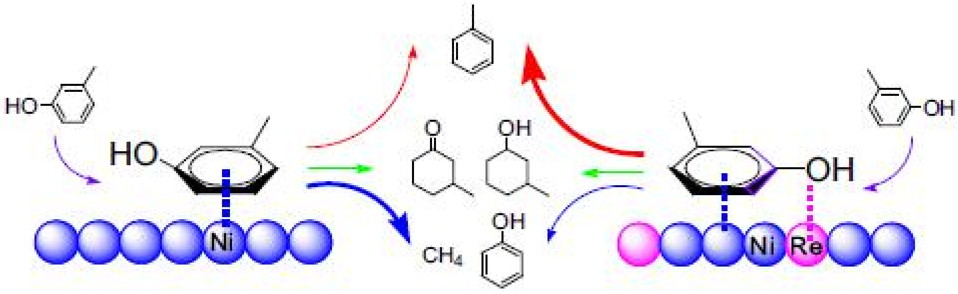
Catalytic hydrodeoxygenation of lignin derived phenolics to aromatics represents an important approach to convert lignin waste from renewable biomass to valuable chemicals and fuels with low hydrogen consumption. The hydrodeoxygenation consists of a number of reactions, such hydrogenation, deoxygenation, C-C hydrogenolysis. Selective deoxygenation of phenolics to aromatics remains a challenge under mild conditions. In this work, we showed bimetallic Ni-Re catalyst enables selective deoxygenation of m-cresol, a model compound of phenolics, to toluene. Addition of Re to Ni breaks Ni into small ensembles, which provides the active sites of Ni-Re neighboring site to adsorption of C-O, which facilitates the deoxygenation reaction. On the other hand, the reduced Ni ensemble size and the reduced electron density of d orbital of Ni by the presence of Re significantly inhibit the C-C hydrogenolysis reaction to low value methane.



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Hydrogen Production from Algal Biomass

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The unprecedented increase in greenhouse gas emissions we are facing has now been deemed the major culprit of global warming. In an effort to combat global warming and climate change, substantial effort is being made at the global level to explore renewable energy that could replace fossil fuels. Production of hydrogen from biological processes, so-called biohydrogen is increasingly attracting attention of researchers. Biohydrogen is a promising future fuel because of its clean and high energy content. It is an ideal energy carrier to reduce greenhouse gas emissions - its conversion to energy yields only pure water. A challenging issue in establishing hydrogen as a sustainable energy source is the way it is produced. Biohydrogen produced from biological processes has the potential for renewable biofuel, and could replace current hydrogen production through thermo-chemical processes deriving from fossil fuels. One of the promising biohydrogen production approaches is conversion from algal biomass, which is abundant, clean and renewable. Unlike other well-developed biofuels such as bioethanol and biodiesel, production of hydrogen from algal biomass is still in the early stage of development. There are a variety of technologies developed for hydrogen production from algal biomass, and some laboratory- and pilot-scale fermentation systems have demonstrated a good potential for full-scale implementation. This work presents an evaluation of development in biohydrogen production focusing on biological pathways, bioreactor systems and operation, and economic evaluation. Perspectives and prospects of biobiohydrogen production are also outlined.

Carboxylate Ionic Liquids Combining Low Cytotoxicity toward HepG2 Cell and High Separation Efficiency for Bioactive Molecules

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Tocopherols, as the main compositions of natural Vitamin E, play an important role in human health due to their antioxidative capacity and ability to act as free radical scavenger. Endowed with a chromanol head and varied alkyl side chains on that chromanol head, tocopherols have four different homologues, α-, β-, γ-, and δ-tocopherol. Of all those homologues, α-tocopherol possess the highest biological activity. So even tocopherols are widely existed in natural sources, there is still a challenge to highly and effectively separate α-tocopherol from other homologues because of their high structural similarity. In addition, ionic liquids (ILs) have attracted a great deal of attention as solvents in separation processes because of their unique physicochemical properties, especially when ILs were endowed with high basicity. Besides, investigations on the cytotoxicity of ILs towards mammalian cell lines are quite insufficient, and it remains a great challenge to develop ILs with both higher efficiency and less cytotoxicity. Herein we reported the cytotoxicity of cholinium carboxylate ILs toward HepG2 cells and their separation performance for natural bioactive molecules for the first time. At first the cytotoxicity toward HepG2 cells of these ILs was systematically evaluated by MTT cell viability assays, and then their functionality as extractants was investigated through the extractive separation experiments of tocopherol homologues. The results demonstrated that these ILs combined both lower cytotoxicity and higher performance than the widely-used imidazolium chloride ILs. For example, the IC50 of cholinium acetate was 135.53, approximately four times as large as that of 1-ethyl-3-methylimidazolium chloride (35.66). The distribution coefficient of δ-tocopherol and the selectivity of δ-tocopherol to α-tocopherol using cholinium octanoate were 8.24 and 9.84, respectively, which were 37 times and twice of those using 1-ethyl-3-methylimidazolium chloride. These results manifest that ILs can be designed in a win-win strategy to combine low cytotoxicity and high performance, which are highly instructive to improve the application of ILs in drug-related processes owing to the positive impact on both safety and efficiency.

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Promoting Methane Yield from Kitchen Waste with Magnetic Rice-Straw Biochar

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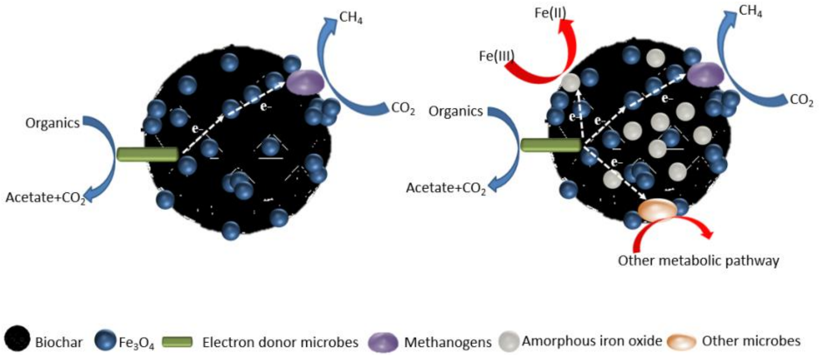
Biochar and magnetite has been shown previously to promote methane (CH_4) yield from anaerobic digestion (AD) by promoting direct interspecies electron transfer (DIET). Magnetic biochar with soft magnetism, high specific surface area and conductibility is a potential economic feasible AD additive. This investigation evaluated the effectiveness of magnetic biochar on AD performance of kitchen waste slurry. The magnetic biochar was fabricated via thermal pyrolysis of $FeCl_3$ treated rice straw under four $FeCl_3$ to rice straw ratio (w/w, 0 to 100 (C), 0.32 to 100 (1Fe), 3.2 to 100 (10Fe), 32 to 100 (100Fe)). Results showed that the addition of (magnetic) biochar resulted in significant reduction of methanization lag phase and improvement of chemical oxygen demand (COD) removal efficiencies comparing with no biochar addition control (CK). Compared to CK treatment, the addition of magnetic biochar 10Fe significantly improved cumulative CH_4 production from 588.9mL to 657.75mL. However, other treatments dramatically reduced cumulative CH_4 production. Closer examination of volatile fatty acids (VFAs) variation, pH, ammonia nitrogen, biogas composition, thickness of iron ion proved that in the AD system with low inhibition risk, magnetic biochar 10Fe can further promote CH_4 production efficiency possibly by promoting DIET during methanogenic process. Furthermore, (magnetic) biochar C, 1Fe and 100Fe can inhibit CH_4 yield possibly by shifting metabolic pathway in the mixed fermentation system. The selection of appropriate synthetic methods of magnetic biochar was important in facilitating the efficiencies of AD.



(a) (b)

Figure 1. Mechanisms for promoting and inhibiting effects of magnetic biochar 10Fe (a) and 100Fe (b)

Carbon Nanotube Hollow Fiber Membrane Accelerates Syntrophic Metabolism and Biogas Production in Anaerobic Digester

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Direct interspecies electron transfer (DIET) between electroactive bacteria and methanogenic archaea via conductive materials is an alternative to interspecies hydrogen transfer (IHT) in anaerobic digester and provides significant benefits to methane production in terms of yield and rate. The present work aimed to investigate effects of carbon nanotube hollow fiber (CHF) supplementation on anaerobic digestion. Experimental results showed that biogas productivity in the reactor with CHF was higher than that of control. This was linked to the results of scanning electron microscopy (SEM) analysis showing that microorganisms attached on the surface of the CHF promoted DIET thereby enhancing both biogas production rate and yield. It was confirmed that the supplementation of CHF accelerated syntrophic metabolism with increased dominance of electroactive bacteria.

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Poster Lectures

Nonenzymatic production of xylooligosaccharide from corn stover by hydrothermal pretreatment and dilute acetic acid hydrolysis

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An efficient strategy was developed for nonenzymatic production of xylooligosaccharide from corn stover in this work. Corn stover was first pretreated by hydrothermal method under 170 ºC for 1h, more than 51 % of the Benzene-alcohol extractives were removed from corn stover. The loss rates of cellulose, hemicellulose and lignin were no more than 5.5%, and the crystallinity index (CrI) of residues increased only slightly. Subsequently, the residues were hydrolyzed by dilute acetic acid. The effects of hydrolysis conditions on degradation of corn stover and xylooligosaccharide production were discussed. When the solid-to-liquid ratio was 1:15 (W: V), the hydrolysis with an addition of 0.01 mol/L acetic acid was operated at 170 ºC for 2 h. The highest hemicellulose removal of 70.0 % was observed, 82.7 % of it was hydrolyzed to sugars, the content of xylooligosaccharide in total sugar also achieved 70.1 %. In this process, more than 96 % of cellulose and 94 % of lignin were reserved in the residues, while generated a relative low level of inhibitors. The residues were analyzed by BET, XRD and SEM. The intact structure of corn stover was disrupted, the specific surface area of residues increased obviously and the surface became rough and porous. These results indicated the biomass recalcitrance of the corn stover was weakened due to the two-step treatment, which was favorable to enhance the efficiency of conversion of hemicellulose to xylooligosaccharide.

Highly-efficient Conversion of Polysaccharide-rich Food Waste into Formic Acid under Mild Hydrothermal Conditions

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The amount of food waste increased dramatically with the rapid growth of population and urbanization. Conventional disposal methods, landfill, incineration and composting, have caused serious problems, such as pollution of soil and underground water, low-efficiency in energy utilization and toxic gases emission.[1] Actually, food waste is a sustainable and carbon-neutral source of organic compounds, thus, developing an efficient approach for conversion of food waste into chemicals and fuels is one of the most promising ways for sustainable development.[2] Hydrothermal process is particularly suitable for the valorization of wet organic wastes in an economical way, since energy-intensive drying process is avoided and nearly cost-free and environmentally benign water as the reaction medium.[3] Herein, a facile and rapid method for the conversion of polysaccharide-rich food waste into formic acid, which is regarded as an excellent hydrogen storage carrier and as fuel cell material recently, was proposed under mild hydrothermal temperatures (Figure 1). The results showed not only purified starch and cellulose which are typical model compounds of food waste but also the main components of food waste, such as rice, wheat, potato, carrot and tissue, as well as simulated food waste could be converted efficiently to formic acid with 50%~80% yield. This study may provide a promising method for the valorization of a high water-content and complex components waste.

Figure 1. Proposed method for conversion of polysaccharide-rich food waste into formic acid.

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Catalytic conversion of Carbohydrate to Methyl Lactate over Mg-MOF-74 in Near-critical Methanol

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Metal organic frameworks (MOFs) are promising heterogeneous catalysts for biomass conversion since MOFs are reported to have many interesting features, such as high thermal stability, high metal content [1], ordered structure, adjustable chemical functionality and unprecedentedly high porosity [2]. In this work, a room temperature synthesis MOF-74 was applied for the conversion of carbohydrate to methyl lactate for the first time. The MOF-74 was characterized by XRD, N_2-BET and the effects of metal site (Co, Ni, Mg, Zn) of MOF-74, catalyst and methanol loadings, reaction temperatures and times were detected. Mg-MOF-74 exhibited the best catalytic activate among the four MOFs. Using Mg-MOF-74 as catalyst, the highest yield of methyl lactate from glucose was 34.9% at 220 °Cfor 6 h. Comparable yields of MLA were produced from glucose and fructose. While sucrose gave a much higher yield of methyl lactate (47.4%). The catalyst showed good reusability for four cycles with a slight reduction in the catalytic activity. This study will expand the application of MOFs on the conversion of biomass.

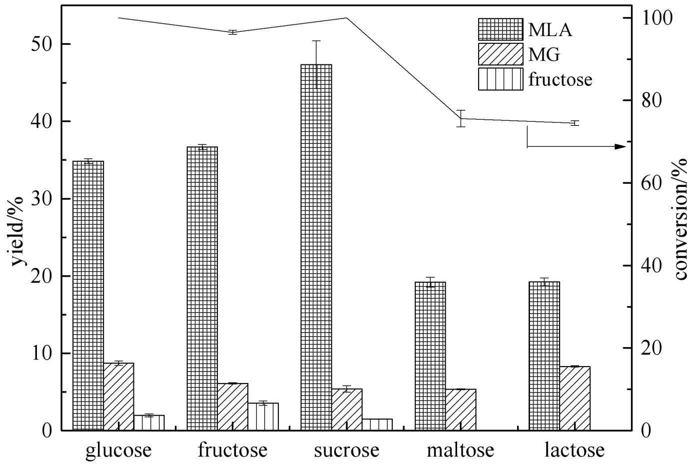

Fig.1 Catalytic performance of the glucose conversion to methyl lactate over Mg-MOF-74 using different sugars as reactants. (MLA: methyl lactate; MG: methyl glycolate)

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Kinetics Study of Levulinic Acid Production from Corncobs by SnCl4 Catalyst in A Single Water Phase

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With the depletion of fossil fuels, a considerable amount of efforts have been focused on the development of an attractive techno-economical and environmentally benign process for the production of biofuels and platform chemicals on a commercial scale. Levulinic acid (LA) is an ideal platform chemical for production of a number of bio-chemicals, which can be produced through acid-catalyzed dehydration and hydrolysis of hexose sugars obtained from lignocellulosic materials. In this study, $SnCl_4$ was identified as an efficient catalyst for hydrolysis of corncob to produce LA. The hydrolysis kinetics of LA production by using $SnCl_4$ as the catalyst was investigated in a single water phase under different reaction conditions. The Box–Behnken design response surface methodology (RSM) was applied to determine the optimized reaction conditions and three individual variables including reaction temperature, duration, and catalyst concentration were evaluated. The highest LA yield of 76.1% was achieved at 193°C and 17 mins with 82 mM $SnCl_4$ catalyst. On top of that, a mechanistic kinetic model was developed to predict the yields of glucose, HMF and LA that are consistent with the experimental results. This kinetic model developed based on the result analysis of corncob can be applied over a wide range of $SnCl_4$ catalyzed hydrolysis reaction for different lignocellulosic biomass. The analysis of the related kinetic parameters and the results of the RSM experiment helped to provide a deep insight into the whole reaction process.

