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酿酒酵母木糖利用和鲁棒性两者拮抗机制初探

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摘　要：针对酿酒酵母木糖利用和抑制物鲁棒性两者此消彼涨的拮抗现象，本研究对前期工作获得的木糖代谢能力高、抑制物抗性高及两者协同提高的三类菌株进行了单抑制物胁迫下生长测试。实验结果表明，菌株对单个抑制物抗性反应各不相同，对乙酸抗性和木糖利用表现为拮抗。随后，利用葡萄糖、木糖和乙酸处理上述三类菌株，从基因扰动及环境扰动角度开展多层次转录组分析，初步筛选出 17 个可能缓解拮抗现象的靶基因；初步证实了 *ASK10* 基因的缺失有助于缓解木糖利用和对乙酸抗性两者之间的拮抗。进一步的研究将结合靶向代谢组和转录组联合分析挖掘更多的调控元件以揭示拮抗分子机制。

关键词：酿酒酵母；拮抗；转录组；*ASK10*

Preliminary study on the antagonistic mechanisms of xylose utilization and robustness in *Saccharomyces cerevisiae*

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Abstract: The xylose utilization and the tolerance to inhibitors in *Saccharomyces cerevisiae* have an antagonistic phenomenon that goes up and down. In our preliminary work, we have obtained three types of strains with higher xylose utilization, higher inhibitor resistance, and synergistic improvement of the two aspects. The growth test under single inhibitor stress indicated that strains have different resistance to individual inhibitors, and they showed antagonistic phenomenon in tolerance to acetic acid and xylose utilization. Subsequently, the above three types of strains were treated with glucose, xylose and acetic acid, and a multi-level transcriptome analysis was carried out from the perspective of gene perturbation and environmental perturbation. We initially screened out 17 target genes that may alleviate the antagonistic phenomenon and revealed that the deletion of the *ASK10* gene can help alleviate the antagonism between xylose utilization and the tolerance to acetic acid. Further research will combine targeted metabolome and transcriptome analysis to discover more regulatory elements to reveal the antagonistic mechanism.

Keywords: *Saccharomyces cerevisiae*; Antagonism; Transcriptome; *ASK10*

生物质热解气 CO/CO_2 生物发酵产醇性能强化：pH 和气液传输调控

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摘　要： 生物质热解过程中会产生大量的热解气，热解气中 CO、CO_2 等无机碳可被细菌利用发酵产乙醇等燃料。微生物利用热解气的过程是一个涉及到气体底物、液体基质以及微生物细胞的气、液、固三相反应过程，为提高 CO/CO_2 等气体在发酵液中的传递能力，提出液体喷雾式气液逆向传输的高效气体发酵生物膜式反应器，雾化的小液滴在下落过程中，与自下而上通入的气体接触强化气液传质，氢气的传质系数（K_La）达 0.785s^{-1}，同比提高了约 70 倍。在此基础上恒 pH 调控菌群生长及乙醇代谢，发现在 pH 为 7 时，利用生长（OD_{600}=1.39）；pH 为 6 时，适合乙醇代谢，乙醇最高达 5.1g/L，也为后续连续气体发酵的生长和产醇的分阶段调控奠定了基础。

关键词：生物质热解气；气体发酵；生物膜反应器；气液传质；pH 调控

Biomass pyrolysis gas CO/CO_2 biological fermentation performance enhancement for alcohol production: pH and gas-liquid transmission regulation

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Abstract: In the process of biomass pyrolysis, a large amount of pyrolysis gas is produced. Inorganic carbon such as CO and CO_2 in the pyrolysis gas can be used by bacteria to produce ethanol and other fuels by fermentation. The process of using pyrolysis gas by microorganisms is a gas, liquid, and solid three-phase reaction process involving gaseous substrates, liquid substrates and microbial cells. The gaseous substrates are dissolved in the liquid substrate and then absorbed by the microbial cells. However, due to the slightly solubility of CO/CO_2, it limits the interaction between gaseous substrates and microorganisms. Therefore, in order to improve the transfer capacity of CO/CO_2 and other gases in the fermentation broth, a liquid spray type gas-liquid reverse transmission of high-efficiency gas fermentation is designed. The atomized droplets are in contact with the bottom-up gas in the falling process and quickly reach a saturated state, thereby achieving the effect of enhancing gas-liquid mass transfer. The mass transfer coefficient (KLa) of which gas reaches 0.785s^{-1}, which is about 70 times higher than that under non-sprayed conditions. On this basis, the effect of pH on the growth and metabolism of the flora was studied by continuous air supply and constant pH control. It was found that the growth condition was optimal at pH 7, and the OD600 reached 1.39. While when the pH was 6, the ethanol output is the highest at 5.1g/L. It also lays the foundation for the subsequent continuous gas fermentation growth and phased regulation of alcohol production.

Keywords: Biomass pyrolysis gas; gas fermentation; biofilm reactor; gas-liquid mass transfer; pH control

玉米深加工废弃物--玉米麸皮预处理及微生物发酵产乙醇

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摘　要：拓展木质纤维素生物质来源是加快二代燃料乙醇工业化生产的重要举措。玉米麸皮是玉米深加工后的废弃物，全国年产生量可达百万余吨，其物理结构相对松散，富含纤维素和半纤维素约 65%、淀粉约 11%、蛋白质约 11%、而木质素仅 5%，是优良的用于生产二代燃料乙醇的木质纤维素原料。本研究主要采用稀酸预处理方法，通过单因素及正交法对固液比、酸浓度、处理温度、处理时间以及物料细度进行优化。实验结果表明，固液比 1：9，酸浓度 0.5%，处理温度 115°C，处理时间 120 min 木糖释放率可达 92%，仅产生乙酸 2.3 g/L。经进一步酶解，12h 葡萄糖和木糖总释放率可达理论值的 91%。限氧发酵结果显示，20h 可消耗 100%葡萄糖和 81%木糖，糖醇转化率为 0.46 g g^{-1}。

关键词：燃料乙醇；玉米麸皮；稀酸预处理；最佳条件

Pretreatment of Corn Bran from Corn Deep Processing and Producing to Ethanol through Microbial Fermentation

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Abstract: Expanding the source of lignocellulosic biomass is an important measure to promote the industrial production of second-generation bioethanol. Corn bran as the waste was generated during corn deep processing, with an annual output of more than one million tons. Its physical structure is relatively loose, composing of 65% cellulose and hemicellulose, 11% starch, 11% protein, and only 5% lignin. Therefore, it is considered as an excellent lignocellulose feedstock for the production of second-generation bioethanol. In this study, corn bran was pretreated by the dilute acid method, and then the solid-liquid ratio, acid concentration, treatment temperature, treatment time and material fineness were optimized through single factor and orthogonal experiments. The results showed that the xylose release rate reached 92% together with only producing 2.3 g/L of acetic acid in the solid-liquid ratio of 1:9, the acid concentration of 0.5%, the treatment temperature of 115℃, and the treatment time of 120 min.. After further enzymatic hydrolysis, the total release rate of glucose and xylose within 12 h can reach 91% of the theoretical value. The results of oxygen-limited fermentation showed that 100% glucose and 81% xylose were consumed in 20 h, with the ethanol yield of 0.46 g g^{-1}.

Keywords: bioethanol; corn bran; dilute acid pretreatment; optimal conditions

运动发酵单胞菌絮凝机理及高效生产乙醇

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摘　要:

运动发酵单胞菌通过 ED 途径代谢葡萄糖高效生产乙醇。具有絮凝表型的 ZM401 是从游离 ZM4 突变而来，不仅能通过沉降有效回收生物质，还增强了细胞的胁迫耐受性。比较基因组分析表明：在基因 ZMO1082 上的单核苷酸删除中断了终止子，使其与下游基因 ZMO1083 融合，编码细菌纤维素合成酶的主要亚基。此外，编码 c-di-GMP 磷酸二酯酶的 ZMO1055 的单核苷酸突变影响了该酶的降解 c-di-GMP 的功能，使其积累强化了纤维素合成。该工作对具有类似表型细菌的絮凝优化具有重要意义。

关键词：运动发酵单胞菌，絮凝，纤维素，c-di-GMP，乙醇发酵

Flocculation mechanism of *Zymomonas mobilis* for efficinet ethanol production

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Abstract:

Zymomonas mobilis metabolizes glucose through the Entner-Doudoroff pathway with high ethanol yield. ZM401, a mutant from ZM4 of *Z. mobilis*, can self-flocculate, and the unique phenotype presents advantages in cost-effective biomass recovery and also robust production. Comparative genome analysis indicated that the single nucleotide deletion in ZMO1082 accidently disrupted its own transcription terminator and the transcription starter of the downstream gene ZMO1083 for their fusion as a new gene ZMO1083/2 to encode the catalytic subunit A of the bacterial cellulose synthesis complex for the synthesis of cellulose fibrils to flocculate the mutant. Moreover, the single nucleotide mutation in ZMO1055 encoding phosphodiesterase for c-di-GMP degradation compromised its function for intracellular accumulation of the messenger to regulate the cellulose synthesis. These discoveries are significant not only for optimizing the self-flocculation of *Z. mobilis*, but also for engineering other bacteria with the phenotype.