Nonenzymatic Sugar Production from Bamboo Shoot Shell by Dilute Acid Hydrolysis in Acetone/water Medium

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The use of lignocellulosic biomass to produce biofuels and biobased products requires the decomposition of cellulose and hemicellulose into its constituent sugars. However, to overcome the recalcitrance barrier of cellulosic biomass for efficient conversion of cellulose to fermentable sugars at a low cost is still the bottleneck problem for industrialization of lignocellulosic biorefinery. Polar aprotic solvent possesses a strong solubility to cellulose while has no or minimal proton donation, thus reduces the occurrence of side-reactions during cellulose degradation reaction. This study investigated a two-step non-enzymatic degradation method of bamboo shoot shell by very low concentration H_2SO_4 acid in an acetone/water polar aprotic solvent system. In the first step, about 88% of hemicelluloses and 84% of lignin were successfully removed, which was carried out at 140℃ for 1h with 0.6% H_2SO_4 and acetone to water ratio of 3:2. Then in the second step, the high cellulose content solids were further degraded by 0.4% H_2SO_4 acid within the temperature range of 160-190℃ for different reaction time in acetone/water medium (4:1). The results indicated that about 70% of the total carbohydrates in lignocellulosic biomass could be recovered as monomer sugars or oligosaccharides in this proposed system. This research could provide valuable insights into valorization of lignocellulosic materials and become a competitive alternative to current biomass-derived carbohydrates production scheme.

The effect of heating rate on the yields and distribution of oil products from the pyrolysis of pubescen

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We studied the effect of heating rate on both the yields and the distribution of the oil products obtained from the pyrolysis of pubescen. The molecular weight of the liquid products was mainly distributed in the range of 200-500 Da (about 77% from GPC). At 15 ^{o}C·min^{-1}, the total yield of small-molecular products from degradation of carbohydrate was 9.53 wt %, and the total yield of identified monophenols reached a maximum of 3.57 wt %. Thus, the liquid products were predominantly present as oligomers. Lignin in pubescen was degraded to stable tetramers. Two kinds of oligomers from lignin (OG-1 and OG-2) have been distinguished. The formation of monophenols and/or oligophenols mostly involved the cleavage of the C-C bonds (C_α-C_β, C_β-C_γ, C_1-C_α) and C-O bonds (β-O-4, β-O-5, C_α-O, C_γ-O and 4-aryl ether linkages). Carbonhydrates derived species interacted with each other and then produced oligomers, the formation pathways of which were explained. A decrease of relative content of the species with Mn = 200-500 Da and an increase of relative content of the species with Mn = 500-1000 Da were observed as the heating rate increased from 2.5 to 15 ^{o}C·min^{-1}. With further increasing heating rate from 15 to 25 ^{o}C·min^{-1}, the molecular weight distribution remained almost unchanged. Increase of the heating rate promoted the cleavage of C_1-C_α bonds, C_β–C_γ bonds in lignin, and the dehydration of C_α–OH units of lignin into C_α=C_β.

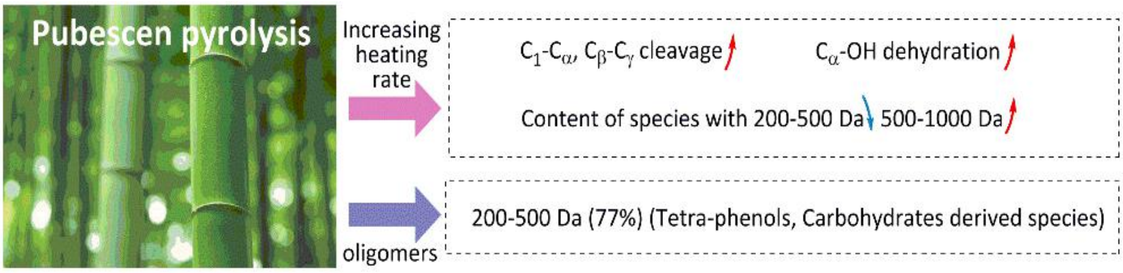

Fig. 1. The effect of heating rate on the pubescen pyrolysis.

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Simultaneous Conversion of Hexose and Pentose to Methyl Lactate in Near Critical Methanol with Metal Chlorides

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The catalytic conversion of biomass to methyl lactate is important, but the utilization ratio of biomass is low since previously only separate reactants, either C5 or C6 sugars, have been studied. Cellulose and hemicellulose make up about 2/3 of lignocellulose [1]. Cellulose and hemicellulose mainly consist of glucose and xylose, respectively. The simultaneous conversion of glucose and xylose in near critical methanol has been studied in this work, and the catalytic reactions with 15 different types of metal chlorides have been measured. The trends of the catalytic conversions of glucose and xylose with 15 different metal chlorides have been found to be similar. The yield of methyl lactate has initially increased and has then decreased steadily with an increase in the pKa value of the metal ions, suggesting that medium Lewis acidity is favorable for the production of methyl lactate. A possible reaction mechanism involving metal ion Lewis acidity and methyl lactate production has been proposed for the preparation of heterogeneous catalysts for simultaneous conversion of cellulose and hemicellulose.

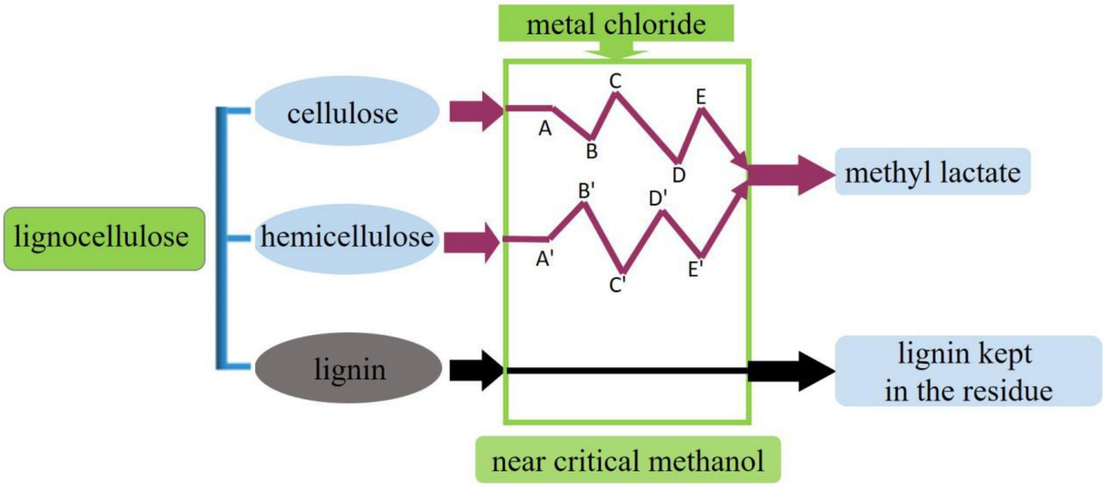

Fig.1 Schematic diagram for the simultaneous conversion of cellulose and hemicellulose to methyl lactate in near critical methanol.

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Evolution of functional groups during corn stalk torrefaction and its impact on pyrolysis

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Torrefaction (at 200, 230, 260, 290℃) of corn stalk and its influentce on pyrolysis were investigated. The in situ IR technique and two-dimensional perturbation correlation IR spectroscopy were used to describe the evolution of functional groups during torrefaction processes.The results showed that the associated hydroxyls decreased with the increase of torrefaction temperature,and the removal of-OH functional groups during torrefaction were mainly from dehydration.TG analysis showed that torrefaction played a significant influence on the kinetic parameters of pyrolysis.With the increase of torrefaction temperature,the activity of pyrolysis was enhanced and the activation energy was improved.

Catalytic conversion of cellulose into polyols over bimetallic Pd-Fe nanoparticle catalysts

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Recently, renewable biomass resource has attracted worldwide attention in the production of valuable chemicals for their abundance and availability [1-5]. Much effort has been taken into the conversion of inedible cellulosic materials into valuable chemicals. Among all the valuable chemicals, sorbitol, EG, 1,2-PG and Gly are very important platform molecules in the plastic, food and pharmaceutical industry. Liu et al. obtained about a 40% yield of polyols on Ru/C [1]. Zhang et al. achieved a 61% yield of ethylene glycol starting with cellulose using a nickel-promoted W_2C catalyst [2]. However, there are still many challenges in the direct utilization of cellulose for its robust structure [2].

In this work, a series of carbon nanotube (CNTs) supported monometallic Pd and bimetallic Pd-Fe catalysts were synthesized and employed to the catalytic hydrogenolysis of cellulose into polyols, including hexitol, ethylene glycol (EG), 1,2-propanediol (1, 2-PG) and glycerol (Gly). The physicochemical properties of these catalysts were characterized by nitrogen physical adsorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) techniques. The total yields for hexitol, EG, 1,2-PG and Gly were as high as 37%, 55% and 53% for Pd/CNTs, Pd-Fe/CNTs (Pd:Fe=1:1) and Pd-Fe/CNTs (Pd:Fe=1:2) in the hydrolytic hydrogenation of cellulose, respectively. The addition of Fe to Pd significantly modified the physicochemical properties of nanoparticles and catalytic performance, especially for hexitol selectivity. The promoting effect of Fe, especially for the hexitol selectivity, over the bimetallic catalysts is due to the fact that the incorporation of Fe may stabilize the Pd^0 nanoparticles and lead to a downshift of the d-band center of Pd metal nanoparticles by the charge transfer from Fe to Pd. The recycle experimental results showed that the leaching of Fe resulted in a significant decrease in the hexitol yield over Pd-Fe/CNTs after the first recycle, which further demonstrates that the Fe element plays a promoted role in the formation of hexitol.

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Butyl acetate production integrated with acetone-butanol- ethanol fermentation, esterification and in situ extraction

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Butyl acetate is an excellent organic solvent with a pleasant fruity smell, which is widely used in solvents, coatings, pharmaceuticals, spices and other industries. In this study, acetone-butano-ethanol (ABE) fermentation by Clostridium acetobutylicum NJ4, esterification catalyzed by lipase and in situ extraction was integrated to achieve direct butyl acetate production from renewable resources. The esterification conditions were firstly optimized, including the amount of enzyme and sodium acetate, addition time of lipase and sodium acetate, the type of extraction agents, such as hexadecane, biodiesel etc., and the type of carbon sources, like glucose, xylose. Under the optimal conditions when 100U lipase and 30 mM sodium acetate were added at the time points of 48 and 96h with pH adjusted to 5.5 using hexdecane as the extractant, butyl acetate production could reach up to 4.6 g/L from 60 g/L glucose. This study represents the first investigation and the highest butyl acetate production through biological processes.

Vegetable oil based polyols prepared by thiol-ene photo-click reaction and waterborne polyurethane dispersion therefrom

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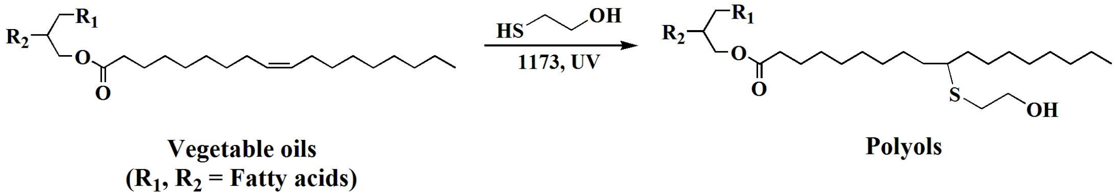
Recently, global efforts are dedicated to find efficient routes to transform renewable resources to valuable monomers for bio-based PU production. In this study a series of bio-based polyols were prepared from olive, castor, corn, canola, rice bran, grape seed and linseed oil by thiol-ene photo-click reaction with a home-made photochemical reactor (Scheme 1). The effect of reaction parameters, including photoinitiators, reaction time, molar ratios of thiol to carbon-carbon double bond and power of mercury lamp on the structures of the resulting polyols was investigated. The mechanism of thiol-ene photo-click reaction was also discussed. The relationship between carbon-carbon double bonds in the backbone of vegetable oil fatty acid chains and the functionalities of the polyols was elucidated. Four of these polyols were used to prepare polyurethane dispersions. The effect of functionalities and molecular structures of the bio-based polyols on the thermo-physical and mechanical properties of the resulting polyurethane films was discussed (Fig. 1). It is found that thiol-ene photo-click reaction offers a bio-based platform to create a variety of polyurethane dispersions that promises economic and environmental benefits.



Scheme 1. Synthesis route of vegetable oil based polyols by thiol-ene photo-click reaction.

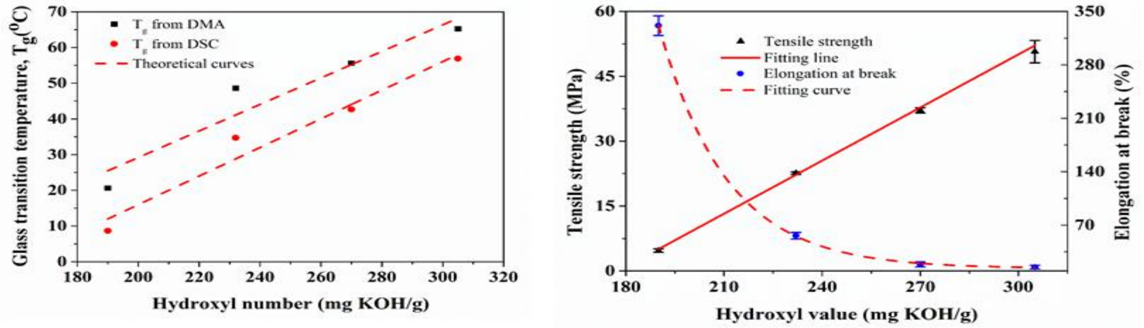


Fig. 1. Dependence of glass transition temperature, tensile strength and elongation at break of PU films on the hydroxyl value of the corresponding polyols.

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Low temperature depolymerisation of pyrolyzed oligomers In alcohol over Pd/NbOPO4catalysts

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Pyrolysis bio-oil contains hundreds of compounds and the majority of them are oligomers which lead to its direct utilization difficult due to some unfavorable properties, such as high instability derived from oxygenated compounds[1-2], so the upgrading bio-oil process is actually to make the oligomers to be depolymerized.

The bio-oil obtained from the low temperature torrefaction (LTT)of pubescens, which mainly contained lignin-oligomers[3], was subjected to mesoporous niobium phosphate supported palladium bifunctional catalyst with ethanol as solvent over the temperature range of 220-280℃. Hydrogenation to depolymerize the oligomers; alkylation, hydrogenation, esterification of monomeric derivatives, simultaneous occurred in the process. The results from GC–MS, FT-IR and GPC analysis showed that the functional groups and compositions were changed dramatically and the major components were monomer phenolic derivatives. The average molecular weight of products reduced from Mw=320Da (Mn=298 Da) to Mw=273Da (Mn=254 Da).The carbon content increased from 61.19 to 79.09 wt% and oxygen content decreased from 29.53 to 9.78 wt %.The atomic H/C ratio increased from 1.55 to 1.62 and atomic O/C ratio decreasing from 0.36 to 0.09, meanwhile the heating value was increased from 27.62 to 39.22 MJ/kg after hydrogenation. Furthermore, the mesoporous niobium phosphate has an amount of acidic sites including both BrÖnsted acid sites on PO_4 and Lewis acid sites on NbO_x prone to the cleavage of C-O-C bond. The above synergistic effects with the excellent hydrogenation performance of Pd contribute to the depolymerization of oligomers.

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Enhancing fermentative hydrogen production with removal of volatile fatty acids by electrodialysis

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Hydrogen is considered as a promising alternative to fossil fuels, due to its high energy density by mass and clean utilization products. Clean hydrogen production may be achieved by dark fermentation. In dark fermentation, the carbohydrate-rich substrates are anaerobically degraded to hydrogen, carbon dioxide, and soluble metabolites (mainly acetic and butyric acids). However, the accumulated volatile fatty acids (VFAs) can be inhibitory to the hydrogen fermentation process. In this study, a three-chamber electrodialysis bioreactor was proposed to continuously remove VFAs during dark fermentation. This reactor contained fermentation chamber, cathode chamber and anode chamber with graphite electrodes. Hydrogen production was greatly enhanced at a voltage of 4 V. A specific hydrogen yield of 187.8 mL/g $_{\text{glucose added}}$ was achieved in the fermentation chamber, which is 41.1% higher than the control group without voltage (133.1 mL/g $_{\text{glucose added}}$). Gas production was not noted in cathode and anode chambers. The hydrogen contents in biogas were in the range of 58.7%-83.2%, exhibiting 13.2%-93.8% increases as compared with the control group without voltage. This can be attributed to the partially removal of bicarbonate from the fermentation chamber, which reduced the carbon dioxide content in gas phase, thereby improving the hydrogen content. Meanwhile, the maximum concentration of acetic acid and butyric acid in the fermentation chamber were 8.2 mM and 8.5 mM, respectively, which are 59.8% and 66.3% lower as compared with the control group without voltage. This suggests the three-chamber bioreactor can successfully reduce the VFA level whilst improving the specific hydrogen yield and hydrogen content.

Acknowledgements

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Hybrid membranes using tung oil-based polyurethane and graphene oxide for gas separation

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The depletion of petroleum and the emission of CO_2 have inspired the research on bio-based polymers and CO_2 capture. Tung oil-based polyols were used to partially replace polyether polyols from petroleum for the preparation of sustainable polyurethane. Tung oil-based polyurethane, TBPU, was prepared via two-step method, i.e. bulk prepolymerization and chain extension reaction. The graphene oxide (GO) was prepared via Hummer method. Then TBPU was blended with the GO at different ratios in dimethylacetamide (DMF). The solvent evaporated while forming TBPU/GO hybrid film. The GO/TBPU films were characterized by FTIR, DSC, TGA and SEM, followed by the measurement of mechanical properties and gas permeability. The results showed that the addition of tung oil-based polyols enhanced the glass transition temperature and thermal stability of TBPU. The graphene oxide improved the thermal stability of the hybrid membrane. The mechanical properties of the hybrid film were improved, and the tensile strength and elongation at break were twice as those of the bulk TBPU film. When the GO content is more than 2.0%, the hybrid film would appear brittle fracture. The increase of GO content in hybrid films improved the selectivity of CO_2/N_2 separation. However, the GO agglomeration reduced the gas separation and permeation properties when the GO content is higher than 0.35%.

Facile and high-yield synthesis of methyl levulinate from cellulose

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Herein, we reported a facile and economically feasible and high-yield synthesis of methyl levulinate from cellulose over metal salt catalyst aluminium sulfate under microwave condition. Microwave irradiation is a volumetric and selective dielectric heating, which may greatly accelerate the reaction rate and reduce the requisite reaction time, thereby preventing cellulose from decomposition to carbonaceous side products at thermal condition. Different metal salt catalysts were investigated in the alcoholysis reaction. The influences of reaction parameters on the product selectivity, as well as the reaction kinetics, were studied. Critical role of additive water in the reaction was discussed. Mechanism studies about the reaction pathway were also proposed.

Efficient production of chemicals from cellulose provides sustainable routes for the utilization of natural renewable resources to meet the requirments of human society.[1-2] Herein, we reported a highly efficient and simple metal salt catalyst $Al_2(SO_4)_3$ for the cellulose conversion to methyl levulinate under microwave condition. A highest ML yield of 70.6% was obtained at 180 °C within a very short time of 40 min. The introduction of water could reduce humin/coke formation and solvent consumption, and can also switch the reaction pathway via the more reactive intermediate glucose. Kinetic and mechanisim study of the subreactions showed that both cellulose hydrolysis and alcoholysis pathways were exisited in the cellulose conversion to ML, with the former as the main route in the presence of water. The reaction with microwave heating showed accelerated reaction rates of 25 times the reaction with conventional oil heating, and even more times of the rates of glucose and methyl glucoside dehydrations, resulting in higher reaction selectivity toward ML prodcution. The catalyst was also successfully recycled and applied to the conversion of cellulose to other alkyl levulinates, as well as the conversion of raw biomass to ML with high yields. The homogeneous nature of $Al_2(SO_4)_3$, together with its high efficiency and excellent recyclability, make it potential catalyst for the large-scale prodcution of ML in industry.

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Superior Performance of Fe/ZSM-5 Catalyst in Hydrothermal Liquefaction of Nannochloropsis sp.

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Hydrothermal liquefaction (HTL) is a promising approach for the conversion of algal biomass into oily substances. This study investigated the influence of heterogeneous catalyst Fe/ZSM-5 on HTL of Nannochloropsis sp. The experiments were specifically conducted at 320~410 °C with a retention time of 60 min and an initial pressure of 2.9 MPa. As for the control experiment, with the increase in temperature, the biocrude oil yield increased firstly and then decreased, whilethe char yield was constantly declined. Upon the loading of Fe/ZSM-5 catalyst, the production of biocrude oil was promoted, and the formation of char was inhibited. Especially, at 365 °C, biocrude oil yield increased from 30.40% to 38.10%. Moreover, the catalyst significantly impacted on the elemental distribution in products of HTL (biocrude oil, aqueous phase, char and gas). The content of C in biocrude oil increased by 7.94%, and the N content decreased by 6.12%. The increased C content in biocrude oil was probably due to the migration of C from aqueous phase, while the decrease N content resulted from the transfer of N to aqueous phase. In addition, Fe/ZSM-5 catalyst resulted in increased generation of H_2 and CH_4. This study reveals that Fe/ZSM-5 catalyst not only enhanced the production of biocrude oil, but regulated distribution of carbon and nitrogen elements in products.

Comprehensive evaluation of combining hydrothermal pretreatment (autohydrolysis) with enzymatic hydrolysis for efficient recovery of monosaccharide and ferulic acid from corn bran

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Corn bran, as agricultural byproduct, is a renewable source for sugars and natural ferulic acid production. However, corn bran is a particularly recalcitrant substrate and the complete enzymatic hydrolysis is not achieved in the ever reported papers. In this study, corn bran was treated by autohydrolysis followed by enzymatic hydrolysis for monosaccharide and ferulic acid recovery. The autohydrolysis conditions had great influences on depolymerization and solubilization of carbohydrates, ferulic acid and acetyl group, and on the enzymatic hydrolysis of autohydrolysis residues. Arabinan was depolymerized and solubilized more easily during autohydrolysis compared to xylan, esterfied ferulic acid and acetyl group. Besides, the enzymatic xylose yield showed strong linear correlation with the contents of arabinan, ferulic acid and acetic acid in autohydrolysis residues while correlations between enzymatic glucose yield and hemicellulose contents were separated into two stages with different slopes. The addition of a few debranching enzymes to commercial cellulase and xylanase hardly enhanced enzymatic hydrolysis of autohydrolysis residues, whereas enzyme blend from Aspergillus oryzae and Eupenicillium parvum showed significant synergistic effect, making it superior to individual crude enzyme or commercial enzyme mixture. Desirable combined hydrolysis yields of glucose (72.26%), xylose (75.87%), arabinose (76.95%) and ferulic acid (74.13%) were obtained after autohydrolysis at 165°C for 40 min and subsequent hydrolysis by enzyme blend produced by A. oryzae and E. parvum.

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The Non-Hydrolytic Proteins from Actinomycetes M2 Enhance the Hydrolysis of Cellulose by Cellulase

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Bioethanol can be produced by using microorganism-fermentable sugars biochemically converted from lignocellulose. However, the high cost of lignocellulose degrading enzymes limits the large-scale industrial application of bioethanol using bioconverted fermentable sugars as material. Therefore, to make it more approachable to bioethanol converted from lignocelluloses hydrolysis, it's necessary to get optimisation of lignocellulolytic enzyme cocktails. There are some non-hydrolytic proteins (also called "cellulase synergistic protein") which can interact synergistically with cellulase in cellulose hydrolysis, leading to lower cellulase loadings and lower cost. In this study, a new isolated synergistic protein-producing strain strain of Actinomycetes M2 was cultivated on the Gauserime synthetic medium containing 2 gL-1 beef extract， 5 gL-1 peptone(w/v) for 120 h and the resulting culture was centrifugated. The pellet was washed twice with distilled water and was then sonicated on ice. The cell lysate(intracellular proteins) was collected after centrifugation by 85% ammonium sulfate precipitation. The mixed proteins were divided into ten parts(components) through hydrophobic chromatography by non-continuous linear gradient elution. The cellulase and synergistic activity of each parts of the proteins were determined. It was showed that every component could promote the hydrolysis activity of cellulase on filter paper. The highest sugar yield was 1.5-fold greater than what it was in the presence of cellulase alone at a cellulase concentration of 0.4 FPU/g of. filter paper. But all of them could't degrade filter paper without cellulase. It was also showed that there was a variety of non-hydrolytic protein from Actinomycetes M2 enhancing cellulose hydrolysis by cellulase. Further studies are necessary to determined these intracellular non-hydrolytic proteins including the purification and the mechanism of enhancement of enzymatic hydrolysis of cellulose and structure analysis of the proteins.

Effects of Ice Plant (Mesembryanthemum crystallinum) Callus Extract on Gene Expression of Human Dermal Fibroblast under UV Exposure

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UV exposure is the principal cause of extrinsic aging, often referred to photoaging. The photoaged skin typically shows a variety of clinical manifestations, including thickened epidermis, mottled discoloration, deep wrinkles, laxity, dullness and roughness, which are resulted from the reduction of collagen, elastic fibers and glycosaminoglycans (e.g., hyaluronic acid). Antioxidant-related genes (SOD2 and CAT) and collagen-related genes (COL1A1 and TIMP1) were selected for analysis of the mRNA expression in human dermal fibroblasts (CCD-966SK) by qPCR. In present study, UVA-treated (15 J/cm^2) cells showed a decrease in SOD2, CAT ($p < 0.001$) and COL1A1 ($p < 0.05$) gene expression indicating the decline of antioxidant ability and collagen formation. However, treating with Cell Young® Ice Plant (2 mg/mL, 24 h) before UVA exposure, SOD2, CAT, COL1A1 and TIMP1 genes were up-regulated significantly ($p < 0.01$) for 9.5, 2.7, 1.7 and 3.8 times, respectively, compared to those of the control group, and for 10.2, 4.3 ($p < 0.001$), 2.1 and 3.8 times, respectively, compared to those of the UVA (only) group. Therefore, it was demonstrated that Ice Plant extracts affects the antioxidant- and collagen-related gene expression, and shows positive effects on endogenous antioxidant activity and skin collagen preservation.

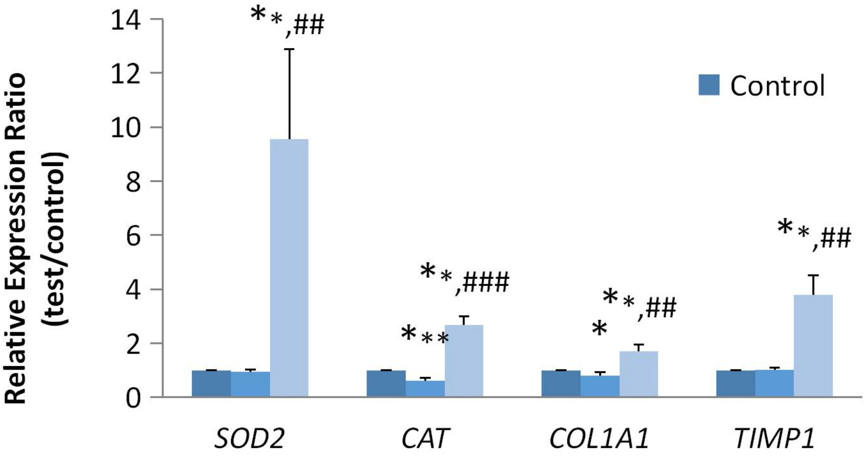

Figure 1.

Potential of Microbial Community in the Bioconversion of Lignocellulose into Biofuels

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Biofuels, widely considered to be an attractive and sustainable alternative to replace fossil fuels, can be produced from various environmental biomass. Lignocellulosic biomass is regarded as a potential renewable source for biofuels conversion because of its wide and abundant distribution. However, it still offers a worldwide difficult problem on how to effectively utilize, and there has been limited investigation on the microbial consortia on the conversion of lignocellulose into biofuels. In the present study, two stable microbial consortia were achieved through the serial subcultures under the anaerobic condition by using cellulose or xylan as the sole carbon source, respectively. Improvement of the substrate degradation as well as the generation of biofuels (e.g., butanol, ethanol and hydrogen) was both observed from the cultures with the exogenous consortium. Analysis from the 16S rRNA gene high-throughput sequencing further pointed out the microbial richness (OTUs number) was strongly related to the substrate during the generation transferring. The major microbial strains were determined to belong to Clostridium genus when using cellulose as the substrate, while bacteria from Ruminococcus genus played an important role in the utilization of xylan. By comparing the relationship between various microbial consortia, the results demonstrated that the specific interaction of microflora will be beneficial to the lignocellulose utilization, and a strategy by combining the microbial consortia with high biofuels-producing bacterial strain was also developed for the bioconversion of lignocellulosic materials into biofuels.

Proper Evaluation and Representation of MFC Performance and Electrochemistry

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Currently, performance evaluation methods of a microbial fuel cell (MFC) are not properly defined in the MFC field. In this study, we compared 4 different methods for MFC power evaluation: IV curve method with three different scan rate and an external resistor method. IV curves were measured at three different scan rates of 0.1, 1 and 10 mV/s, and an external circuit of an MFC was connected and fixed for 30 minutes for each resistance in the external resistance method. In the IV curve, maximum power densities were 1,253 mW/m^2 for the external resistance method, 1,518 mW/m^2 for 0.1 mV/s, 2,287 mW/m^2 for 1 mV/s, and 3417 mW/m^2 for 10 mV/s. Maximum power densities for 0.1, 1, 10 mV/s were 49, 83, and 173% higher than that of the external resistance method. Cyclic voltammetry (CV) showed similar performance among the experiments, confirming that there was negligible change in anode and cathode in the experiments. In maximum power density comparison between 3 scan rate and external resistance method, the scan rate of 10mV/s showed much difference from the external resistance method. The scan rate of 1mV/s showed about twice the external resistance method. Finally, the scan rate of 0.1mV/s showed the most similar value with the external resistance method.

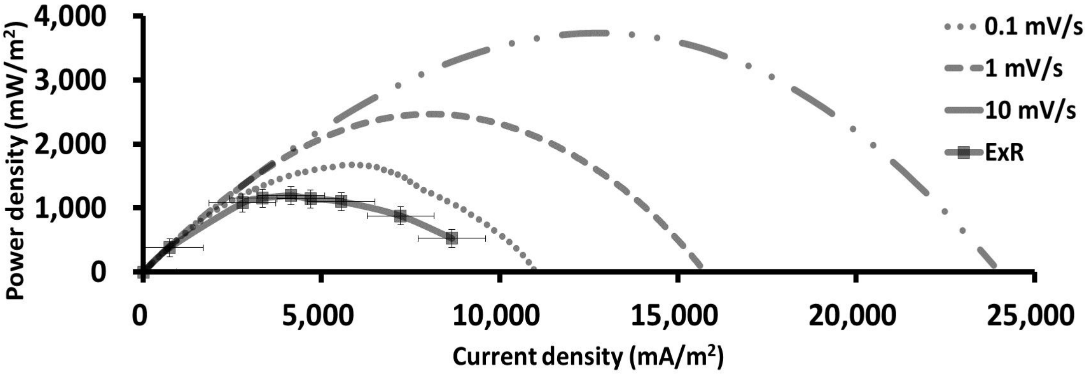

Figure. Power density curves of different scan rate and ExR.