Keywords: *Zymomonas mobilis*, flocculation, cellulose, c-di-GMP, ethanol fermentation

磷钼酸对 NH_2-MIL-68 (Rh)的协同作用促进 CO_2 的选择性光催化还原

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摘　要：化石燃料燃烧释放的 CO_2 是全球温室效应的主要原因，CO_2 的捕获和有效利用是一个重要的问题，光催化还原 CO_2 以其清洁高效、环境友好、反应条件温和的特点引起了人们的广泛关注。本研究以金属有机骨架(NH_2-MIL-68 (Rh))为载体，以磷钼酸（PMA）为活性组分，通过水热法成功合成了复合催化剂。通过 FTIR、XPS、DRS 光谱对 PMA@NH_2-MIL-68(Rh)复合材料的电子结构进行了分析，结果表明，磷钼酸的末端氧与 MOF 相互作用，形成了 Rh-O 键，并伴随 Mo5$^+$活性物质的形成。光催化 CO_2 还原性能测试表明，0.63%的 PMA@NH_2-MIL-68(Rh)复合材料的催化性能最佳，产生 387.28 mol·g-1 CO 和 11.75 mol·g-1 CH_4。在 CO 的收率方面，0.63%的 PMA@NH_2-MIL-68(Rh)是 NH_2-MIL-68(Rh)的近 15 倍，循环和稳定性结果表明，PMA@NH_2-MIL-68(Rh)复合材料在重复使用 5 次后，光催化降解 CO_2 的效果没有明显变化，说明其稳定性较好。

关键词：NH_2-MIL-68(Rh)；山竹状结构；磷钼酸；选择性催化；CO_2 还原；

Synergistic effect of phosphomolybdic acid on rhodium-based metalorganic frameworks promotes efficient selective photocatalytic reduction of CO_2 to CO

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Abstract: Carbon dioxide CO_2 is the main product released from fossil fuels incineration process and serves as the important greenhouse gas for global warming. In this work, the catalyst PMA@NH_2-MIL-68(Rh) of molybdophosphate supported NH_2-MIL-68(Rh) was successfully synthesized by hydrothermal method, with a metal-organic framework (NH_2-MIL-68 (Rh)) as the carrier and PMA as active component. The electronic structure of PMA@NH_2-MIL-68(Rh) composite was analyzed by FTIR, XPS and DRS spectra. The results showed that the terminal oxygen of molybdophosphate interacted with MOF to form Rh-O bond, accompanied by the formation of Mo5$^+$ active substance. The photocatalytic CO_2 reduction performance test shows that the 0.63% PMA@ NH_2-MIL-68(Rh) composite achieves optimal catalytic performance, yielding 387.28 μmol·g^{-1} CO and 11.75 μmol·g-1 CH4, respectively. In terms of the yield of CO, 0.63%PMA@NH_2-MIL-68(Rh) is nearly 15 times of NH_2-MIL-68(Rh). The results of cycling and stability showed that the photocatalytic effect of PMA@NH_2-MIL-68(Rh) composite did not change significantly after repeated use for 5 times, indicating that it had good stability.

Keywords: NH_2-MIL-68(Rh); mangosteen-like spherical structure; Phosphomolybdic acid; Selective catalysis;

CO_2 reduction;

纤维素类生物质废弃物-甘薯渣的丁醇发酵研究

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摘　要：本研究以纤维素类生物质废弃物-甘薯乙醇发酵残渣为原料，丙酮丁醇梭菌（Clostridium acetobutylicum）为发酵菌株，考察了不同硫酸浓度和酸水解时间对原料酸水解后糖分的变化以及发酵生产丙酮、丁醇、乙醇(ABE)总溶剂的影响。同时进一步研究残渣酸水解液不同脱毒方式，添加碳源和营养物质对 ABE 总溶剂产量的影响。结果表明，硫酸水解处理的甘薯发酵残渣含有葡萄糖、木糖、阿拉伯糖等可被丙酮丁醇梭菌所利用的底物，1%(v/v)硫酸 121°C酸水解 30min，利用 $Ca(OH)_2$ 过中和酸水解液脱毒，发酵 72h 最终 ABE 总溶剂量 8.92g/L，发酵效率 91.11%，添加葡萄糖碳源和其它营养成分并不能显著提高 ABE 总溶剂产量和缩短发酵时间，表明甘薯废渣酸水解液中的营养成分已能满足丙丁梭菌发酵生产 ABE 溶剂所需。

关键词：纤维素类生物质废弃物，丙酮丁醇梭菌，丁醇发酵

Butanol fermentation from cellulosic biomass waste of sweetpotato residue

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Abstract: Studies were performed to produced Acetone butanol ethanol (ABE) from bioethanol production residues using *Clostridium acetobutylicum* CICC 8012. The effects of sulfuric acid concentration and hydrolysis time on sugar and ABE yield were investigated. At the same time, the effects of different detoxification methods, carbon sources and nutrients on the ABE yield were compared. The results showed that the hydrolyzed sweetpotato residue contained glucose, xylose and arabinose. The culture produced 8.92 g/kg ABE（91.11 of the theoretical yield）from $Ca(OH)_2$ over-limed sweetpotato residue hydrolysate (1% v/v sulfuric acid at 121°C for 30 min) though 72 h fermentation. Extra carbon source and other nutrients could not significantly increase the ABE yield and shorten the fermentation time, which indicated that the nutrients in the hydrolysate of sweetpotato residue could meet the requirements of *Clostridium acetobutylicum* to produce ABE.

Keywords: Cellulosic biomass waste, *Clostridium acetobutylicum*， ABE production

固有无序蛋白(IDPs)提高酿酒酵母细胞的耐高温和抗干燥能力

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摘　要: 二代燃料乙醇经济有效生产所需酿酒酵母菌株的理想特性之一是耐高温，酿酒酵母最适生长温度为 25~30℃，通常不会在高于 40℃下生长，获得在高温下生长状况良好的重组菌株具有实际应用价值。固有无序蛋白（IDPs）可以通过形成玻璃态或高阶组件(如可逆聚合体、颗粒等)来保护细胞免受不同的应力。本研究以酿酒酵母 CEN.PK 102-5B 为出发菌株，通过着丝粒质粒分别异源表达多种来源的 IDP 基因，初步筛选得到几株具有明显高温耐受性的重组菌株。下一步实验对其高温耐受性进行验证，及筛选潜在的耐干燥及抑制物的菌株，以期制备二代燃料乙醇专用活性干酵母菌株。

关键词：酿酒酵母、耐高温、抗干燥、活性干酵母

Improvement of high temperature and dryness resistance in *Saccharomyces cerevisiae* by expression of intrinsically disordered proteins (IDPs)

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Abstract: One of the ideal characteristics of the *Saccharomyces cerevisiae* strains needed for efficient production of second-generation fuel ethanol is the high temperature resistance. The optimal growth temperature of *S. cerevisiae* is 25 ~ 30 ℃, which usually does not grow above 40 ℃. Intrinsic disordered proteins (IDPs) can protect cells from different stresses by forming non-crystalline amorphous solid (vitrify) or by forming high-order components such as reversible polymers or granules. In this study, Saccharomyces cerevisiae CEN.PK 102-5B was used as the starting strain, and the IDP genes from various sources were heterologously expressed through centromeric plasmids. Several recombinant strains with obvious high temperature tolerance were obtained by preliminary screening. The next step is to verify its high temperature tolerance and screen potential strains that are resistant to desiccation and inhibitors, in order to prepare active dry yeast strains for second-generation fuel ethanol.

Keywords: *Saccharomyces cerevisiae*, High temperature resistance, Desiccation resistance, Active dry yeast

甘油-水混合溶剂中微藻和稻杆共液化制备生物油研究

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摘 要:

本文开展甘油-水混合溶剂中微藻和稻杆共液化制备生物油的研究。研究了反应温度、催化剂(K_2CO_3)、停留时间、原料质量比、水相循环对产品分布和生物油特性的影响。结果表明，微藻和稻杆共液化表现出较明显的协同效应。在 350℃、10 分钟、5wt.%K_2CO_3、原料质量比为 1：1 反应条件下，微藻和稻杆共液化的生物油产率为 42.22%，协同效应达 8.86%。结合 GC-MS、元素分析、SEM 等对水热液化后生物油、水热碳的特性进行了分析。结果发现共液化生物油中脂肪酸和酮的含量分别高于 30%、10%，酚类含量小于 3%。混合微藻改善了稻秆水热生物油的品质。

关键词：共液化；微藻；稻杆；协同效应；生物油

Study on co-liquefaction of microalgae and rice straw in glycerol-water mixed solvent to produce bio-oil

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Abstract:

This study investigated the co-liquefaction of microalgae and rice straw in a glycerol-water mixed solvent to produce bio-crude oil. The effects of reaction temperature, catalyst (K_2CO_3), residence time, raw material mass ratio, water phase circulation on products' distribution and bio-oil characteristics were explored. The results indicated that microalgae and rice straw showed a synergistic effect during the co-liquefaction process. When the reaction conditions were 350°C, 10 minutes, 5wt.%K_2CO_3 and the raw material mass ratio was 1:1, the bio-oil yield achieved 42.22% and a positive synergistic effect of 8.86% was examined for co-liquefaction. Using GC-MS, elemental analyses, SEM etc., the characteristics of bio-oil and hydrothermal carbon after co-liquefaction were analyzed. It was found that the contents of fatty acids and ketones were higher than 30% and 10% respectively while that of phenols was less than 3% in the co-liquefaction bio-oil, indicating that the introduction of microalgae effectively improved the bio-oil quality of rice straw hydrothermal liquefaction.

Keywords: Co-liquefaction; Microalgae; Rice straw; Synergistic effect; Bio-oil

催化纤维素水相制备酮醇类化合物

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摘　要:

传统上，酮醇产品是从化石资源中经过多步合成的产物，由于其同时含有羰基和羟基，被认为是多种高附加值精细化学品合成的重要中间体。在 W/Ni 原子比为 1.0-5.0 的 Ni-WOx/C 催化剂上，实现了纤维素直接氢解制备 C_3-C_4 醇酮（羟基丙酮和 1（3）-羟基-2-丁酮）的反应。C_3-C_4 酮醇的产率与 W/Ni 比和催化剂焙烧温度密切相关。在碱性/酸性 WOx 和金属 Ni 的最佳平衡条件下，酮醇的产率最高可达 63%。Ni 的引入促进了 W^{5+}碱性位的形成，促进了 Ni-WOx 界面碱性位的形成。碱性 W^{5+}与酸性氧空位（Vö）的协同作用可以激活靶 C-O/C=O 键，促进葡萄糖和 C_3-C_4 醛中间体的异构化。在 Ni-O-W-Vö 界面上-OH 和-C=O 的协同吸附稳定了相邻的酮和羟基，并对其它羟基进行选择性氢解，最终得到了 C_3-C_4 酮醇。本研究拓展了纤维素生物质的应用领域，实现了以木质纤维素生物质为原料绿色、可持续地合成高价值的 C_3-C_4 酮醇产品。

关键词：生物质、纤维素、酮醇、Ni-WOx/C 催化剂、氢解

Selective C_3-C_4 Keto-alcohols Production from Cellulose Hydrogenolysis

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Abstract:

Keto-alcohols, which are traditionally produced from fossil resource with multi steps, are considered as the important intermediates for diversified high value-added fine chemicals synthesis due to their involved carbonyl and hydroxyl groups. Herein, direct cellulose hydrogenolysis to the C3-C4 keto-alcohol products (hydroxyacetone and 1(3)-hydroxy-2-butanone) was achieved over Ni-WOx/C catalysts with the W/Ni atom ratio of 1.0-5.0. The keto-alcohols yield was proposed to strongly depend on the W/Ni ratio and the catalyst annealing temperature. The highest keto-alcohols yield of 63% was obtained at the optimal balance of basic/acidic WOx species and metallic Ni. The introduction of Ni facilitated the formation of the basic W5+ sites, which enhanced the formation of basic sites at the Ni-WOx interface. The synergistic effect between the basic W5+ and acidic oxygen vacancy (Vö) could activated the target C-O/C=O bonds, promoting the isomerization of glucose and C3-C4 aldehyde intermediates with the assistance of the interfacial Ni. The cooperative adsorption of the -OH and -C=O groups at the Ni-O-W-Vö interface stabilized the adjacent ketone and hydroxyl groups and remained the other hydroxyl groups for hydrogenolysis, obtaining the final C3-C4 keto-alcohols. This work expanded the application of cellulosic biomass, enabling the green and sustainable synthesis of the high valued C3-C4 keto-alcohols products using lignocellulosic biomass as raw material.

Keywords: biomass, cellulose, keto-alcohols, Ni-WOx/C catalyst, hydrogenolysis

基于碱性可循环乙二醇苯醚双相体系的稻秆炼制工艺构建

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摘要：

研究开发了一种温和条件下低水耗的碱性两相预处理工艺，经均匀设计优化后，两相乙二醇苯醚体系表现出了出色的脱木素性能，每克稻秆仅 6 毫升水，80℃下，木质素脱除率为 82.16%，即使 55℃下，木质素脱除率仍可达到 78.15%。并根据双相系统特性，构建了溶剂循环过程。乙二醇苯醚和洗涤废水在 80℃下重复使用 3 次后，木质素脱除率依然超过 80%。对应残渣的 72h 酶解率仍超过 80%（乙酸盐缓冲液），甚至在黑液中残渣酶解率依然超过 71%。这显示了基于碱性双相预处理过程，构建低水耗能耗、溶剂循环的生物精炼系统的可能。

关键词：碱性两相预处理；乙二醇苯醚；稻秆；去木质素；循环炼制

Construction of Rice Straw Biorefinery Based on Alkaline Recyclable Biphasic 2-Phenoxyethanol/Water System

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Abstract:

A novel recyclable alkali-assisted biphasic pretreatment process under mild conditions with low water consumption is first developed. After conditions were optimized with the uniform design method, the biphasic 2-phenoxyethanol system presented superior delignification performance with only 6 mL of water consumption per gram of rice straw. Namely, the lignin removal reached 82.16% at 80 °C or 78.15% even at 55 °C. Then, according to the characteristics of the biphasic system, the entire solvent circulation process was constructed. The recycled 2-phenoxyethanol and washing wastewater were directly reused three times at 80 °C, giving more than 80% of lignin removal. Meanwhile, enzymatic digestibility of corresponding residues still exceeded 80% in acetate buffer, or 71% even in black liquor at 72 h. These show the possibility of constructing a biorefinery system based on an alkaline biphasic pretreatment process, with less water and energy consumption, fractionable composition, solvent recyclability, and black liquor utilization.

Keywords: Alkaline biphasic pretreatment, 2-Phenoxyethanol, Rice straw, Delignification, Recyclable biorefining process

熔盐体系耦合固体酸催化纤维素制备 5-HMF

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摘　要：5-HMF 作为重要的可再生平台化合物，而如何利用纤维素作为原料高产制备 5-HMF 是实现纤维素高效利用的关键。本文以微晶纤维素为原料，利用熔盐体系的作用将纤维素水解为葡萄糖，而固体酸将生成的葡萄糖异构化为果糖，最后果糖在熔盐体系下脱水生成 5-HMF。进一步利用有机萃取液在线萃取目的产物 5-HMF，从而实现一锅法合成 5-HMF。在 170℃，20min 的反应条件下，5-HMF 的最高产率达到了 52.78%，5-HMF 的选择性为 66.83%。在制备 5-HMF 的过程中，本研究初步完成了对十种常见的固体酸在熔盐-有机溶剂体系下的筛选工作，也部分揭示了在熔盐-有机萃取剂体系下耦合固体酸催化纤维素一锅法合成 5-HMF 的机理。这为纤维素商业化制备高附加值化学品提供了一种可行的潜在思路。

关键词：纤维素，5-HMF，熔盐体系，双相体系,甲基异丁基酮

Preparation of 5-HMF from Cellulose Catalyzed by Molten Salt System Coupled with Solid Acid

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Abstract: 5-HMF as an important renewable platform compound, how to use cellulose as a raw material to produce 5-HMF in high yield is the key to achieving efficient utilization of cellulose. Microcrystalline cellulose was used as raw material in this article. Under the influence of molten salt system, cellulose was hydrolyzed to glucose. Subsequently, glucose was isomerized to fructose by solid acid. Finally, fructose was dehydrated in molten salt system to obtain 5-HMF. It was further combined with organic extracts to extract the target product 5-HMF on-line to realize the one-pot synthesis way of 5-HMF. A 52.78% yield was achieved at 170°C for 20 min, and the selectivity of 5-HMF was 66.83%. In the process of obtaining 5-HMF, this research has initially completed the screening work of ten common solid acids in the molten salt-organic solvent system, In addition, it also partially have revealed the mechanism of the molten salt-organic extractant system coupled with solid acid in one-pot catalytic conversion of cellulose to 5-HMF. the proposed technique presents a promising strategy for Synthetic 5-HMF in a commercial way.

Keywords: Cellulose, 5-HMF, molten salt hydrate, biphasic system

超临界甲醇中还原 $CuMgAlO_x$ 高效催化木质素模型物内 *β*-O-4 键氢解

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摘　要：发展经济、可持续和绿色的催化系统是木质素加氢转化工艺的关键。但是，目前大多使用贵金属催化剂（Pt，Pd，Re，Ru 等）和高压氢气的反应体系，其成本较高且安全性差。因此，我们开发了一种低成本的、无外加氢气的 $Cu/CuMgAlO_x$-超临界甲醇加氢体系，该体系对木质素中含量最高的 *β*-O-4 连接键的加氢解聚具有高催化活性。以 2-(2-甲氧基苯氧基)-1-苯基乙醇为反应物得到的最高的转化率大于 99.0 mol%，单体产率达 180.3 mol%，相应的断键表观活化低至 13.74 kJ/mol。表征结果显示 Cu^0 和酸性位点起到协同催化作用。绘制了该催化体系下 *β*-O-4 型木质素模型物的详细氢解网络图。最后，通过巨尾桉酶解木质素（EHL）的氢解验证了该催化体系对真实木质素良好的催化氢解效果。

关键词: 木质素，*β*-O-4 键，催化氢解，铜基催化剂，超临界甲醇

Hydrogenolysis of β-O-4 linkage within lignin over reduced $CuMgAlO_x$ catalyst in supercritical methanol

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Abstract: The development of economic, sustainable, and environmentally friendly catalytic system was the key for the hydroprocessing of lignin. However, in most circumstances, noble-based metal catalysts (e.g., Pt, Pd, Re, Ru) were used with high-pressured H2 gas as the hydrogen source, which was neither economically reasonable and safe. Herein, we introduce a low-cost CuMgAlOx catalyst with promising activity towards the hydrogenolysis of β-O-4 linkages within lignin in supercritical methanol through a H2-free method. High conversion (>99.0 mol%) and yields of monomers (180.3 mol%) were obtained from 2-(2-methoxyphenoxy)-1-phenyl ethanol in a short reaction time. The corresponding activation energy for linkage cleavage was as low as 13.74 kJ/mol. Characterizations of CuMgAlOx demonstrated the collaboration of Cu0 and acid sites in the catalysis. Hydrogenolysis of various β-O-4 lignin model compounds were performed to verify the reaction pathways. Chemisorption energies were calculated with CASTEP to prove the experimental results. A detailed network for CuMgAlOx catalyzed β-O-4 linkage cleavage was proposed. Ultimately, the hydrogenolysis of Eucalyptus urophylla enzymatic hydrolyzed lignin (EHL) was performed, where successful β-O-4 linkage hydrogenolysis was accomplished. This work paves the way for the application of Cu-based catalysts and hydrogen transfer method in lignin valorization.