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Whole-Cell Biocatalytic Selective Oxidation of HMF to 5-Hydroxymethyl-2-Furancarboxylic Acid

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Catalytic upgrading of 5-hydroxymethylfurfural (HMF), an important bio-based platform chemical, is of great interest currently. In this work, we reported biocatalytic oxidation of HMF to 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) by using a newly isolated strain Comamonas testosteroni SC1588. Compared to growing cells, resting cells were found to be a better biocatalyst for the synthesis of HMFCA. This strain exhibited high tolerance to HMF (up to 180 mM). However, its catalytic performances were highly sensitive to pH. The product exerted a significantly negative effect on the catalytic performances and viability of the cells, partially due to the acidity of this compound. The product inhibition and toxicity toward this strain were reduced considerably after adjusting pH of the reaction mixtures to 7.0. Excellent substrate conversions (approximately 100%) and good HMFCA yields (88-99%) were obtained when the substrate concentrations were less than 130 mM. In addition, the HMFCA synthesis could be improved significantly by the combination of histidine addition with pH tuning at higher substrate concentrations. Catalytic activities of the cells increased markedly when they were cultivated in the presence of a low concentration of furfural and furfuryl alcohol. HMFCA was afforded in the yield of approximately 98% after 36 h at the substrate concentration up to 160 mM in a scale-up synthesis. The crude product was obtained with the purity of 94% and a recovery of 99% after simple extraction. Besides, this strain was capable of selectively transforming other furfurals to the target acids with good yields of 90-93%.

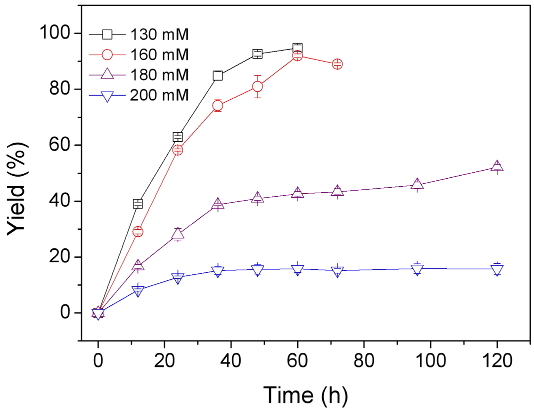

Figure 1. Improved synthesis of HMFCA

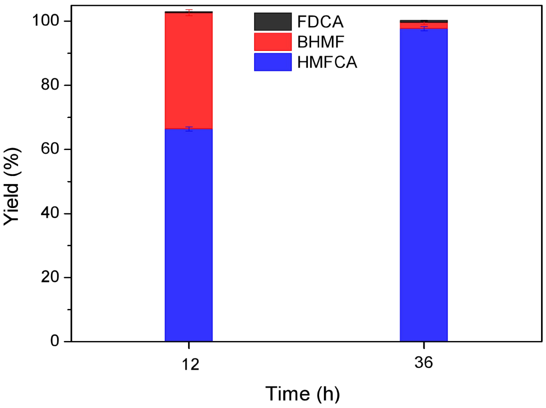

Figure 2. Scale-up synthesis of HMFCA

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A High-Performance Anode for Microbial Fuel Cells Based on Carbon Cloth Modified by Nature Nitrogen-Enriched Material

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Anode modification was an efficient approach to improve the anode performance for the bacteria attachment, substrate oxidation and extracellular electron transfer of microbial fuel cells (MFCs). In this study, we reported a simple process for anode modification, by which a carbon cloth was modified by immersing carbon cloth in the suspension of carbonized chlorella pyrenoidosa. The electrochemical/bioelectrochemical performance of the modified anode were evaluated by chronoamperometry, cyclic voltammograms (CVs) and electrochemical impedance spectroscopy (EIS) in a half-cell system respectively. The results showed that the modified anode obtained a higher maximum current density of 2.12 mA/cm^2 (under controlled potential of +50.00 mV vs. Ag/AgCl) after start up, a higher oxidation current response of 2.86 mA/cm^2 in CV tests and a lower charge transfer resistance of 105.40 Ω, compared to the anode based on unmodified carbon cloth (1.46 mA/cm^2, 1.51 mA/cm^2 and 243.20 Ω), achieving an improvement of current density by 45% and 89%, and a decrease of internal resistance by 57% respectively. These results indicated that the modified anode had a better catalytic activity for substrate oxidation and a lower extracellular electron transfer resistance. Therefore, anode modification by decorating carbonized CP was a simple and effective method to improve the anode performance.

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Assessment of Start-Up Time of Microbial Fuel Cells

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For accurate evaluation, it is necessary to know when an inoculated MFC reaches its maximum performance. For this purpose, performance and electrochemistry of fours MFCs, which consisted of PVDF cathodes and graphite fiber brushes anodes, were characterized over time. Polarization test illustrated that maximum power density of all reactors became stable after 9 weeks. Although there were variations afterwards, but they were negligible. On average, maximum power densities after 9 weeks were 2,994 mW/m^2, 2,983 mW/m^2, 2,444 mW/m^2 and 836.8 mW/m^2 in order of CH 13, CH 11, CH 12 and CH 10. In CH 10, the maximum power density at the 17th week improved considerably. Cyclic voltammetry experiments also indicated same period of operation making the MFC more mature while the current density of each anode achieved stable state. Even though CH 10 showed quiet lower performance, after 11 weeks, its current density increased close to its initial value. This change was in good agreement with other reactors. For the reason that used cathodes and anodes showed the similar performances, it was confirmed that an inoculated MFC needs ordinary start-up time of 9 to 11 weeks to gain its maximum performance, which were manifested by the enlargement of current production and maximum power density in practical.

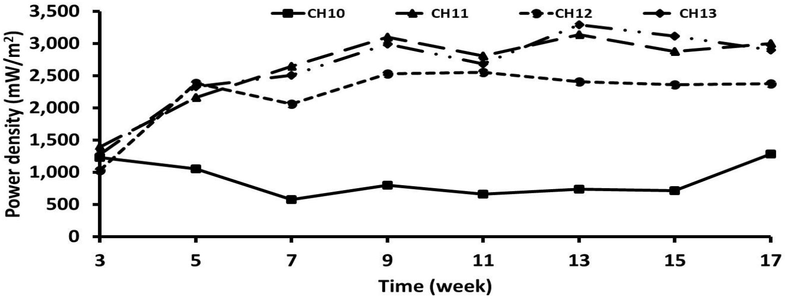

Figure. Time-series Maximum Power Densities of an MFC

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High Butanol Production from Undetoxified Lingocellulosic Hydrolysate by Clostridium Acetobutylicum NJ4

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Biobutanol production has been gained increasing attention due to the concerns on environmental issues and non-renewability of fossil fuels. Bioconversion of lignocellulosic hydrolysate to butanol is impeded by the toxic effects of inhibitors which are generated during pretreatment and hydrolysis processes. Here we describe a wild-type Clostridium acetobutylicum NJ4 with high tolerance to the lignocellulose-derived inhibitors and its capability to transform these inhibitors. Strain NJ4 is capable of tolerating over 60 mM furfural, 60 mM hydroxymethylfurfural, and 6.6 mM vanillin, respectively, and is able to convert 55 mM furfural into furfuryl alcohol within 90 h. The high furfural tolerance enables strain NJ4 to produce 7.45 g/L butanol from dilute sulfuric acid pretreated corn stover hydrolysate that bypassed the detoxification step. The capability of strain NJ4 to produce butanol from un-detoxified hydrolysate lays the foundation of cost-effective biofuel production from lignocellulosic materials.

Butanol Production from Seaweed by Clostridium Acetobutylicum NJ4 via Simultaneous Saccharification and Fermentation (SSF)

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Butanol can be biosynthesized by mesophilic and solventogenic Clostridia from starch or monosugars, however, the costs of substrate account for a relatively high share in the price of butanol production. Although lignocellulose shows great potential as the feedstock for biofuel generation, however, they usually contain high amount of lignin, which cannot be easily degraded. Seaweed, an abundant, renewable and fast-growing bioresource, has attracted more and more attention owning to its low or even no lignin content. In this study, Clostridium acetobutylicum NJ4 possesses a relatively high utilization capacity of various monosugars, like glucose, xylose, galactose etc., and the butanol production achieved 14.0 g/L, 13.9 g/L and 12.4 g/L, respectively. Furthermore, it showed simultaneous utilization capacity of mixed sugars containing different ratios of glucose, galactose, xylose, and the butanol production could achieve 13.7 g/L. Considering glucose, galactose, xylose are the main sugar ingredients of seaweed, this demonstrates the possibility of using seaweed as the potential biomass for butanol production by C. acetobutylicum NJ4. After hydrolyzed of seaweed using thermal acid process, and neutralized with 5 M NaOH, the hydrolysates contained 38, 32, 12, 5 and 3 g/L of L-galactose, D-glucose, D-xylose, L-glucuronate, D-mannitlo etc. Lastly, C. acetobutylicum NJ4 could efficiently convert the seaweed hydrolysate to 11.49 g/L butanol, representing the highest butanol production from seaweed by solventogenic Clostridium sp.

Genome Shuffling: Advances and Applications for Microbial Strain Improvement.

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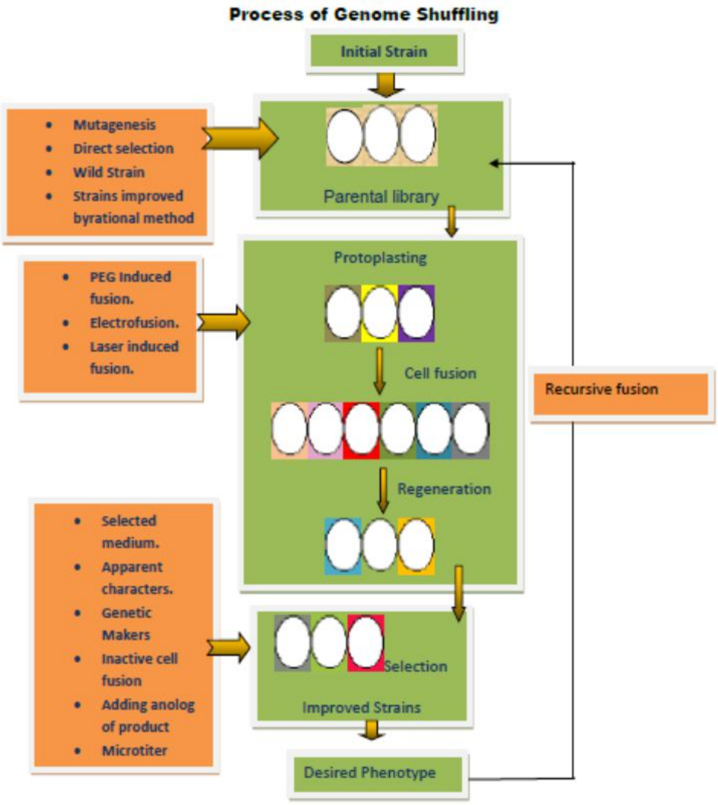
Classical strain improvement technique which involves several rounds of recombination has significantly been successful for microbial strain improvement but this is a slow process. Genome shuffling has demonstrated to be an effective and reliable method for rapid engineering of complex phenotypes, as witnessed in several other examples of improvement in microbial strain development for desired phenotypes [1]. Genome shuffling offers the advantages of accumulated beneficial mutations and the screening of undesired mutations due to simultaneous changes at different positions throughout the genome without the necessity for complete genome sequencing data or genome network information and therefore yields microbes of superior properties[2]. Wild type strains of Clostridium acetobutylicum butanol-producing strain GX01 and Lactobacillus mucosae butanol-tolerant strain M26 were subjected to mutagenesis combining N-methyl-N-nitro-N-nitrosoguanidine induction with genome shuffling. After four successive rounds of genome shuffling, the C. acetobutylicum shuffled strain GS4-3 showing greater levels of fermentation performances compared to the wild type strains was isolated [3].This review makes an effort to look the advantage of genome shuffling, introduce the procedure of this technology, recent strides and applications of this method for microbial strain phenotype improvement and then discuss future opportunities in the development of this technology.



Acknowledgement

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Chlorella Pyrenoidosa Derived Nitrogen-Doped Porous Carbon as Monolithic Air Cathodes for Microbial Fuel Cells

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Nitrogen-doped porous carbon has been demonstrated as a cost-efficient oxygen reduction reaction (ORR) catalyst for microbial fuel cells. However, conventional technique used for fabricating carbonaceous cathode is complex and time consuming. Herein, we report an easy-fabricating, three-dimensional and monolithic air-cathode derived from Chlorella pyrenoidosa (CP-cathode). The scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS) indicated that the porous structure of CP-cathode can provide sufficient channels for oxygen and proton transfer, and inherent nitrogen can serve as the active sites for the ORR activity. In addition, cathodes with different pore sizes and the same CP loading were also used to study the effect of pore size on the oxygen supply of cathode performance of MFCs. Results indicated that an optimal CP-cathode can realize a higher power density than that of Pt/C cathode. Therefore, the proposed CP-cathode can be used as a cost-efficient and easy-fabricating air cathode for MFC application.

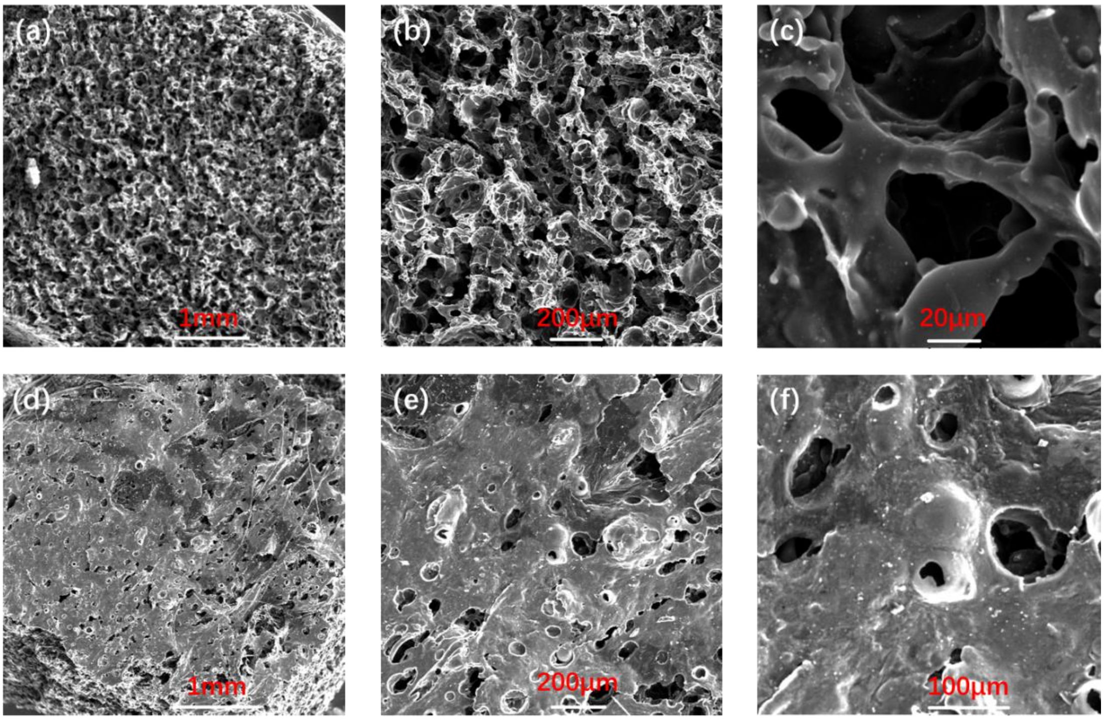

Fig.1 SEM images of CP-cathode (a-c) cross section and (d-f) outside surface.