Keywords: Lignin; β-O-4 linkage; copper; hydrogenolysis; supercritical methanol

TiO_2 促进的 Ru/ TiO_2-Al_2O_3 催化剂用于愈创木酚的低温还原

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摘　要：采用共沉淀法制备了 Al/Ti 比 2：1 的 TiO_2 -Al_2O_3 复合氧化物载体，通过浸渍法制得高分散 5%Ru/ TiO_2-Al_2O_3 催化剂，用于木质素解聚产物愈创木酚的低温还原反应，并进行了 XRD、SEM、TEM、NH_3-TPD 等表征。实验发现 5%Ru/ TiO_2-Al_2O_3 催化剂具有优异的低温加氢活性，在温度 50℃、Al/Ti 比 2：1 和氢压 2.0 MPa 的条件下，愈创木酚的转化率可达 97.2%，主要产物为 2-甲氧基环己醇，其选择性为 88.9%，少量转化成环己醇、2-甲氧基环己酮、2-甲氧基环己烷，其中环己醇的选择性为 8.9%。结果表明 TiO_2 对所负载的 Ru 具有良好的促进作用，催化剂中合适的 Al/Ti 比可获得优化的低温还原活性，高分散的 Ru 与催化剂表面的酸量之间存在协同作用。

关键词：催化加氢，Ru/ TiO_2-Al_2O_3，愈创木酚

TiO_2-promoted Ru/ TiO_2-Al_2O_3 catalyst for the catalytic hydrogenation of guaiacol at low temperature

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Abstract:
Mixed oxide Al2O3-TiO2 with Al/Ti ratio 2:1 was synthesized by coprecipitation method, and highly dispersed 5%Ru/Al2O3-TiO2 catalyst was effectively prepared by impregnation and characterized by means of XRD、SEM、TEM、NH3-TPD. The catalyst is of the excellent catalytic hydrogenation activity of guaiacol under the low temperature condition. It was found that the conversion of guaiacol can reach 97.2% at 50℃ and 2.0MPa hydrogen pressure, the main product is 2-methoxycyclohexanol with a selectivity of 88.9%, a small amount is converted to cyclohexanol with a selectivity of 8.9%, and 2-methoxycyclohexanone and methoxyethoxycyclohexane. The results show that TiO2 has a good promotion effect on Ru, and the optimal reduction activity at low temperature can be obtained by appropriate Al/Ti ratio in the mixed oxide carrier. There is a synergistic effect between highly dispersed Ru and the amount of surface acidity on the catalyst.

Keywords: catalytic hydrogenation, Ru/ TiO2-Al2O3, guaiacol

稻秆与餐厨废油共液化强化生物油制备

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摘　要:

在亚临界水条件下开展稻秆与餐厨废油模化物水热共液化制备生物油的研究。探究反应温度、催化剂(K_2CO_3)、停留时间、原料比对共液化产物分布及生物油特性的影响。结果表明共液化制备生物油存在显著的协同效应。在 300℃、10min 时，稻杆：油质量比为 1：3 时，协同效应达 11.74%，生物油产率最高达 88.77%，水热残碳的产率由稻杆单独水热液化的 21.98%降低至 0.53%。结合 GC-MS、元素分析、SEM 等对水热共液化后生物油、水热残碳的特性进行了分析，发现添加餐厨废油模化物有效改善了稻秆水热液化生物油的品质。

关键词：水热共液化；餐厨废油；水稻秸秆；协同效应;生物油

hydrothermal co-liquefaction of rice-straw and model waste cooking oil for enhanced bio-crude production

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Abstract:

Hydrothermal co-liquefaction of rice straw and model waste cooking oil was investigated under subcritical water conditions to produce bio-crude. The effects of reaction temperature, catalyst (K2CO3), residence time, and mass ratio of raw material on the distribution of co-liquefied products and the characteristics of bio-crude oil were explored. Significant synergistic effect for bio-crude production was observed. At 300°C, 10 min and rice straw to model oil ratio of 1:3, the synergistic effect was as high as 11.74% and the highest bio-oil yield of 88.77% was achieved with the solid residue carbon yield dropped sharply from 21.98% for the hydrothermal liquefaction of rice straw alone to only 0.53%. Using GC-MS, elemental analyses, SEM etc., the characteristics of bio-crude and solid residue carbon produced from hydrothermal co-liquefaction were analyzed. The addition of waste cooking oil model compounds was proved to effectively improve the quality of bio-crude during rice straw hydrothermal liquefaction.

Keywords: Hydrothermal co-liquefaction; Waste cooking oil; Rice-straw; Synergistic effect; Bio-crude oil

木质素衍生酚类模化物原位加氢脱氧制取苯的研究

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摘　要：木质素，地球上最大的自然芳香物质的来源，其转化利用受到了研究者的广泛关注。为了将木质素衍生的酚类物质转化为苯、甲苯、二甲苯（BTX），我们的研究提出在温和的条件下（230°C，1 atm N_2）采用甲醇水相重整制氢，使用廉价的甲醇作为氢源，与酚类加氢脱氧（HDO）耦合，以提高酚类物质的转化率和 BTX 收率。本研究使用 Ru/C 催化剂，分别催化苯酚、愈创木酚、2,6-二甲氧基苯酚进行反应，一段时间后转化率均接近 100％。此外，实验发现甲醇的添加量存在一个较优的值，过多氢源反而会造成苯环过度加氢，抑制直接脱氧。当醇油比（甲醇与模化物摩尔比）为 2.5:1 时，实现酚的全部脱氧，BTX 的摩尔收率可达 76%。本实验反应条件温和，所用催化剂稳定且易于获得，BTX 的收率高，该方法对于木质素的利用具有一定的意义。

关键词：木质素衍生酚类，原位加氢，酚类加氢脱氧，Ru/C 催化剂，BTX

In-situ hydrodeoxygenation of lignin-derived phenolics to produce BTX

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Abstract:

Lignin is the largest source of aromatic substances in nature. In order to convert lignin-derived phenolic compounds into BTX, using cheap methanol as a hydrogen source under mild conditions (230°C, 1 atm N2) was proposed. Hydrogen production by methanol-aqueous phase reforming was coupled with phenol hydrodeoxygenation (HDO) to achieve a high conversion rate of phenols and a high yield of BTX. In this study, a commercial Ru/C catalyst was used, and the conversion rate of different model compound was close to 100% after reacting for a period of time. In addition, experiments have found that using more methanol didn't work better. In fact, too much hydrogen source caused excessive hydrogenation and inhibited deoxygenation. When the molar ratio of methanol to raw material was 2.5:1, the yield of BTX was as high as 80%, and the complete deoxygenation of phenol was realized. The experimental conditions were mild, the catalyst used was stable and readily available, and the yield of BTX was extremely high, which provides insightful ideas for the valorization of lignin.

Keywords:

Lignin-derived phenolics, in-situ hydrogenation, phenol hydrodeoxygenation, Ru/C catalyst, BTX

多级结构 Ni 基催化剂强化生物质热解制富氢合成气研究

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摘 要：摘要—黑体/小五；摘要内容—宋体/小五；行距为 1.25 行

本研究采用简单的水热合成方法成功制备出具有多级结构的 Ni-Zn、Ni-Al 催化剂并将其应用于生物质催化热解制备富氢合成气过程。结果表明，在 600 °C 催化反应温度条件下，一维棒状 Ni-Zn 催化剂能够显著提高合成气中氢气选择性，H_2/CO 比例高达 3.05，此时产气量为 655 mL/g 生物质，H_2 产量为 305 mL/g 生物质；而三维花状 Ni-Al 催化剂则能够显著提升气体产量，气体产率达 65.9 wt.%，产气量为 745 mL/g 生物质，此时 H_2/CO 比例为 2.28。结构表征发现，Ni 基活性位点在催化剂表面高度分散，其有序组装有效缓解催化剂因无序堆积导致的活性位点覆盖问题，进而促进反应物与更多的活性位点充分接触，提高催化性能。

关键词：富氢合成气；生物质；催化热解；多级结构；Ni 基催化剂

Promoting hydrogen-rich syngas production from pyrolysis of biomass over hierarchically structured Ni-based catalysts

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Abstract: Novel hierarchically structured Ni-based catalysts (Ni–Al and Ni–Zn) were successfully synthesized by a simple hydrothermal process, and applied for hydrogen-rich syngas production from biomass pyrolysis. Various characterization techniques such as XRD, SEM, BET and H_2-TPR were employed to thoroughly characterize the fresh catalysts. The results reveal that the developed Ni-based catalysts are found to be highly effective for hydrogen-rich syngas production. High gasification efficiencies of 65.9 and 59.6 wt.%, syngas yields of 745 and 655 mL/g biomass, H_2 yields of 316 and 305 mL/g biomass as well as H_2/CO molar ratios of 2.28 and 3.05 were obtained for Ni–Al and Ni–Zn catalysts, respectively, at a moderate catalytic temperature of 600 °C. Based on the results of structure characteristics, this might be due to their unique hierarchical structure (three-dimensional flower-like and one-dimensional nanorods) with Ni species homogeneous dispersed on the surface, which can effectively reduce the coverage of active centre caused by disorder aggregation and improve the thermal stability. As a result, more active sites can be accessible for reactants to promote the cracking/reforming reactions of pyrolysis volatiles. The resulting syngas are favored for further Fischer–Tropsch synthesis reaction and other synthesis reactions for the production of liquid hydrocarbons.

Keywords: H_2-rich Syngas, Biomass, Catalytic pyrolysis, hierarchically structured, Ni-based catalysts.

芬顿试剂改性 ZSM-5 分子筛及催化烯烃齐聚反应性能研究

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摘　要:

采用浸渍法分别制备了不同浓度芬顿试剂改性的 ZSM-5 分子筛催化剂，通过表征及烯烃齐聚反应考察了各催化剂的理化性质和催化性能。结果表明：随芬顿试浓度增大，ZSM-5 分子筛脱铝加强，结晶度逐渐降低，分子筛中 Fe 含量明显增加。且逐渐由外部进入分子筛骨架，骨架内的 Fe 主要以四配位的 Fe^{3+}形式存在。5wt.%芬顿试剂改性后的 ZSM-5 分子筛还存在四配位的 Fe^{2+}。5wt.%芬顿试剂改性后的 ZSM-5 分子筛的比表面积、介孔体积最大，酸性最强。相比母体 ZSM-5 分子筛，丙烯转化率从 77.1%增加至 85.8%。长链组分选择性从 78.3%增加至 85.7%，催化剂在 60h 内具有良好的稳定性，且保持在 80%以上。

关键词：芬顿试剂；ZSM-5；烯烃齐聚

Research on propene oligomerization reaction over the Fenton reagent modified ZSM-5

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Abstract:

A series of different concentrations of Fenton's reagents were used to modify the ZSM-5 molecular sieve, respectively. All these catalysts were characterized and evaluated in propene oligomerization process. They were characterized by XRD, ICP-OES, N_2 adsorption-desorption, NH_3-TPD, Py-IR. The results demonstrated that with the increase in the concentration of Fenton's reagents for modification, the dealumination of the ZSM-5 molecular sieve enhanced, the crystallinity gradually decreased, and the Fe in Fenton's reagents gradually entered into the molecular sieve framework from the outside increasing its content. After modified by 5 wt.% Fenton's reagents, the Fe in the framework mainly existed as four-coordinated Fe^{3+}, and there also existed some four-coordinated Fe^{2+}. In addition, the modified ZSM-5 molecular sieve exhibited the largest specific surface area, mesopore volume and the strongest acidity. During the oligomerization of propylene, the conversion increased from 77.1% to 85.8%, compared to the original ZSM-5 molecular sieve. The selectivity of components with long carbon chain increased from 78.3% to 85.7%. And the catalyst showed good stability within 60 h.

Keywords: Fenton reagent; ZSM-5; propene oligomerization;

不同种类生物质的气化特性及相关性分析

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摘　要　本文在固定床反应器和热重分析仪上研究了 13 种生物质（包含壳类、木质类、秸秆类）的蒸汽气化特性和非等温气化反应性，探讨了样品气化反应性与原料特性之间的关联。结果表明，热解阶段失重行为和动力学特性主要受纤维素和半纤维素含量的影响；焦炭气化阶段失重量、最大失重速率和其对应温度主要由固定碳含量决定，反应性则主要受灰分含量和组成的影响。总气体产率与生物质有机质含量呈现一定相关性，而 H_2 产率则主要与固定碳含量相关，其中壳类生物质最高；温度升高利于烃类气体重整，H_2 产率相应提高，但高温会导致焦油的芳香性增加；提高蒸汽浓度也会促进烃类气体重整，且更利于含 2 个以上芳环的焦油的裂解和开环。

关键词　生物质，蒸汽气化，失重特性，反应性，关联性分析

Gasification characteristics and correlation analysis of different kinds of biomass

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ABSTRACT: In this paper, the steam gasification characteristics and non-isothermal gasification reactivity of 13 kinds of biomass (including shells, woods, and straws) were studied on the fixed bed reactor and thermogravimetric analyzer respectively, and the relationship between gasification reactivity and feedstock characteristics were discussed. The results showed that the weight loss behavior and kinetic characteristics of the pyrolysis stage are mainly affected by the content of cellulose and hemicellulose. The weight loss, maximum weight loss rate and the corresponding temperature in the char gasification stage were mainly determined by the fixed carbon content, and the reactivity was mainly affected by the ash content and composition. The total gas yield had a certain correlation with the biomass organic matter content, while the H_2 yield was mainly related to the fixed carbon content, and shell biomass is the highest. Increasing temperature was conducive to the reforming of hydrocarbon gas, and the H_2 yield increased accordingly, but high temperature also increased the aromaticity of tar. Increasing the steam concentration also promoted the reforming of hydrocarbon gas, and was more conducive to the cracking and ring opening of tar containing more than two aromatic rings.

KEY WORDS： Straw biomass, Steam gasification, Thermogravimetric characteristic, Gasification reactivity, Correlation analysis

生物质钙基吸附增强气化制氢研究

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摘　要：本研究以 ASPEN PLUS 软件为平台，建立了生物质钙基吸附增强气化模型，结合固定床的实验数据，研究了温度、CaO 添加量、水蒸气添加量等参数对制氢过程的影响。当气化温度在 650~700℃时，可获得较好的吸附增强效果，670℃时有最大 H_2 浓度 56%，温度大于 750℃后，CaO 对气化过程无强化作用；随着 CaO 添加量的增加，H_2 浓度和产率均增加，当 CaO/生物质摩尔比大于 0.75 后，对气化过程基本无影响；随着水蒸气/生物质质量比增加，H_2 浓度和产率都在逐渐增加，但水蒸气气化率快速下降，当比例超过 1.2 后，水蒸气分压的增大导致的体系中 CO_2 分压开始减小，CaO 的增强气化作用不再明显。

关键词：生物质；CaO；增强气化；氢气；ASPEN PLUS

Ca-based Sorbent Enhanced Biomass Steam Gasification for Hydrogen Production

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Abstract: A model of Ca-based sorbent enhanced biomass steam gasification for hydrogen production was built using ASPEN PLUS. Combined with the experimental data of a fixed bed, the effects of temperature, CaO/biomass molar ratio, Steam/biomass mass ratio on gasification characteristics were analyzed. When the temperature of gasification is between 650~700℃, a better adsorption enhancement effect can be obtained, and it reaches the maximum value of 56% at 670℃. CaO has no enhanced effect on gasification after the temperature is higher than 750℃. As the CaO/biomass molar ratio increases, both concentration and yield of H_2 increase, and there is no more changes in gasification when the ratio is greater than 0.75. The concentration and yield of H_2 increase with the increase of Steam/biomass mass ratio, but the gasification rate of steam decreases rapidly. The partial pressure of CO_2 in the system decreases due to the increase in the partial pressure of steam after Steam/biomass mass ratio is greater than 1.2, and the enhanced effect of CaO is no longer obvious.

Keywords: biomass; CaO; enhanced gasification; hydrogen; ASPEN PLUS

生物质熔融盐快速热解及挥发分重整研究

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摘　要：本文在在固定床上利用三元熔融碳酸盐进行棉杆快速热解特性以及热解挥发分的裂解重整研究，结果表明在 450~550°C 热解时，熔融盐对挥发分二次成焦作用较强；随着温度的升高，熔融盐对挥发分二次裂解作用增强，反应中间物发生脱羧、脱甲基、脱甲氧基以及芳香化反应,伴随着大量 CO、CH_4、H_2 析出。当温度进一步升高至 850°C 时，气体产率大幅升高而热解焦炭和生物油明显降低，生物油中稠环芳烃超过 90%，主要来源于热解中间体的进一步脱氧和芳香化反应，同时析出大量的气体，气体产率超过 91%，合成气产量达到 29.51 mmol/g。

关键词：熔融盐；热解；挥发分；生物质

Biomass rapid pyrolysis and derived volatiles reforming on molten salts

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Abstract:

In this paper, the rapid pyrolysis characteristics and derived volatiles reforming of cotton stalks were investigated in a fixed bed by using ternary molten carbonate. The results shows that molten salts promoted secondary coking of volatiles under the temperature of 450~500ºC. With the increasing of temperature, molten salts accelerated the cracking of volatiles, the intermediates were decarboxylated, methylated, demethoxylated and aromatized to produce CO, CH_4 and H_2. When the temperature was 850ºC, the gas yield increased significantly while the oil and char decreased. The polycyclic aromatic hydrocarbons (PAHs) occupied more than 90% of the liquid oil. They mainly came from further deoxidation and aromatization of pyrolysis intermediate, which resulted in the releasing of gas. The gas yield was 91 wt% and 29.51 mmol/g.