Maximum Power Density, Polarization Resistance and Impedance of Microbial Fuel Cells Differing in Anodic Number and Configuration

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In order to improve the performance of the microbial fuel cell (MFC), proper placement of cathode and anode is required. In this study, electrochemistry and performance of an MFC with different anodic number and configuration were compared. In the horizontally arranged anode to a cathode (H form), resistance of the anode electrode decreased from 15.9 Ω to 1.6 Ω as number of brushes increased from 1 to 4. Maximum power density was also increased from 1,114 mW/m^2 to 1,721 mW/m^2 as number of brushes increased from 1 to 4. In the vertically arranged anode, as a number of the bush anode more than 2 did not decrease internal resistance greatly, and maximum power density was slightly improved. However, current density in the vertically arranged anode was 64.5 mA/m^2, which was 18.7 mA/m^2 higher than the horizontally arranged anode (45.8 mA/m^2). In conclusion, it was found that the horizontally arranged anode is better for increasing power production and the vertically arranged anode is better for increasing current production.

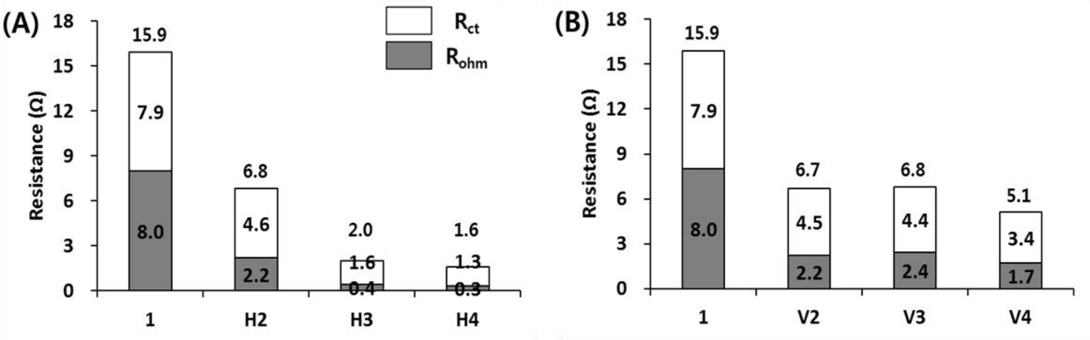

Figure. Distributions of charge-transfer impedance (□) and ohmic impedance (■) of the horizontally-located anodes (A) and the vertically-located anodes (B).

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Direct Conversion of Food Waste into Biobutanol by An Amylolytic Clostridium Sp. Strain XF10

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In this study, a one-step fermentation process for production of butanol and hydrogen from food wastes by using amylolytic Clostridium sp. strain XF10 is developed. This strain is able to excrete indigenous amylases (induced by starchy materials), which naturally hydrolyzes 180 g/L of food wastes and produce 14.1 g/L of butanol. Enzymatic structure and activity analysis show that calcium could promote the activities of amylases. Moreover, supplementation of external calcium ions to the food wastes medium could further improve butanol to 15.6 g/L, which is 25% higher than that in a similar study (12.5 g/L). The promoted amylase activities could further shorten the fermentation duration and enhance the butanol productivity to 0.17 g/L/h, which is comparable to that (0.20 g/L/h) in glucose based medium, indicating a sustainable approach to solve environmental sustainability issues and generate bioenergy.

Enhancing the Thermostability of A Recombinant B-Agarase Agaxa Fermented from E. Coli

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As a renewable resource, marine biomass (e.g., algae) are currently considered to be the next-generation source for bioenergy production, and agarases from marine bacteria are regarded as the most important enzymes that utilize marine biomass, such as agar. In this study, AgaXa, an agarase that was previously identified, was fermented from a recombinant E. coli strain, and the process was optimized to increase its production level by investigating the carbon and nitrogen sources in the medium, culture temperatures as well as the types of fermentation. Linear fed-batch cultivation within a 5 L bioreactor (25 ^{o}C and 0.1 mM IPTG induction) resulted in the highest production (1.5×10^{4} U/L), demonstrating a six-fold improvement over the non-optimized conditions. For further ideal industrial applications, effective protective reagents are used to enhance the stability of AgaXa, and the optimal protective reagent concentrations to maintain enzymatic activity were determined to be the addition of Na^{+} (1.8 mM), glucose (1.37%), glycerol (16.97%), and pectin (0.21%). By applying such protective reagents, more than 80% of enzymatic activity was retained even when the agarase was incubated at 85 ^{o}C.

Comprehensive Investigation of 2-Phenylethanol Production by Using Yarrowia Lipolytica

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2-Phenylethanol (2-PE) is considered as an important fragrance ingredient broadly used in food and cosmetic industries due to its mild, warm and rose-honey-like odor. It can be extracted from some plants and chemically synthesized, but the costly production process and low quality of 2-PE hinder their wide application in the market. To meet the increasing demand of consumers for natural flavors, biological production of 2-PE has emerged as a vivid alternative to the traditional extraction processes[1].

Yarrowia lipolytica is a promising candidate in biotechnological processes due to its safe and robust property and wide carbon utilization spectrum[2]. This study further explored the potential of Y. lipolytica for 2-PE production. After comprehensive investigation of the effects of various nitrogen sources and the addition time on 2-PE production, it was confirmed that the 2-PE production closely associated with cell growth. Furthermore, compared to glucose, glycerol is more superior for 2-PE production (1.35 g/L) as it can provide more NADH for Ehrlich pathway. Interestingly, a high production of 2.65 g/L of 2-PE with a yield of 0.53 g/g (2-PE/L-Phe) was obtained with sodium acetate as the carbon source and 5g/L L-Phe as the nitrogen source after 244 h fermentation, representing the highest report by Y. lipolytica[3]. This study provides a promising alternative to turn the waste of industry into more value added product.

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Impairment of NADH Dehydrogenase and Regulation of Anaerobic Metabolism by the Small RNA RyhB and NadE for Improved Biohydrogen Production in Enterobacter Aerogenes

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Background

Enterobacter aerogenes is a facultative anaerobe and is one of the most widely studied bacterial strains because of its ability to use a variety of substrates, to produce hydrogen at a high rate, and its high growth rate during dark fermentation. However, the rate of hydrogen production has not been optimized. In this present study, three strategies to improve hydrogen production in E. aerogenes, namely the disruption of nuoCDE, overexpression of the small RNA RyhB and of NadE to regulate global anaerobic metabolism, and the redistribution of metabolic flux. The goal was to clarify the effect of nuoCDE, RyhB, and NadE on hydrogen production and how the perturbation of NADH influences the yield of hydrogen gas from E. aerogenes.

Results

NADH dehydrogenase activity was impaired by knocking out nuoCD or nuoCDE in E. aerogenes IAM1183 using the CRISPR-Cas9 system to explore the consequent effect on hydrogen production. The hydrogen yield from IAM1183-CD(ΔnuoC/ΔnuoD) and IAM1183-CDE (ΔnuoC/ΔnuoD/ΔnuoE) increased by 24.5% and 45.6% in batch culture (100mL serum bottles). The hydrogen produced via the NADH pathway increased significantly in IAM1183-CDE, suggesting that nuoE plays an important role in regulating NADH concentration in E. aerogenes. Batch cultivating experiments showed that by the overexpression of NadE (N), the hydrogen yield of IAM1183/N, IAM1183-CD/N, and IAM1183-CDE/N increased 1.06-, 1.35-, and 1.55-fold, respectively, compared with IAM1183. Particularly worth mentioning is the strain IAM118-CDE/N reached 2.28 mol in H_2 yield, per mole of glucose consumed. IAN1183/R, IAM1183-CD/R, and IAM1183-CDE/R showed increasing H_2 yields in batch culture. Metabolic flux analysis indicated that increased expression of RyhB led to a significant shift in metabolic patterns. We further investigated IAM1183-CDE/N, which had the best hydrogen-producing traits, as a potential candidate for industry applications using a 5-L fermenter; hydrogen production was up to 1.95 times greater than that measured for IAM1183.

Conclusions

Knockout of nuoCD or nuoCDE and the overexpression of nadE in E. aerogenes resulted in a redistribution of metabolic flux and improved hydrogen yield. Overexpression of RyhB had an significant change on the hydrogen production via NADH pathway. A combination of strategies would be a novel approach for developing a more economical and efficient bioprocess for hydrogen production in E. aerogenes. Finally, the latest CRISPR-Cas9 technology was successful for editing genes in E. aerogenes to develop our engineered strain for hydrogen production.

Utilization of Energy Crop Italian Ryegrass in Cd Contaminated Paddy Field

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Cadmium (Cd) is one of the most toxic heavy metal elements. Intake of Cd from rice caused Itai-itai disease in the past and it is still a threat for human health and far more people are affected by Cd exposure than previously thought. China is faced with the land problem of heavy metal pollution, especially Cd-pollution. Rice (Oryza sativa), an important staple food for nearly a half of the world's population, is a major source of Cd intake. Italian ryegrass (*Lolium multiflorum* Lam) is a fast establishing, winter active herbaceous annual or biennial grass. It is considered as a high-potential bio-ethanol resource and due to its stress resistance of Cd, it could be applied to phytoremediation. It is an approach to plant Italian ryegrass in Cd-contamination paddy field in winter fallow paddy field to harvest lignocellulosic biomass. It could avoid occupation of cultivated land competed with staple crop, simultaneously accomplish phytoremediation of soil. In our study, we conducted the Italian ryegrass–Rice Rotation (IRR) plots field experiment in a middle level Cd-contamination paddy field (1.73-2.71mg/kg) in Hunan province. All of the treatments including four duplicates: winter fallow plots, cutting plots and non-cutting plots were randomly distribution. We research the Cd contents of different parts in Italian ryegrass and rice. The results show that : (1) in Italian ryegrass, the Cd concentrations of different parts are root>culm>blade, and there is no significant difference in blade and culm between cutting plots and non-cutting plots, but in root the Cd content of cutting plots is significant higher than non-cutting plots. (2) In rice, the Cd concentrations of different parts are root>culm>leaf>branch>rice hull>brown rice. Similar with other plants, the Cd accumulation of Italian ryegrass and rice is a strong gradient in Cd concentrations: roots > shoots. In the system, rice yield does not have significant different with all treatments. Also profit from this rotation system, 117.67kg/plot fresh weight and 16.14kg/plot dry weight feedstock were harvested in cutting plots, and 113.27kg/plot and 15.13kg/plot dry weight feedstock were harvested in non-cutting plots. It demonstrates that the cutting Italian ryegrass could enhance the annual biomass. With IRR system, we could not only harvest bio-energy feedstock to solve the problem of planting energy crop competed with staple crop, but also extract the heavy metals (special the Cd) from paddy field to mitigate excessive Cd contaminated soil.

Mechanistic Study on NaCl-Promoted Conversion of Xylose to Furfural

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Furfural is an important value-added chemical, widely used in oil refining, plastics, medicine, and pesticide industries, with an annual output about 300,000 tons. Industrially, inorganic acid catalysts, such as HCl, were used for the conversion of hemicellulose component in the agricultural waste and wood residue to furfural, with a yield of about 40-50%.

In this work, the mechanism for the NaCl promoted conversion of xylose to furfural in H_2O was studied. The conversion of xylose under different temperatures (373-433 K) and time (15-360 min) with or without addition of saturated NaCl was firstly studied. It was found that the conversion of xylose and the yield of furfural gradually increased with increasing temperature, while the conversion of xylose and the yield of furfural increased with increasing NaCl. At 433 K for 5 h, the conversion of xylose increased from 40.9% (without NaCl) to 64.4% (in presence of saturated NaCl). And the yield of furfural increased from 26.6% (without NaCl) to 37.4% (in presence of saturated NaCl). The interaction between NaCl and xylose was investigated respectively using DMSO-d_6 and D_2O as solvent. Due to the strong hydrogen bond acceptability of Cl^- in DMSO-d_6 solvent, it is easy to attack C-OH-2,3,4 of xylose, which promoted the dehydration of xylose. According to the literature, xylose dissolved in H_2O exists in the form of furan ring. It was found that Cl^- have an effect on the ring hydrogens after more activated hydroxyl groups was attacked by D_2O. This suggested that Cl^- had a weak effect on the C of xylose. *In situ* IR results indicate that increasing the temperature or NaCl concentration accelerated the cleavage of the xylose C1-O6 bond, which promoted the formation of furfural.

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Mechanistic Study on NaCl-Promoted Conversion of Xylose to Furfural

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Furfural is an important value-added chemical, widely used in oil refining, plastics, medicine, and pesticide industries, with an annual output about 300,000 tons. Industrially, inorganic acid catalysts, such as HCl, were used for the conversion of hemicellulose component in the agricultural waste and wood residue to furfural, with a yield of about 40-50%.

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High Value-Added Utilization of Industrial Lignin: Preparation of Lignin-Based High Specific Capacity Supercapacitor

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The abundant renewable lignocellulosic biomass derived from plant sources has received wide attention in recent years. Especially, the high value-added extensive development and utilization of biomass is of great meaningful to the sustainable development of human society. As an important by-product from paper industry, the high value-added utilization of industrial lignin has a more important practical significance for mitigating environmental pollution and resource crisis. Recently, we demonstrated a novel lignin-based carbon/zinc oxide (LC/ZnO) hybrid composite using industrial lignin that was extracted from paper pulping waste liquor as the carbon source. The LC/ZnO hybrid composite was prepared through a facial one-pot carbonization method. The prepared LC/ZnO is composed of well dispersed ZnO nanoparticles embedded on a lignin-based carbon nanosheet. The LC/ZnO composite shows high specific surface, large-size nanographites and good electrical conductivity, which demonstrated excellent electrochemical performance. The LC/ZnO hybrid composite obtained at 700 ℃ displayed very high specific capacitance (192.8 F g^{-1}), outstanding durability and superior rate performance in two-electrode systems in 6M KOH. The capacitance maintained 178.9 F g^{-1} after 3000 galvanostatic charge-discharge cycles. On account of the facile preparation of LC/ZnO hybrid composite, we believe that this research gives a facile alternative method for the preparation of lignin-derived high specific capacity supercapacitor and other advanced energy storage/conversion devices.

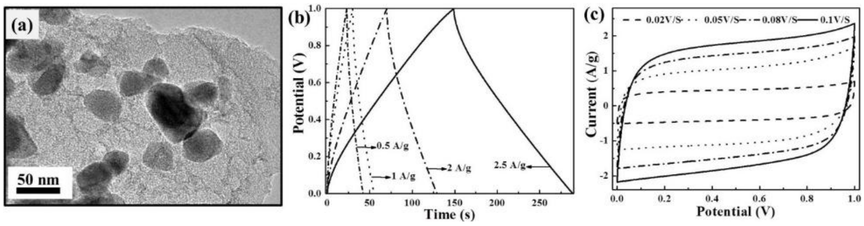

Fig. 1. (a) TEM image of the LC/ZnO, GCD (b) and CV (c) curves of the LC/ZnO.