Keywords: Molten salt, pyrolysis, volatiles, biomass

B 掺杂对 Ni/半焦催化剂催化甲苯水蒸气重整反应的影响研究

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摘　要:

Ni/半焦催化剂用于甲苯水蒸气重整反应中，半焦载体易与水蒸气发生气化反应而被逐渐消耗。因此，如何抑制半焦载体的气化消耗，以提高 Ni/半焦催化剂的寿命是其亟待解决的问题。本研究通过构筑 B 掺杂的 Ni-B/半焦催化剂探究 B 对甲苯水蒸气重整中 Ni/半焦催化剂稳定性的影响及作用机理，主要包括 B 掺杂对半焦载体中固有碱金属及碱土金属和碳质结构的影响。对以未处理生物质为原料制得的 Ni/半焦催化剂，适量 B 掺杂可以提高半焦载体的石墨化程度、抑制半焦中 K 的催化作用，有利于提高其稳定性。对以酸洗生物质为原料制得的 Ni/半焦催化剂，B 掺杂虽然略微降低了催化剂的石墨化程度，但是可以提高其抗积碳与抗烧结性能。

关键词：水蒸气重整；甲苯；B 掺杂；稳定性；Ni/半焦

Effects of Boron doping on the performance of Ni/Biochar catalyst in toluene steam reforming

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Abstract: Biochar support can be consumed quickly by steam when Ni/biochar catalysts are used in the toluene steam reforming process. Thus, how to inhibit the consumption of biochar support to improve the catalyst lifetime becomes an urgent problem. In this study, we doped Ni/biochar catalysts with Boron and investigated the catalyst performance and mechanism of Ni-B/biochar catalysts. B doping influenced both the inherent alkali and alkali earth metals and the carbon structures of biochar. For Ni/biochar catalysts prepared from raw biomass, a suitable amount of B can increase the graphitization degree of the biochar support and inhibit the catalytic effects of K, which were conducive to the improvement of catalyst stability. For Ni/biochar catalysts prepared from acid-washed biomass, B doping improved the anti-coking and anti-sintering ability of the catalyst, although the graphitization degree was lowered slightly.

Keywords: Steam reforming; Toluene; Boron doping; Stability; Ni/biochar.

CeO_2 和 ZrO_2 改性的 SAPO-34 的制备及其合成气制备低碳烯烃催化性能

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摘　要:

采用水热法制备了 CeO_2 和 ZrO_2 改性的 SAPO-34 分子筛，同时通过共沉淀法制备了 ZnCr 氧化物，通过机械混合的方法制备了金属氧化物分子筛复合催化剂。用 X 射线衍射、N_2 吸脱附（BET）和透射电镜（TEM）等方法对催化剂的结构进行了表征。采用加压固定床反应器测定了催化剂的催化性能，与常规的 SAPO-34 分子筛对比 CeO_2-ZrO_2 改性的 SAPO-34 催化剂显示了较高的 CO 转化率和低碳烯烃选择性，催化性能更佳。

关键词：水热合成法；SAPO-34；合成气转化；低碳烯烃

Preparation of CeO_2 and ZrO_2 modified SAPO-34 for syngas conversion to olefins

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Abstract:

SAPO-34 molecular sieve were synthesized by hydrothermal methods and was modified with CeO_2 and ZrO_2..A series of CrZn oxide catalysts with different Cr/Zn ratios were synthesized by co-precipitation. The composite catalyst was prepared by mechanically mixing CrZn oxide and SAPO-34 molecular sieve . The structures of synthesized catalysts was characterized with several methods such as XRD, BET and SEM. The catalytic performance of the catalyst was tested in a fixed bed reactor. The results show that the catalyst using CeO_2 and ZrO_2 modified SAPO-34 molecular sieve show higher conversion of CO and selectivity to C2–C4 olefins than that of the unmodified SAPO-34.

Keywords: hydrothermal synthesis；SAPO-34；syngas conversion；light olefins

FexC@C 催化剂的可控制备及其费托合成性能研究

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摘　要:

铁碳化合物（FexC）作为费托合成主要活性相，在反应过程中其组成的变化及烧结是其失活的主要原因。本文以金属有机框架材料为前驱体，制备一系列碳包裹的铁碳化合物催化剂（FexC@C），通过控制制备条件，实现碳包裹层厚度和铁碳化合物种类的连续可调，将其进行费托合成评价，催化剂表现出较高的反应性能和良好的稳定性。对其进一步表征结果表明，催化剂的碳包裹外层对铁碳化合物的稳定作用和对铁烧结的限制作用，可能是其表现出优异性能的主要原因。

关键词：FexC@C 催化剂；结构可调；费托合成

FexC@C catalyst with continuous adjusted structure and its application in FTS

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Abstract:

Generally, it has been widely accepted that the iron carbides are active phases in FTS reaction, and the iron carbides phase transformation, sintering and carbon deposition are the main reason for the catalysts deactivation during the FTS reaction. In this paper, a series of FeCx@C core-shell catalysts are prepared from metal organic framework precursors, and evaluated on the FTS reaction. These catalysts present good activity and stability in the FTS reaction. The characterization results of the catalysts suggest that iron-carbon compounds stabilization and restriction iron sintering by the carbon-coated outer layer of the catalyst, which may be the main reason for its excellent performance.

Keywords: FexC@C catalyst, continuous adjusted structure, FTS reaction

毛竹加工剩余物催化热裂解研究

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摘　要：为解决毛竹加工过程剩余物有效利用问题，本研究通过加入不同负载率的金属铜改性 ZSM-5 沸石催化剂，采用热裂解-气相色谱/质谱联用技术，对于毛竹加工剩余物进行了催化热裂解研究。结果表明，加入 Cu(2)/ZSM-5 的毛竹加工剩余物的热裂解的有机液体产物中酚类物质的相对含量最高，占 22.39%，其次是酮类物质和呋喃类物质，分别占 13.56 %和 13.55%。醇类物质、糖类物质的含量有明显增加；研究结果可为毛竹废料资源的有效利用提供基础数据，对毛竹热裂解技术的发展提供参考。

关键词：毛竹加工剩余物，催化热裂解，Py-GC/MS

Study on Catalytic Pyrolysis of Bamboo Residue

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Abstract:

In order to solve the problem of effective utilization of bamboo residues, this study uses pyrolysis-gas chromatography/mass spectrometry technology to study catalytic pyrolysis of bamboo residues by adding different loading rates of copper-modified ZSM-5 catalyst. The results showed that when loading rates of copper-modified ZSM-5 catalyst was 2 wt.%, the relative content of phenols was highest one, which was 22.39%; the relative contents of ketones and furans ranked second and third, which were 13.56% and 13.55%, respectively; in addition, alcohol and sugar substances in catalytic pyrolysis of bamboo processing residues have increased significantly. The research can provide basic data for the effective utilization of bamboo waste resources and provide a reference for the development of bamboo pyrolysis technology.

Keywords: Bamboo residues, Catalytic pyrolysis, Py-GC/MS

四氢呋喃/水共溶剂预处理提升木糖渣酶解糖化的研究

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摘　要：本研究采用四氢呋喃（THF）/H_2O 共溶剂预处理方法，提升了木糖渣（CRs）的酶解糖化效率，获得了高产率、高浓度的葡萄糖。首先，通过 Box-Behnken 实验设计中的响应面优化，得到了最优的预处理条件（THF 浓度 53.7%，时间 1 h，温度 202.3 °C），并获得了最大糖产率 498.2 mg/g CRs。然后，将最优条件预处理后回收的 CRs 应用于高基质（15-20%）酶水解，得到了 128.6 mg/mL 的高浓度葡萄糖。最后，通过 9 个与底物相关的因子与纤维素转化的相关性分析，发现预处理后残留的 Klason 木质素和表面缩聚的假木质素是酶水解的主要抑制因子。

关键词：纤维素；响应面；高基质；葡萄糖；假木质素；

Tetrahydrofuran/H_2O co-solvent pretreatment enhance enzymatic hydrolysis of corncob residues

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Abstract: To obtain high yield and high concentration glucose from corncob residues (CRs), tetrahydrofuran (THF) + H_2O co-solvent pretreatment was employed. The pretreatment parameters were firstly optimized by Box-Behnken Design of response surface method, and the maximum glucose yield (498.2 mg/g CRs) was obtained via enzymatic hydrolysis after pretreated under optimized conditions (53.7% THF concentration, 202.3 °C, 1.05 h). Then, the pretreated CRs under optimized conditions were enzymatically hydrolyzed at 20% solid loading, and then obtained the high concentration glucose production (128.6 mg/mL). Finally, the interactions between the 9 substrate-related factors and cellulose conversion were analyzed through correlation analysis, and found that Klason lignin remained in the cellulose-rich fractions and pseudo lignin condensed on the surface of the recovered substrate were the predominant inhibitors for enzymatic hydrolysis.

Keywords: cellulose; response surface method; high solid loading; glucose; pseudo lignin;

生物油选择性改质制备对二甲苯研究

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摘　要:

利用可再生生物质热解生物油可以制备石油化工中重要的大宗化工原料对二甲苯和高辛烷值汽油。本工作制备了 Zn/Ga/SiO_2/HZ 多功能催化剂，发现多功能催化剂提高了生物油的催化改质过程中对二甲苯的选择性和收率。SiO_2 负载层降低了催化剂表面的酸性，显著提高了对二甲苯的选择性。在催化剂中加入锌、镓等活性元素，可以促进脱羰、脱羧和芳构化反应，进一步提高对二甲苯的收率。获得对二甲苯收率最高为 18.7%，对二甲苯在二甲苯中选择性为 93.8%。通过对不同生物油的催化裂化反应及产物中官能团的详细考察，提出了反应机理。从生物油中得到的对二甲苯产品可用于高附加值的化工或高辛烷值汽油添加剂。

关键词：生物油；催化提值；对二甲苯；多功能催化剂

Preparation of P-xylene from Bio-oil by Selective Catalytic Upgrading

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Abstract:

P-xylene and gasoline with high octane number can be prepared by the catalytic pyrolysis of bio-oil from renewable biomass. In this work, Zn/Ga/SiO_2/HZ multifunctional catalyst was prepared. It was found that the multifunctional catalyst improved the selectivity and yield of p-xylene in the catalytic upgrading of bio-oil. The surface acidity of the catalyst was decreased by loading SiO_2 and the selectivity of p-xylene was significantly improved. The addition of zinc and gallium in the catalyst can promote the decarbonylation, decarboxylation and aromatization reactions, and further improve the yield of p-xylene. The highest yield of p-xylene was 18.7%, and the selectivity of p-xylene in xylene was 93.8%. The reaction pathways were proposed according to the detailed investigation for the catalytic cracking of different bio-oils and the functional groups in the products. The p-xylene product obtained from bio-oil can be used as high value-added chemical or high octane gasoline additive.

Keywords: Bio-oil; catalytic upgrading; p-xylene; multifunctional catalyst

木质素热解工况条件对寡聚物形成的影响

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摘要：为探究降低木质素热解油中寡聚物含量的有效调控途径，本实验研究了热解温度与气氛对碱木素液相产物中寡聚物含量及其组成特性的影响。结果表明，600°C 热解得到的寡聚物含量相对较低，单酚含量相对较高。一定量氢气的存在($H_2/Ar = 1:9$, v/v)能够促使木质素在热解过程中优先发生不饱和键的加氢反应，由此抑制了二次反应的发生。因此，木质素在 600°C 下热解时，建议通入适量的氢气，以减少寡聚物的含量、提高单酚收率。

关键词：热解油；温度；气氛；寡聚物；调控途径

Effects of temperature and atmosphere on the oligomers during the pyrolysis of lignin

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Abstract: To obtain effective regulation pathways for the reduction of the oligomers content in alkali lignin (AL)-derived pyrolysis oil (PO), the effects of pyrolysis temperature and atmosphere on the oligomer-rich fractions were investigated. The results showed that under a pyrolysis temperature of 600°C, the content of oligomers and main monophenols was relatively low and high, respectively. More notably, a certain amount of hydrogen ($H_2/Ar=1:9$, v/v) promoted a preferential hydrogenation on unsaturated bonds during pyrolysis, leading to the reduction of oligomers and enhancing the yield of monophenols, accordingly.

Key words: Pyrolysis oil; Temperature; Atmosphere; Oligomers; Regulatory pathways

改性分子筛催化木质素加氢脱氧的研究

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摘　要：木质素是最丰富的天然可再生芳香高分子聚合物，木质素加氢脱氧制备的烃类物质，可用作生物燃料。本研究设计了一种金属 Al 改性的分子筛 HZSM-5 负载活性金属 Ru 的催化剂，对从桉木粉中提取的有机溶剂木质素进行加氢脱氧反应。在氢气压力 4MPa、水为溶剂、转速为 600rpm 的条件下，通过实验考察了催化剂用量、反应时间、反应温度对木质素加氢脱氧的影响，确定最佳反应条件为木质素与催化剂用量比 1：1、反应时间 10h、反应温度 270℃，此时轻组分物质总收率为 21.89wt%，其中烃类物质收率为 15.47wt%，丙酸乙酯收率为 4.22wt%，其它含氧物质收率为 2.21wt%。

关键词：木质素；加氢脱氧；金属改性分子筛；烃类物质

Study on Catalytic Hydrodeoxygenation of Lignin by Modified Molecular Sieves

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Abstract: Lignin is the most abundant natural renewable aromatic polymer. Hydrocarbons prepared by lignin hydrodeoxygenation can be used as bio-fuel. In this study, metal Al-modified HZSM-5 molecular sieve loaded with metal Ru catalysts was designed for organosolv lignin extracted from eucalyptus powder hydrodeoxygenation. Under the conditions of hydrogen pressure of 4MPa, water as solvent, rotation speed of 600rpm, influence factor catalyst dosage, reaction time and reaction temperature are explored . The optimal reaction conditions were weight ratio of lignin to catalyst dosage 1: 1, reaction time 10h and temperature 270℃. As a result, the total yield of light components was 21.89wt%, in which the yield of hydrocarbons, ethyl propionate,other oxygen compound was 15.47wt%, 4.22wt%, and 2.21wt% respectively.

Keywords: Lignin; hydrodeoxygenation; metal modified molecular sieve; hydrocarbons

Co 基催化剂上酚类加氢脱氧研究

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摘 要:

以 Co 为加氢脱氧的主要活性组分，采用固定床流动态连续反应工艺，通过不同载体、助剂对 Co 基催化剂性质及其加氢脱氧性能影响的研究，开发了适合于生物油中酚类组分定向加氢脱氧的高活性和稳定性的微球 SiO_2 负载 Co 和 Pt 的双金属 Co-Pt/SiO_2 催化剂，在 400 ºC、1.0MPa 氢气压力和 0.5 h^{-1} 的反应条件下，其对酚类混合物的转化率可达 98%，转化产物基本为苯、甲苯和二甲苯，并能在反应过程中长时间保持稳定。

关键词：酚；钴；二氧化硅；加氢脱氧；催化剂

Co-based catalysts for hydrodeoxygenation of phenols from biomass oils

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Abstract:

In this paper, hydrodeoxygenation (HDO) of phenols as the model compound of aromatic oxygenated compounds in biomass oil over Co-based catalysts was studied. Co-Pt/SiO_2 catalyst with high HDO activity and stability for the conversion of guaiacol and phenols into aromatic hydrocarbons was developed. Under the temperature of 400 ºC, hydrogen pressure at 1.0 MPa and weight hourly space velocity of 0.5 h^{-1}, the HDO activity for phenols reached 98%, and the products were almost all benzene, toluene and xylene with outstanding stability..

Keywords: phenols; hydrodeoxygenation; Co; SiO_2; catalyst

烘焙耦合分级冷凝对核桃壳和蒸馏残渣共热解液体产物分布的影响

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摘 要:

生物质热解耦合分级冷凝技术有助于实现生物油中高附加值产物的分离和富集。而烘焙可以有效改变生物质的结构，从而影响生物质热解及其产物分布。基于此，本研究以探究生物质预处理耦合分级冷凝技术对生物质热解液体产物的分布及对高附加值产物分离和富集的影响为目的，采用配置三级冷凝系统的小型固定床热解装置对生物油蒸馏残渣和核桃壳进行烘焙预处理耦合共热解实验。结果表明：随着烘焙温度的升高，热解液体产物的总产率逐渐下降；烘焙预处理有助于共热解液体产物中酚类产物的富集，且酚类产物倾向于在第二冷凝级富集；烘焙预处理不利于第一和第二冷凝级中烃类和呋喃类产物的富集。

关键词：烘焙预处理；分级冷凝；共热解；高值化学品

Effect of torrefaction coupled with fractional condensation on the distribution of co-pyrolysis liquid products of walnut shells and distillation residue

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Abstract:

Biomass pyrolysis coupled with fractional condensation helps to realize the separation and enrichment of high value-added products in bio-oil. Torrefaction pretreatment can effectively change the structure of biomass, thereby affecting biomass pyrolysis and its products distribution. Based on this, the purpose of this study is to explore the impact of torrefaction pretreatment coupled with fractional condensation on the distribution of biomass pyrolysis liquid products and the impact on the separation and enrichment of high value-added products. A small fixed-bed pyrolysis device equipped with a three-stage condensation system was used to conduct torrefaction pretreatment coupled with co-pyrolysis of bio-oil distillation residue and walnut shells. The results show that with the increase of torrefaction temperature, the total yield of pyrolysis liquid products gradually decreases. Torrefaction pretreatment is helpful to the enrichment of phenolic products in co-pyrolysis liquid products, and phenolic products tend to be enriched in the second condensation stage. Torrefaction pretreatment is not conducive to the enrichment of hydrocarbons and furan products in the first and second condensation stages.

Keywords: Torrefaction pretreatment; Fractional condensation; Co-pyrolysis; High value-added products

$AlCl_3$ 溶液室温预处理毛竹的 200^{o}C 烘培研究

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摘　要：基于 $AlCl_3$ 室温预处理对毛竹的影响研究，进一步研究了金属盐浸渍对毛竹在烘培过程中转化的影响。经 $AlCl_3$ 预处理的毛竹在烘培过程中生成的液体及小分子产物收率的明显提高，其最大转化率及液体收率分别可达 44.2 *wt.%* 和 32.1 *wt.%*，对应半纤维素转化达 96.0 *wt.%*，纤维素转化 32.1 *wt.%*，可获得 2.4 *wt.%*单糖，5.1 *wt.%*羧酸，2.6 *wt.%*呋喃化合物以及 10.5 *wt.%*酚类物质。结果表明，残留的 $AlCl_3$ 对烘培过程中三种主要成分的分解具有显著的催化作用。

关键词：烘培，预处理，氯化铝，毛竹，木质素

200^{o}C Torrefaction of *Pubescens* Pretreated with $AlCl_3$ Aqueous Solution at Room Temperature

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Abstract: Based on the room temperature pretreatment of *pubescens* by $AlCl_3$ aqueous solution, metal salts soaking-Torrefaction conversion technology was investigated ulteriorly. It was found that $AlCl_3$ pretreatment of *pubescens* favored observably the yield of liquid and small molecular products in the torrefaction via changing the composition and structure of the raw material. For Pretreated Samples, the maximum conversion and Y_{liquid} reached 44.2 *wt.%* and 32.1 *wt.%*, respectively, along with 96.0 *wt.%* of hemicellulose, 31.8 *wt.%* of cellulose converted, yielding 2.4 *wt.%* monosaccharides, 5.1 *wt.%* carboxylic acid, 2.6 *wt.%* furan compounds as well as 10.5 *wt.%* phenols, indicating obvious catalytic effects of residual $AlCl_3$ on the decomposition of the three major components in torrefaction.