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In Situ Precipitation of CuS Nanocrystals on Cellulose Nanofibers with Quaternized Chitosan as Stabilizer and Adhesive to Prepare Highly Conductive Paper

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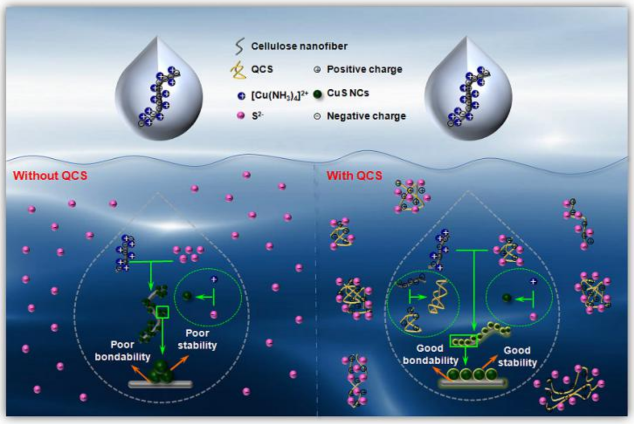
This work reports a feasible method to *in situ* precipitate uniform copper sulfide nanocrystals (CuS-NCs) on cellulose nanofibers (CNF) by untilizing quaternized chitosan (QCS), which act as stabilizer and adhesive to prepare the highly conductive paper. QCS provides a gap confinement effect to avoid the aggregation of CuS-NCs, and anchors NCs on the surface of negatively charged CNFs by electrostatic self-assembly to form a homogeneous coating due to the highly positive charge. In this way, CuS-NCs show a very uniform distribution on CNFs, which enhances the conductivity of composite paper from 30.33 $\mathrm{Scm^{-1}}$ to 110.56 $\mathrm{Scm^{-1}}$. The highly conductive paper has promising application in electric devices, sensors, super capacitors, and solar cells. This study not only provides a novel strategy to develop the uniform distribution of CuS-NCs on CNFs for fabricating the highly conductive paper, but also allows the biopolymer to obtain high value applications.



Doubly pH-Responsive Pickering Emulsion Stabilized by Lignin Nanoparticles

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Pickering emulsions play an important role in many industrial processes and commercial products.[1] Currently, there is growing interest in developing stimulus-responsive particulate emulsifiers for Pickering emulsions because of their significant advantages over conventional surfactant systems.[2] pH-responsive Pickering emulsions have attract special attention, as they are the simple and easily realizable thanks to a breadth of chemicals and materials available.[3] A simple reversible oil-in-water pH-responsive Pickering emulsion based on the alkali lignin (AL) from pulping black liquor was developed. AL was first modified by quaternization to synthesize amphoteric alkali lignin (AAL). AAL with pH-responsive characteristics and is soluble in acidic and basic water. However, in neutral solution, AAL becomes insoluble and particles are formed, which could be used as emulsifier for doubly pH-responsive Pickering emulsions. Emulsions are stable at pH values between 3 and 10. Above and below this pH range, the system demulsifies, resulting in a reversible Pickering emulsifier having two pH-controlled, reversible transitions. Five organic solvents (n-decane, liquid paraffin, n-hexane, toluene, and dichloromethane) were chosen as the oil phase. Reversible emulsions were formed for all five oils. Lignin-based Pickering emulsions can be cycled between stable and unstable many times upon alternating the pH of the aqueous phase, the droplet size did not change significantly and had good storage stability. The high salt tolerances of lignin-based Pickering emulsions are highly beneficial in various applications including oil recovery. The method for in situ formation of pH-responsive Pickering emulsions based on lignin will open up a new route to the preparation of a wide range of reversible emulsions.

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Enhanced Cr(VI) Removal by Polyethylenimine-Functionalized Phosphorus Doped Hierarchical Porous Biochar

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The amino-functional phosphorus-containing biochar derived from oil-tea shell are facilely fabricated through a two-step strategy, phosphoric acid (H_3PO_4) activation and amino (polyethylenimine, PEI) modification. Herein, the as-synthesized biosorbents were prepared for the removal of Cr(VI) from aqueous solutions. Efforts were focused on establishing relationships between textural and physical-chemical properties of the precursor and the resulting materials, and their adsorption capacity toward Cr(VI). The influence of contact time, adsorbent dose, Cr(VI) concentration, pH and temperature were also investigated. The adsorption of Cr(VI) by the functionalized biochar followed the pseudo-second-order kinetic model and the Langmuir-Freundlich adsorption isotherm model. The maximum adsorption capacities of H_3PO_4 activated precursor and PEI modified biosorbent were 183.4 mg/g and 306.8 mg/g, respectively. The Thomas models fitted very well with the breakthrough curves obtained in a continuous column process. The biosorbents before and after amino functionalization, and the one after sorption of Cr(VI) were characterized by Fourier transformed infrared spectroscopy, X-ray photoelectron spectroscopy and other analytical instruments. The H_3PO_4 activated biochar exhibited a high specific surface area (1056 m^2/g) with abundant functional groups, which is in favor of PEI grafting. The excellent removal performance toward Cr(VI) is demonstrated to be a structure-dependent surface chemical process between Cr(VI) and heteroatoms (N and P), as well as the effect of high surface area and pore structure. This work may provide insights for designing other functional materials for high-efficiency removal of other heavy metals from polluted water. The results herein revealed that the PEI modified biochar had a good potential as a suitable material for sorption of Cr(VI) from aqueous solution.

Production of 1,3-Propanediol: Co-Expression of Glycerol Dehydratase and 1,3-Propanediol Dehydrogenase Genes of Clostridium Perfringens and Biotransformation

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1,3-propanediol (1, 3-PD) is a promising versatile chemical compound which has a wide range of application in cosmetic, food, solvent, pharmaceutical industries. Especially, 1,3-PD is being used as a monomer for the synthesis of various polyesters and feedstock. With the increasing development of important applications of 1,3-PD, the demand for its production has been burgeoning around the world. 1,3-PD is usually produced by chemical method, and it also can be biosynthesized through two serialized glycerol's conversion by glycerol dehydratase (GDHt) and 1,3-propanediol dehydrogenase (PDOR). In view of various merits of biosynthesis of 1,3-PD, much focus has been attracted into the research of this area. In the present study, the *dhaB* gene encoding glycerol dehydratase and the *dhaT* gene encoding 1,3-propanediol dehydrogenase were cloned from an isolated strain of *Clostridium perfringens*, and then were co-expressed in *E. coli* BL21. The recombinant GDHt and PDOR were analyzed by bioinformatics methods based on the sequences of nucleotides and amino acids, respectively. Then, the recombinant enzymes were purified by nickel-chelate chromatography and characterized via pH and temperature optimization, substrate specificity assay and kinetic analysis. Subsequently, the biosynthesis conditions of 1,3-PD was optimized through biotransformation using the whole cell of BL21-*dhaT*-*dhaB*. Furthermore, based on the optimal conditions, the profile of 1,3-PD production was investigated via biotransformation. The bioconversion result showed that 1,3-PD production by whole cell of BL21-*dhaT*-*dhaB* was improved largely compared with the wild type strain of *Clostridium perfringens*. The result of this research may form a basis for the future work of 1,3-PD biologically synthesized.

Acknowledgement

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Preparation of a Light Colour Alkali Lignin with Hydroxypropyl Sulfonating and Application as Dye Dispersant

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Lignin dispersant has the good heat stability to the dye dispersion compared to naphthalene series dispersants. But the sulfomethylated alkali lignin has some disadvantages, such as high fiber staining, low sulfonate group and low molecular weight. The fiber staining of lignin is greatly dependent on the dark brown color, at the same time the hydroxy groups in lignin molecule can form hydrogen bond with the fibers. Some methods for reducing fiber staining by adding 5% ~ 15% of naphthalene sulfonate-formaldehyde condensates and chelating agent (EDTA) and modifying lignin with epoxy chloropropane [2]. A two-step method for reducing the color of lignin by first blocking the phenolic hydroxyl and then oxidizing the blocked lignin [3]. However, the reduction in hydroxyl of lignin by chemical methods can decrease dispersity and high temperature stability [4]. The acetylation can reduce lignin color, but substantially decrease water solubility [5]. A light-colored hydroxypropyl sulfonated alkali lignin (HSAL) was synthesized using pine alkali lignin by grafted-sulfonation and crosslinking reaction processes. The sulfonic group content and the molecular weight (*Mw*) of HSAL significantly increased while the phenolic hydroxyl groups reduced by around 80% of alkali lignin. More importantly, HSAL whitened the dark brown color of alkali lignin to light yellow; it exhibited very lower staining on fiber. The dispersity, heat stability and dye uptake of dye bath with HSAL had significantly improved compared to sodium lignosulfonate, sulfomethylated alkali lignin and naphthalene series dispersant.

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Effect of Lignin-Based Amphiphilic Polymers on the Absorption and Enzymatic Hydrolysis Kinetics of Cellulase on the Lignin and Cellulose Films

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The origin, amount, hydrophilicity, charge, molecular weight and distribution of lignin had significant influences on the enzymatic hydrolysis of lignocelluloses. Lignin-based polyoxyethylene ether (EHL-PEG) enhanced the enzymatic hydrolysis of lignocelluloses better than PEG4600, while effect of lignosulfonate (LS) was inferior to PEG4600. Effect of LS, EHL-PEG and PEG4600 on the absorption and enzymatic hydrolysis kinetics of cellulase on the lignin and cellulose films were investigated by Quartz Crystal Microbalance with dissipation monitoring (QCM-D). Results showed that LS and EHL-PEG combined with cellulase mainly by electrostatic attractive interaction and hydrophobic interaction respectively, and formed hydrophilic cellulase aggregates, that significantly reduced the nonproductive adsorption of cellulase on lignin. Both EHL-PEG nonionic amphiphilic polymers directly synthesized from EHL, and LS synthesized from EHL followed by combining with CTAB to form LS-CTAB catanionic surfactant, could be used to enhance enzymatic reaction of lignocelluloses, that not only improve the enzymatic hydrolysis and decrease the cellulase dosage, but also realize the efficient utilization of enzymatic hydrolysis lignin.

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Synthesis of Tannin-Immobilized on Cellulose and Its Adsorption Properties for Berberine Hydrochloride

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Cellulose was oxidized by sodium periodate to prepare aldocellulose, and then tannins were immobilized on aldocellulose by the reaction between the phenol ring of tannin and the aldehyde group of aldocellulose, where toxic crosslinking agents were not used. Tannin-immobilized on cellulose was characterized by scanning electron microscopy (SEM), infrared spectrum (IR) and X-Ray diffraction (XRD), and the adsorption properties for berberine hydrochloride were evaluated. The adsorption properties of tannin-immobilized on cellulose were improved due to the introduction of tannin. The maximum adsorption capacity of tannin-immobilized on cellulose for berberine hydrochloride was 149.6 mg/g, and the adsorption equilibrium could be obtained within 60 min. The isothermal adsorption for berberine hydrochloride fitted to the Freundlich model well. The sorption kinetics fitted well to a Pseudo-first-order rate model. The adsorption of tannin-immobilized on cellulose for berberine hydrochloride was mainly chemical adsorption, and the adsorption process was endothermic. The tannin-immobilized on cellulose have potential application value in the field of the separation and purification.

Adsorption of Uranium(VI) from Aqueous Solution Using Chemically Modified Aerial Root of Ficus Microcarpa

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Different from other heavy metals, uranium (U) is an element possessing both radioactivity and chemical toxicity (Chen, et al., 2017), which could be largely derived from nuclear energy production, such as nuclear power plants operation, uranium mining and milling activities, generating great deal of uranium containing wastewater. The treatment of uranium wastewater using waste biological material is of great significance. The adsorption behavior of U(VI) from aqueous solution using chemically modified aerial root of *Ficus microcarpa* (CMARFM) was comprehensively studied in the present work, in the terms of parameters such as adsorption time, solution pH, temperature, initial uranium concentration and adsorbent dosage via static batch experiments.

The results show that the adsorption capacity and removal rate of U(VI) from aqueous solution were significantly elevated after the aerial root of Ficus microcarpa was modified with KMnO4 solution, compared with the unmodified scenario. In general, the U(VI) removal rate and adsorption capacity by CMARFM increased in the early stage and then decreased with the increase in pH value, achieving an equilibrium at 60 min and almost irrespective of the temperature. Under the optimum adsorption conditions of 0.25 g CMARFM at pH 6.0, the maximum removal rate of 99% was achieved with 2.5 $mg\cdot L^{-1}$ U(VI) solution. The adsorption could be described by the Langmuir isotherm model and met pseudo- second - order kinetics equation in dynamics. Scanning electron microscopy Energy Dispersive X-Ray Spectroscopy (SEM-EDS) confirmed that the aerial root of Ficus microcarpa has a naturally microporous honeycomb structure, which possessed the structural characteristics of excellent U adsorbent. Fourier transform infrared spectroscopy (FT-IR) has shown that the main adsorption sites on CMARFM which adsorbed uranium in solution were mainly attributed to hydroxyl and amino. The results of this work indicated that chemically modified aerial root of *Ficus microcarpa* exhibited great potential in uranium containing wastewater control applications.

Figure 1 The photo of aerial root of *Ficus microcarpa* studied

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The Potential Inhibitory Mechanisms of the Soluble Compounds Derived from Steam Pretreated Biomass on the Current Commercial Enzyme Cocktail

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Although thermochemical pretreatment methods such as steam explosion have been widely used to pretreat various lignocellulosic biomass, it generates various soluble products that could strongly inhibit the enzyme medicated cellulose hydrolysis. Although water washing has been used to remove these soluble inhibitors, it requires large amount of water and energy, adds extra processing steps, and decreases final sugar concentration after enzymatic hydrolysis. In order to develop more efficient strategies to mitigate the enzyme inhibition, it is essential to better understand how these soluble compounds might affect the performance of cellulase cocktail and their detailed inhibition mechanisms behind. Most of previous studies mainly used various synthetic “model” inhibitors and only focused on the “traditional” cellulase cocktails such as Celluclast, while how the soluble compounds may affect the hydrolytic potential of the current enzyme cocktails remains unclear. In this study, the effects of the major inhibitory soluble compounds, derived from a range of “real-life” steam pretreated lignocellulosic biomass, on the major groups of enzyme activities (exo/endo-glucanase/β-glucosidase/xylanase activities) present in the state-of-the-art Novozymes Cellic CTec3 cellulase preparation were systematically evaluated. In addition, the major mechanisms behind these inhibitions such as the reversible/irreversible inhibition were assessed, and the potential strategies to overcome these inhibitory effects were discussed.

Doubly pH-Responsive Pickering Emulsion Stabilized by Lignin Nanoparticles

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Pickering emulsions play an important role in many industrial processes and commercial products.[1] Currently, there is growing interest in developing stimulus-responsive particulate emulsifiers for Pickering emulsions because of their significant advantages over conventional surfactant systems.[2] pH-responsive Pickering emulsions have attract special attention, as they are the simple and easily realizable thanks to a breadth of chemicals and materials available.[3] A simple reversible oil-in-water pH-responsive Pickering emulsion based on the alkali lignin (AL) from pulping black liquor was developed. AL was first modified by quaternization to synthesize amphoteric alkali lignin (AAL). AAL with pH-responsive characteristics and is soluble in acidic and basic water. However, in neutral solution, AAL becomes insoluble and particles are formed, which could be used as emulsifier for doubly pH-responsive Pickering emulsions. Emulsions are stable at pH values between 3 and 10. Above and below this pH range, the system demulsifies, resulting in a reversible Pickering emulsifier having two pH-controlled, reversible transitions. Five organic solvents (n-decane, liquid paraffin, n-hexane, toluene, and dichloromethane) were chosen as the oil phase. Reversible emulsions were formed for all five oils. Lignin-based Pickering emulsions can be cycled between stable and unstable many times upon alternating the pH of the aqueous phase, the droplet size did not change significantly and had good storage stability. The high salt tolerances of lignin-based Pickering emulsions are highly beneficial in various applications including oil recovery. The method for in situ formation of pH-responsive Pickering emulsions based on lignin will open up a new route to the preparation of a wide range of reversible emulsions.

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Effect of Solids Retention Time on the Performance of Membrane Bioreactors Treating Aromatic Hydrocarbon-Containing Wastewater

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Petroleum refining process produced large amount of oil refinery effluent, which is about 0.4-1.6 times the volume of refined oil[1]. It is a problematic stream account of abundant hazardous aromatic substances: polycyclic aromatic hydrocarbons (PAHs), benzene, toluene, ethylbenzene, xylene (BTEX)[2]. Membrane bioreactor (MBR) technologies, which combine biological treatment with membrane filtration, had been extensively employed for industrial wastewater treatment due to excellent effluent quality. Three submerged membrane bioreactors operated at different solid retention time (10d, 30d and 60d) were carried out to investigate the performance of MBR for treating aromatic hydrocarbon-containing wastewater. Good COD removal rate was achieved in three MBRs, but only 80% NH_4^+-N removal rate was in MBR operated at 10 days. Toluene and anthracene were efficiently (>99%) eliminated from wastewater during MBR process, and slightly higher removal rate was achieved at longer SRT. Volatilisation contributed significantly to toluene removal, and anthracene was almost completely biodegradable. LB-EPS content in MBR operated at 10 days was approximately four times higher than two other MBRs with SRT at 30 and 60 days. Mixed liquor filterability measured specific resistance to filtration (SRF) was positively correlated to the amount of LB-EPS, and best sludge dewaterability was found in R-30. Thus, suitable SRT should be designed for both good aromatic hydrocarbon removal efficiency and sludge dewaterability.

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Cells' Disruption and Directional Regulation of Hydrolysate of Microalgae During the Medium-Low Temperature Hydrothermal Hydrolysis Process

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Due to the complex structure of microalgae cells' wall, the wall disruption is a obstructive process for efficient energy utilization of microalgae biomass. To rapidly break the multi-layered three-dimensional structure of microalgae cell wall, the catalyst-free hydrothermal hydrolysis was studied. The microstructures of microalgae cells were analyzed by scanning electron microscopy and transmission electron microscopy. It was found that microalgae cell membrane was destroyed at 100 °C, while the cell wall loosed at 150 °C. The material inside the cells started to release after cell membrane destroyed but not the cell wall. With the reaction temperature and residence time increased, the particle size of microalgae cells decreased, the cells were destructed more severely, and the precipitation rate of internal organelles was increased. However, the ratio of substance that could be directly used for biogas fermentation in hydrolysate, such as reducing sugar, was limited due to side reactions that happened without catalyst. Therefore, formic acid was choosed to directional regulate the hydrolysate for the late fermentation. Under 3% diluted formic acid-assisted hydrothermal hydrolysis, the yield of reducing sugar in the hydrolysate was increased by 458% to 189.79 mg/g dry biomass compared to that in the hydrolysate without acid. Compared with the alkali-assisted hydrothermal hydrolysis, diluted formic could obviously inhibit the side reactions. And there was no HMF in hydrolysate. The hydrolysate obtained by low-content formic acid-assisted hydrothermal hydrolysis could match the need of the late biogas fermentation.

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Effect of Lignin-Based Amphiphilic Polymers on the Absorption and Enzymatic Hydrolysis Kinetics of Cellulase on the Lignin and Cellulose Films

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The origin, amount, hydrophilicity, charge, molecular weight and distribution of lignin had significant influences on the enzymatic hydrolysis of lignocelluloses. Lignin-based polyoxyethylene ether (EHL-PEG) enhanced the enzymatic hydrolysis of lignocelluloses better than PEG4600, while effect of lignosulfonate (LS) was inferior to PEG4600. Effect of LS, EHL-PEG and PEG4600 on the absorption and enzymatic hydrolysis kinetics of cellulase on the lignin and cellulose films were investigated by Quartz Crystal Microbalance with dissipation monitoring (QCM-D). Results showed that LS and EHL-PEG combined with cellulase mainly by electrostatic attractive interaction and hydrophobic interaction respectively, and formed hydrophilic cellulase aggregates, that significantly reduced the nonproductive adsorption of cellulase on lignin. Both EHL-PEG nonionic amphiphilic polymers directly synthesized from EHL, and LS synthesized from EHL followed by combining with CTAB to form LS-CTAB catanionic surfactant, could be used to enhance enzymatic reaction of lignocelluloses, that not only improve the enzymatic hydrolysis and decrease the cellulase dosage, but also realize the efficient utilization of enzymatic hydrolysis lignin.

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Seed-Induced Synthesis and Physicochemical Characterization of Hierarchical ZSM-5: Effect of Organosilanes on Catalyst Properties and Performance in the Catalytic Fast Pyrolysis of Biomass

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Lignocellulose is one of the most attractive biomass resources in nature. ZSM-5 showed an optimum for conversion of biomass towards aromatic species due to the similarity between the diameter of benzene and the size of the largest micropore openings in the zeolite[1]. In addition, the micropore diameter, internal pore space and steric hindrance played a determining role for aromatic production[2]. In this paper, the hierarchical HZSM-5 zeolites were synthesized based on the seed-induced hydrothermal method and organosilanes (phenylaminopropyltrimethoxysilane, PATMOS) mediated method. The synthesised HZSM-5 zeolites are referred to as the SNZ5-x samples, where x represents the amount of PATMOS.

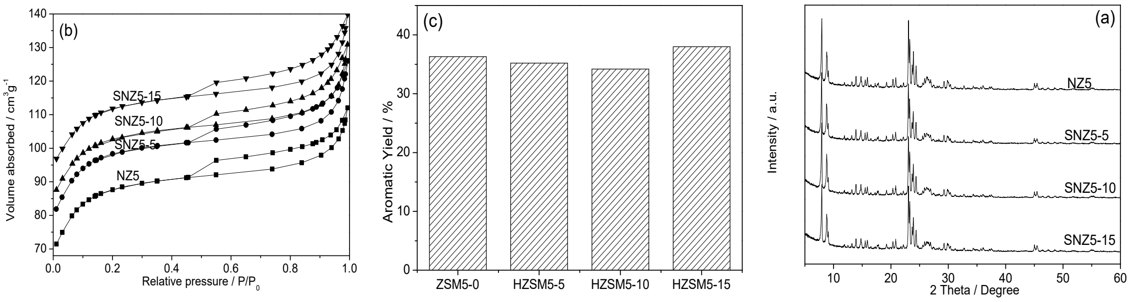

Fig. 1 (a) XRD patterns and (b) N_2 adsorption and desorption isotherms of the hierarchical ZSM-5 samples, (c) Aromatic yields obtained for the catalytic fast pyrolysis of cellulose over the hierarchical HZSM-5 zeolites

The XRD patterns of the synthesised zeolites exhibit characteristic diffraction peaks of MFI topology Fig. 1(a). Fig. 1(b), the isotherms of the HZSM-5 zeolites exhibit a hysteresis loop in the range of p/p_0 = 0.43-0.99, which strongly suggests that an open mesopores connected to the external surface for the hierarchical HZSM-5 zeolites[3]. Fig. 1(c) shows that the highest yield of aromatic was obtained for the mesoporous sample with the greatest microporosity, thus the right balance between meso- and microporosity is critical to achieve high yields.

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A Novel Method to Dry the Digested Sludge Combined Solar Energy and Porous Medium

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Generally, there is still more than 55% water content in the digested sludge, and to dry it to lower than 40% water content is necessary process for the further use as organic fertilizer, and it consumes large heat during its further dryness. The exiting dryness ways may be two: one is heated by traditional energy (such as fossil fuel) and another is heated by waste heat or solar energy. It is certainly a sustainable and clean way for the latter one. However, caused by the high viscosity of the sludge, there is the heat transfer question for either of the ways, which leads to a long dryness period and low dryness efficiency. In this study, a novel approach that dry sludge by solar energy and heat transfer enhancement by porous medium has been presented. The completed set of approach of dry process and the adding and screening of porous medium are described in the first section, and then an operation state has been given which carried out under the practice condition. Ceramic pellets with 10 mm and 20 mm dimeter mixed with sludge for different proportion. The warm air heated by solar and then reheated by heat pump to 70 °C. The operation results show that this approach has save energy more than 45% and speeds up the dry process at least 50%.

Laponite as Immobilization Agent of AgNP in Chitosan-Based Film for Keeping Litchi Freshness

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Silver nanoparticle (AgNP) is an excellent antimicrobial agent with broad-spectrum, but its application is limited in food field due to its small size and resulting in easy leakage. In this paper, laponite immobilized silver nanoparticle (L@AgNP) was synthesized with chitosan (CS) as green reductant, in which AgNPs were embeded in the interlayer of laponite due to its confinement effect. Subsequently, CS nanocomposite films were prepared with L@AgNP as safe antimicrobial agent for keeping litchi freshness. The results show that only about 5.6% of AgNP was released from the films with the addition of laponite, which are much lower than that of the films without laponite (about 29.1%). Furthermore, mechanical properties, water solution and swelling behavior, water vapor permeability (WVP) and oxygen transmission rates of chitosan nanocomposite films were improved due to the suitable addition of laponite. In particular, compared with the pure CS films, the solubility of CL2/L@AgNP films decreased from 24.6% to 4.62%, oxygen transmission rates reduced from 959.09 to 3.95 cm^3/m^2·d·atm, and the films' WVP decreased 28.42%. Furthermore, since AgNP from in situ synthesis was stably embedded into laponite, it hardly showed toxicity to cells, but the films exhibited high antimicrobial activity against Staphylococcus aureus and Escherichia coli. As a packaging, CL2/L@AgNP films effectively extended the storage life of litchi by comparing with commercial cling wrap. Therefore, this chitosan hybrid film is a suitable biodegradation material as food packaging for keeping freshness and extending shelf-life of food.

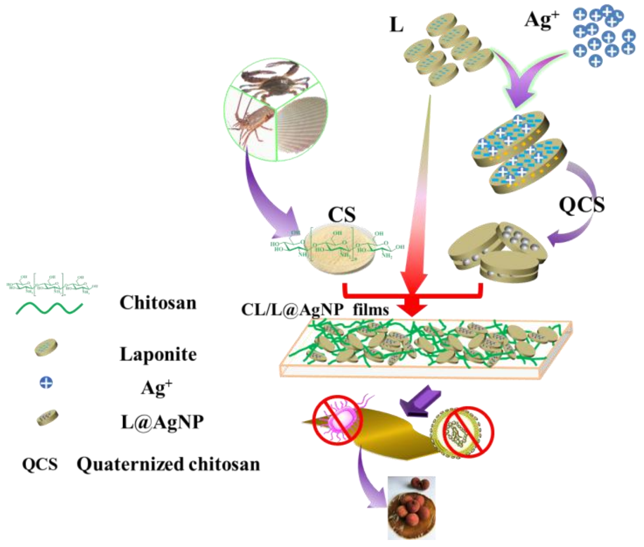

Fig. 1 Schematic illustration for the prepare of CL/L@AgNP films

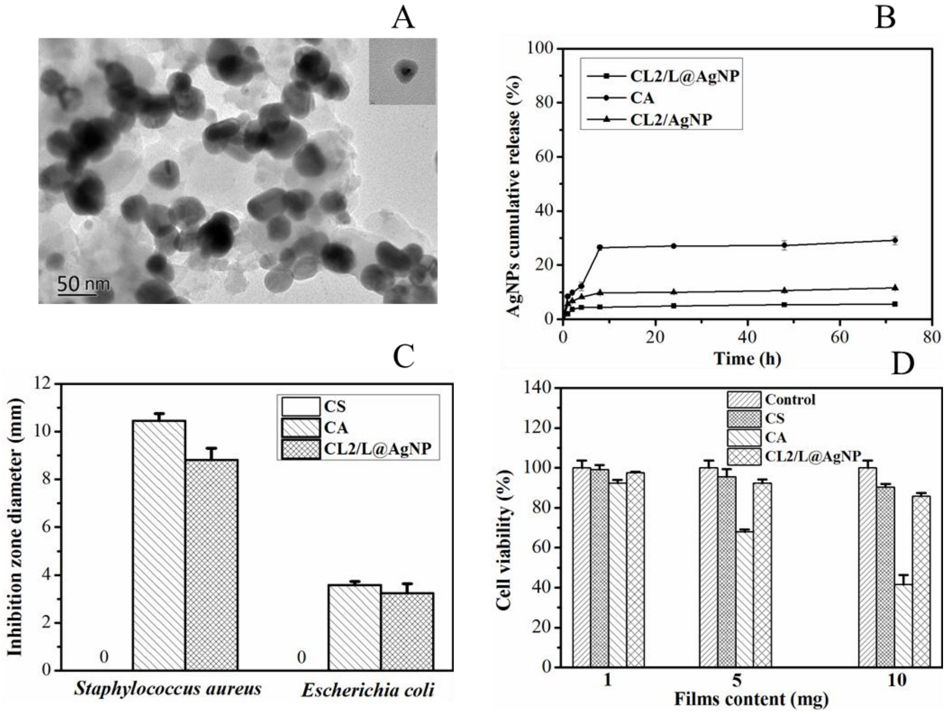

Fig. 2 TEM micrograph of L@AgNP (A), AgNP release from chitosan films (B), inhibition zone (C) and cytotoxicity of chitosan composite films (D).

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Selective Catalytic Transfer Hydrodeoxygenation of Oleic Acid over Bimetallic PdCu and PdNi Alloy Supported Catalysts for the Production of Diesel Like Hydrocarbons

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Fixed bed autoclave catalytic hydrodeoxygenation of a model monosaturated fatty acid to diesel range hydrocarbons over monometallic catalysts (Pd/C, Ni/C, Cu/C) and a wide compositional range of bimetallic $Pd_xNi_{(1-x)}/C$ and $Pd_xCu_{(1-x)}/C$ catalysts is reported. The surface and bulk properties of both monometallic and bimetallic catalysts are determined by an array of techniques including XPS, BET, ICP-OES, PXRD, CO Pulse Titration, TGA and HRTEM. The synthesized materials are used for catalytic hydrodeoxygenation of oleic acid using 1,2,3,4 – tetrahydronapthalene as a hydrogen donor molecule at 603 K with autogenous pressure. The results demonstrated that bimetallic $Pd_{75}Cu_{25}$ catalyst outperforms monometallic catalysts in terms of both activity and selectivity to diesel range (C_{17}+C_{18}) hydrocarbons. The promoting effect is understood by the capacity of Pd to dehydrogenate 1,2,3,4 – tetrahydronapthalene to naphthalene, leading to a much higher availability of molecular hydrogen for the catalytic reaction as compared to monometallic Ni and Cu catalysts. In short, alloying Pd with Cu and Ni lead to very active catalysts in terms of oleic acid conversion with substantial alteration in selectivity towards diesel products as compared to monometallic catalysts.

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Switchable Synthesis of Furfurylamine and Tetrahydrofurfurylamine from Furfuryl Alcohol over Raney Nickel

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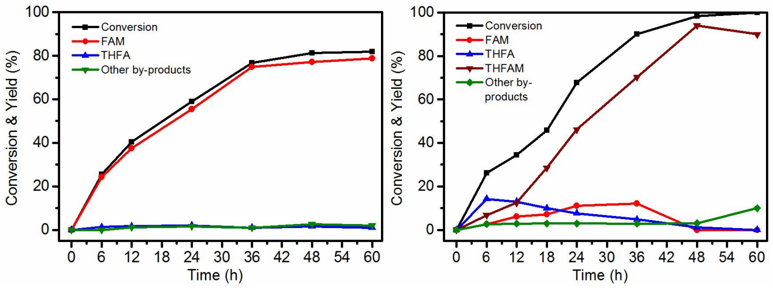
Reductive amination of alcohols takes advantage of using inexpensive starting material and exhibiting higher atom efficiency, and deserves increasing attention[1]. Herein, the heterogeneous hydrogenation/dehydrogenation catalysts such as Pt/C, Pd/C, Ru/C, Rh/C, Raney Co and Raney Ni were employed to catalyze the reductive amination of furfuryl alcohol.

Under 0.35 MPa NH_3, all the tested catalysts were totally inactive except for Raney Ni, over which the furfuryl alcohol could be converted into furfurylamine. After introducing 1.0 MPa of hydrogen, a considerable amount of tetrahydrofurfuryl alcohol was formed over each tested catalyst. Only tetrahydrofurfurylamine of the amination product was found over Raney Raney Ni. Our DFT (density functional theory) calculation demonstrated that the difference of adsorption energy between NH_3 and H_2 on Ni is lower than noble metals[2], indicating that less metal active sites would be occupied by NH_3 due to competitive adsorption, this might be the main reason that Raney Ni is most active in reductive amination[3]. Thus, the switchable synthesis of tetrahydrofurfurylamine and furfurylamine from furfural alcohol is feasible by simply control the introduction of H_2 over Raney Ni (Fig. 1). In absence of H_2, the yield of furfurylamine reached 78.8% after 60 h reaction at 180 °C and 0.35 MPa of NH_3. After introducing 1.0 MPa of hydrogen, the yield of tetrahydrofurfurylamine reached 94.0% after 48 h reaction.



(a) (b)

Fig. 1 Reaction kinetics of reductive amination of furfuryl alcohol for synthesis of (a) furfurylamine in absence of H_2 and (b) tetrahydrofurfurylamine in 1.0 MPa of H_2.

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Catalytic Transfer Hydrogenation of Cinnamaldehyde into Cinnamyl Alcohol over Co-Re/TiO_2 Bimetallic Catalyst

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Selective hydrogenation of cinnamaldehyde (CAL) to cinnamyl alcohol (COL) has attracted much attention in recent years since COL is widely used in the synthesis of various fine chemicalsare and pharmaceuticals[1-4]. Compared with hydrogenation reactions involving molecular hydrogen (H_2), transfer hydrogenation is much safer and easier to handle since. In this study, we attempt to develop Co-Re/TiO_2 bimetallic catalyst for selective hydrogenation of CAL to COL using formic acid (FA) as hydrogen source.

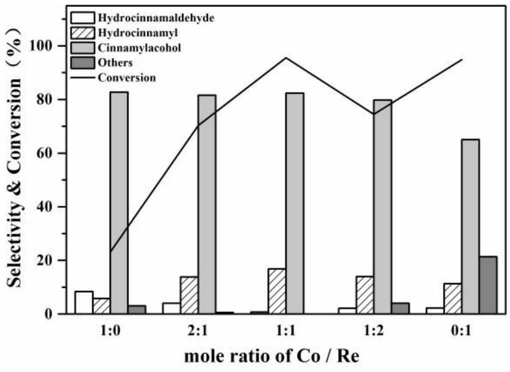

Figure 1. Effect of different molar ratio of Co/Re for cinnamaldehyde hydrogenation. Reaction conditions:80 mg cat, 160 ºC

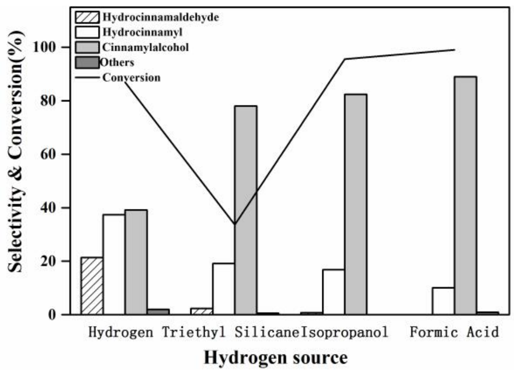

Figure 2. Effect of hydrogen source for cinnamaldehyde hydrogenation over Co-Re/TiO_2. Reaction conditions:80 mg cat.

As is shown in Figure 1, the Co-Re/TiO_2 catalyst with 1:1 molar ratio of Co/Re exhibited the highest yield of COL. The yield of COL decreased either increasing the Co/Re ratio to 1:0 or decreasing to 0:1. These results clearly demonstrate that Co and Re have synergistic effect, which causes electron density of carboxylic cardon atom in CAL to change, on COL yield. A number of cheap chemicals were used as hydrogen donors (Figure 2), FA being the most representative, which can not only provide high throughput of hydrogen atoms, but also avoid the contamination of products by releasing the CO_2 into gas phase. By further optimization of reaction conditions, a highest COL yield of 88% was obtained when using formic acid as hydrogen source and no obvious deactivation of the Co-Re/TiO2 catalyst was observed after using 5 times.

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Biomass-derived Porous Functional Carbon Loaded with $CuFe_2O_4$ for Tandem C-H Activation/ Sonogashira for New Solvatochromic Fluorescent Dyes

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Galactose, as a common biomass, was converted into a good porous functional carbon through one step hard template method for loading with $CuFe_2O_4$. Several critical variables for this highly porous functional carbon had been optimized. This new catalyst displayed excellent activity for the tandem C-H activation/ Sonogashira reaction. This catalyst could be easily recovered through magnetic separation and reused without significant loss of catalytic efficiency after being used for 20 times. Furthermore, many new dyes with excellent solvatochromic fluorescent property has been synthesized through this strategy in good yields.

Activated Carbon Cathode with Reduced Graphene oxide for Enhanced Performance of a Microbial Fuel Cell

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A microbial fuel cell (MFC) is an emerging technology that produce bio-electricity from organics and reduced inorganics in wastewater stream. Because electricity production of MFC is closely related with treatment efficiency, increasing power of MFC is important. An air-cathode used in MFC needs to have a high catalytic activity for oxygen reduction. And it should be easy to fabricate and have good electro-catalytic performance. Reduced graphene oxide (rGO) has high electrical conductivity and becomes a more common carbon material. So, in this study, cathode performance was evaluated by adding rGO to the activated carbon cathode. rGO was added at various ratios to the cathode to replace carbon black: 0 mg (rGO 0 mg, CB 30 mg), 5 mg (rGO 5 mg, CB 25 mg), 15 mg (rGO 15 mg, CB 15 mg) and 30 mg (rGO 30 mg, CB 0 mg). Maximum power density of rGO15 was 2,642 mW/m^2, which was higher than that of rGO5 (2,124 mW/m^2), rGO30 (2,120 mW/m^2) and AC (1,955 mW/m^2). In addition, cathode performance was tested by CV, LSV and EIS measurements.

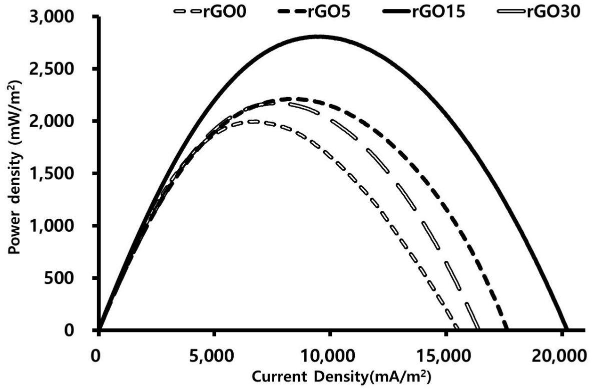

Figure. Comparison of Polarization test according to rGO ratio

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Novel Strategy for Chitin Nanofibrils Extraction from Swelling, Ball Milling and Mashing Processing

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Chitin nanofibril (ChNF) is a biomass-based nanomaterial extracted from the native chitin, which has been reported to be widely used in the development of optically transparent nanocomposites, chiral separation membranes, and functional foods or drugs for inflammatory bowel disease patients [1]. The traditional methods of preparing the ChNF are the chemical oxidation [2] and the high-pressure homogenization [3], which involves the use of highly-toxic chemicals (TEMPO) or costly equipment (Masuco or Microfluidizer). A novel strategy of continuous mechanical treatment based on the swelling, ball milling and mashing was proposed to isolate the chitin nanofibrils with the stable structure and property from the marine biomass resources (crab shells and squid pens). The swelling of raw chitin (α- or β-chitins) was performed on the four kinds of solvents possessing different polarities, including the H_2O, ethylene diamine (EDA), N,N-dimethylformamide (DMF) and n-octanol, with the aim at the effective separation of the chitin fibrils from the intercalation effect of solvent molecules. The subsequent ball milling treatment can further peel off the wrapped long fibrils and cut off the amorphous regions of the native chitin, leaving the short and nanoscaled chitin chains. Finally, the stable dispersion of chitin nanofibrils in the aqueous suspension was achieved by the high-speed shear of crusher processing. We investigated the separation effects of the swelling solvents to the chitin, and the influence of milling conditions (duration and milling ball diameters) to the structure and stability of the prepared ChNF. Getting rid of the chemical reaction and special equipment, the promising ChNF nanomaterials with the average diameter of less than 60 nm (as shown in Figure 1) can be prepared by the proposed continuous mechanical treatments, which can be widely applied in the laboratory or industrial production.

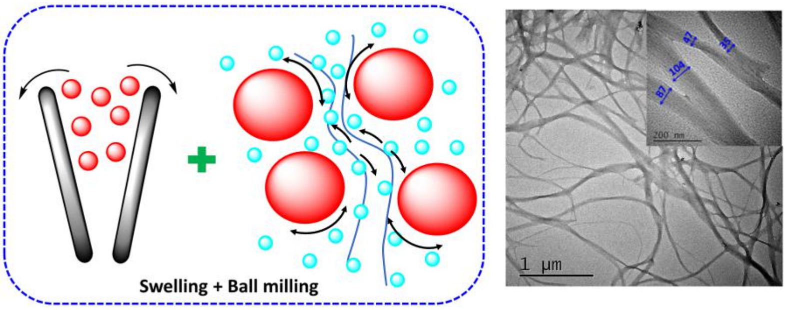

Figure 1. The proposed mechanism of swelling and ball milling and TEM images of the obtained chitin nanofibrils in this study.

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Simulated Moving Bed Chromatography for the Separation of Ethylesters of Eicosapentaenoic Acid and Docosahexaenoic Acid

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Ethyl esters of eicosapentaenoic acid and docosahexaenoic acid were separated with simulated moving bed (SMB) chromatography, where the stationary phase were C18 silica gel and polystyrene type resin with particle size of 10 μm packed in eight columns, and the mobile phase was pure methanol. The Henry constants, transport parameters and total porosity were measured from pulse response chromatographic experiments using a single column. The Henry constants were obtained from the first moment analysis. The transport parameters including axial dispersion coefficients and effective mass transfer coefficients were obtained from the second moment analysis. Nonlinear adsorption equilibrium isotherms for the pure components and their mixture were determined from adsorption-desorption method. The Langmuir model was used to fit the experimental data, and the corresponding parameters were further used to predict the competitive adsorption equilibria of the mixture. The validity of mathematical model parameters was checked by a frontal chromatography experiment. The simulated results of the SMB process using these parameters agreed well with the experimental results. At the feed concentration of 10 g/L, 50 g/L and 100 g/L, the SMB separation was able to produce both solutes with relative purity above 99%.

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Concentration of Docosahexaenoic Acid and Eicosapentaenoic Acid from Fish Oil Fatty Acids by Urea Complexation

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Eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) are popular research objects due to their important roles in biological functions for human being. The simplest and most efficient technique for obtaining polyunsaturated fatty acid concentrates is urea complexation. A quick, low cost and greener method is designed in this article. In the process, the single factor effect of urea-to-fatty acid ratio, the ratio of solvent to fatty acid, crystallization temperature, and crystallization time were studied, respectively. The composition of fish oil fatty acids was determined by GC. Based on the results, a simple and effective orthogonal experiment was used to optimize the separation conditions. With full consideration of various factors that have opposite effect on the total purity and the recovery, the optimal conditions in the urea complexation were as follows: the ratio of urea to fish oil fatty acids is 1:1(wt/wt), the crystallization temperature is 0℃, and the crystallization time is 2 h. Under the optimal conditions, the total content of EPA and DHA reached up to 80% from 63% with a high recovery 85%. Besides, a possible method to recycle urea is designed by adding water and petroleum ether to the urea complexes, and then the aqueous solution was evaporated in order to recycle urea.

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Efficient Sucralose-Derived Solid Acid Catalysts with Suitable Properties for Hydrolysis of Cellulose

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Lignocellulose can be hydrolyzed by acid catalyst to reduce sugars which can be used to produce lipid by fermentation. Solid acid catalyst bearing cellulose adsorbing and catalytic site was studied currently for its advantage of the synergistic effect of cellulose adsorbing and catalytic groups. In this paper, preparation of the carbon-based catalysts were according to the method reported in reference 1. Results showed that the samples carbonized or sulfonated at high temperature (above 648K and 413K, respectively) become more rigid by reason of growth and stacking of large polycyclic aromatic carbon sheets. On the one hand, with the the degree of polymerization increased, accessible sites for attachment of -SO_3H groups as well as -Cl groups decreased and thus led to bad performance in conversion of cellulose and obviously decline the selectivity of glucose. The optimized catalyst showed excellent catalytic activity and resulted in 71% yield of glucose with 97% of selectivity for catalyzing the hydrolysis of ball-milled cellulose. Hydrolysate from hydrolysis of cellulose by the catalyst prepared under the optimal conditions was employed as fermentation liquor. Lipid yield and biomass accumulation have no obvious different between the tested hydrolysate and the control group (as shown in figure 2) that has none inhibits implying that the HMF generated at the hydrolysis process hasn't reach the concentration that would affect lipid production of Yeast strain T. fermentans CICC 1368.

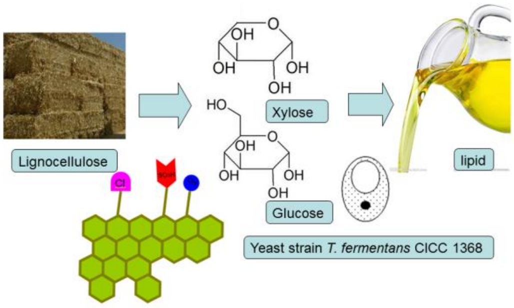

Figure 1 Flow chart

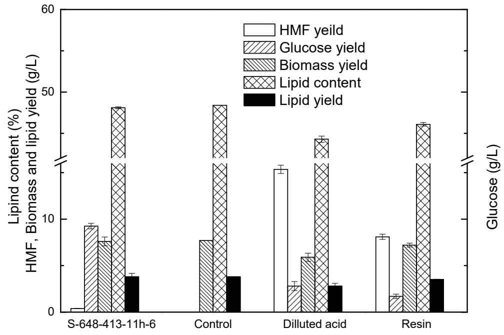

Figure 2 Relationship between lipid accumulation and 5-HMF yield

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Production of Hydrocarbon Fuels from Pyrolysis of Plant Acidification Oil Using Different Basic Catalysts

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In order to obtain low cost diesel-like bio-fuel oil, plant acidification oil was selected to as a raw material to crack. The bio-fuel oil was analyzed by FTIR, ^{1}H-NMR, ^{13}C-NMR and GC-MS to provide complementary information. And yield of plant acidification oil at different catalysts was measured. Acid value, calorific value and viscosity of bio-fuel oil were also analyzed. It was found that basic catalyst gave a product with relatively low acid value. But different basic catalyst showed different decarboxylication role. And it was found that metallic oxides have excellent role of decarboxylication. The acid value of bio-fuel oil with KOH, K_2CO_3 and Mg-Al hydrotalcite was 96.56 mg KOH/g, 113.56 mg KOH/g, 69.29 mg KOH/g, respectively. And yield of bio-fuel oil was 71.84 %, 66.67 %, 70.81 %, respectively. The soap-like matter was found using the KOH, K_2CO_3 catalyst, but not in Mg-Al hydrotalcite. It suggested that Mg-Al hydrotalcite was suitable base catalyst for plant acidification oil pyrolysis. And maybe it revealed the essence reason, which showed the acid value difference with different catalyst. The probable reason of acid value difference was proposed in the paper. Plant acidification oil was potential renewable source to obtain bio-fuel oil using cracking method.