Keywords: Torrefaction, Pretreatment, $AlCl_3$, *Pubescens*, Lignin

氯化镁溶液室温预处理对毛竹热解行为和其热解油性质的影响

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摘 要：研究了毛竹在不同浓度 $MgCl_2$ 溶液及同等 pH 盐酸溶液中浸渍处理后其热解行为的变化。对热解前的固体进行了热重分析，对热解油进行了 GC-MS、GC-FID、HPLC、GPC、ESI-MS 以及 2D HSQC NMR 分析。$MgCl_2$ 促进了热解中半纤维素的脱水，有利于毛竹热解油中糠醛收率的提升，从 0.27 *wt.%* (raw *pubescens*)升高到 2.61 *wt.%* (20 *wt.%* $MgCl_2$)。热解油的 ESI-MS 以及 2D HSQC NMR 分析结果表明：$MgCl_2$ 促进了半纤维素的解聚，热解油中寡聚物的含量增加。此外，2D HSQC NMR 检测到了一个源于纤维素和半纤维素共同降解得到的新结构（X-MeGlcA4）,进一步证实了该条件下的共同解聚作用。

关键词：氯化镁，预处理，毛竹，半纤维素，木质素

Effects of $MgCl_2$ Solution Pretreatment at Room Temperature on the Pyrolytic Behavior of Pubescens and the Properties of Bio-oil

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Abstract: Pyrolytic behaviors of pubescens samples pretreated by 0, 5, 10, 15, and 20 *wt.%* $MgCl_2$ solution and HCl solution (with equal pH value to designed $MgCl_2$ solution) was studied. The solid samples before the pyrolysis were analyzed by TGA, and the bio-oil was analyzed by GC-MS, GC-FID, HPLC, GPC, ESI-MS, and 2D HSQC NMR. Dehydration of hemicellulose during pyrolysis was promoted in the presence of $MgCl_2$, which was conducive to increase the Y_{furfural} (raising from 0.27 to 2.61 *wt.%*, corresponding to raw *pubescens* and 20 wt.% $MgCl_2$ used). The ESI-MS and 2D HSQC NMR results further confirmed the depolymerization of hemicellulose by $MgCl_2$, which increased the content of oligomers in the pyrolysis oil obtained. Moreover, a new structure (X-MeGlcA$_4$) derived from degradation of cellulose and hemicellulose was detected，which further confirmed the co-degradation of cellulose and hemicellulose under this condition.

Keywords: Pretreatment, Liquids, Oligomers, Biofuels, Pyrolysis

xNi/HTASAO5 催化剂上二氧化碳低温重整甲烷制氢反应稳定性的研究

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摘要：生物质热解尾气主要含有二氧化碳和甲烷等，可通过干法重整反应（DRM）获得氢，从而增加热解尾气的商业价值，减少环境污染，提高生物质的利用率。本文选择镍物种作为反应活性成分，HTASAO5 材料作为载体，制备了 xNi/HTASAO5 催化剂,研究了其在 DRM 反应中的催化性能，并用 TPR、XRD、TG-Ms、XPS、TEM、BET 等表征方法对催化剂进行分析。研究发现在反应中适量的 Ni 不仅能够达到较高的活性，而且能够抑制积碳生成，提高催化剂的稳定性。

关键词：甲烷　　二氧化碳　　稳定性　　催化性能

The study on the stability of xNi/HTASAO5 Catalyst for the production of H_2 via carbon dioxide reforming of methane at low temperature

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Abstract: The off gas from the pyrolysis of biomass mainly contains carbon dioxide and methane, which could be used to produce hydrogen by DRM. In the present work, nickel species were selected as active components and HTASAO5 was used as support to prepare xNi/HTASAO5 catalysts, and its catalytic performance in DRM reaction was studied. The catalysts were analyzed by TPR, XRD, TG-MS, XPS, TEM, BET and other characterization methods. It was found that Ni with a suitable amount can not only have higher activity, but also inhibit the formation of carbon deposits and improve the stability of the catalyst.

Keywords: methane**;** carbon dioxide; stability; catalytic performance

Ni-HTASO5 催化甲烷蒸汽重整和水汽变换反应提高制氢效率研究

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摘　要:

研究了不同载体制备的镍基催化剂上水蒸汽甲烷重整（SMR）制氢工艺。采用 BET、AAS、XRD、H_2-TPR、CO-TPD、NH_3-TPD、XPS、TG-DSC-MS 和 Raman 光谱对催化剂进行了表征。以 CeZrOx 修饰的 Al_2O_3 (HTASO5)为载体，该催化剂对 SMR 反应表现出良好的催化性能和抗积碳性能，CeZrOx 能够增强水汽变换(WGS)反应，提高氢产率。研究发现，Ni-HTASO5 可以减少催化剂的强酸位点，这不仅有利于形成低石墨化的积碳，还可以降低积碳生成量。

关键词：水汽甲烷重整；水汽变换反应；CeZrOx；氢；碳沉积

Promoted H_2 Production via Simultaneous Methane Steam Reforming and Water-Gas Shift Reaction on Ni-HTASO5

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Abstract:

Steam methane reforming (SMR) was studied on Ni-based catalysts with different supports for hydrogen production. The catalysts were characterized by BET, AAS, XRD, H_2-TPR, CO-TPD, NH_3-TPD, XPS, TG-DSC-MS and Raman spectroscopies. Using CeZrOx-modified Al_2O_3 (HTASO5) as support, the catalyst exhibited good catalytic performance and carbon resistance for SMR reaction, whereas CeZrOx was able to enhance water-gas shift (WGS) reaction, promoting more hydrogen production. It was found that Ni-HTASO5 could decrease the strong acid sites of the catalyst, which would not only contribute to the formation of low graphited carbon, but also decrease the amount of carbon deposition.

Keywords: steam-methane reforming; water-gas shift reaction; CeZrOx; hydrogen; carbon deposition

磷酸二氢铵催化生物质选择性热解生产糠醛和左旋葡萄糖酮的机理研究

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摘　要:

糠醛（FF）和左旋葡萄糖酮(LGO)是木质纤维素类生物质热解的典型高附加值产物，前期研究发现磷酸铵盐可有效提升 FF 和 LGO 的收率。本工作旨在揭示糠醛和左旋葡萄糖酮在催化热解过程中的生成路径，采用 TG-FTIR 和 Py-GC/MS 对负载了不同质量磷酸二氢铵的稻壳开展热解实验。结果表明，在 ADP 作用下，C=O 官能团和碳水化合物在 300℃以下的释放大大加强，说明 ADP 能促进糖苷键的断裂并增强脱水反应。在热解产物中，脱水糖类产物和呋喃类产物的产率和相对含量明显提升。ADP 对 FF 和 LGO 均显示出良好的选择性。随着 ADP 剂量的增加，FF 和 LGO 的产量和相对含量先增加然后保持稳定。当热解温度为 400℃时，LGO 和 FF 的相对峰面积之和可达 52.23％。根据上述结果，推测出基于磷酸和氨气联合催化作用的选择性热解生物质制备 FF 和 LGO 的反应路径。

关键词：催化热解，生物质，糠醛，左旋葡萄糖酮，磷酸铵盐

Investigation on the Catalytic Effects of Ammonium Dihydrogen Phosphate on the Pyrolysis of Lignocellulosic Biomass

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Abstract: Furfural (FF) and levoglucosenone (LGO) are typical high-value biomass pyrolytic products of lignocellulosic biomass. Previous research found that ammonium phosphate can effectively improve the yield of FF and LGO. The catalytic effects of ammonium dihydrogen phosphate (ADP) on the biomass pyrolysis were investigated in this study. via TG-FTIR and Py-GC/MS. Results showed that ADP greatly enhanced the release of C=O groups and carbohydrates below 300 °C, indicating the breakage of glycosidic bond and dehydration reaction during pyrolysis were promoted by ADP. ADP showed good selectivity for both FF and LGO. With the increased ADP dose, the yield and relative content of FF and LGO increased firstly and then kept stable. 400 °C was found the optimal temperature for the production of FF and LGO, where the sum of the relative peak area of LGO and FF could reach 52.23%. Finally, a possible formation pathway of LGO and FF under the catalysis of ADP was speculated.

Keywords: catalytic pyrolysis, biomass, furfural, levoglucosenone, ammonium phosphate salts

升温速率对重质生物油理化特性演变影响的试验研究

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摘　要:

重质生物油的提质技术往往涉及到热处理过程。本研究以揭示升温速率对重质生物油理化特性的影响为目的，利用核磁共振波谱仪与气相色谱/质谱联用仪进行表征。结果表明：慢速升温速率对 400 至 800°C 下重质生物油的理化特性无明显影响。而在快速升温速率下热解温度为 300-500°C 时焦油产率明显增加。然而，进一步提高热解温度（600-800°C）则会降低焦油产率。元素分析表明焦油中碳含量随热解温度的升高而增加，而氮含量变化较小。NMR 结果发现焦油中羧基官能团在高温下易断裂。此外， GC / MS 分析表明随着热解温度的提高，芳族化合物的含量不断增加，而苯酚的含量则呈现相反的趋势。

关键词：重质生物油；热解；升温速率；演变

Effects of heating rate on the evolution of heavy fraction of bio-oil during its pyrolysis

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Abstract:

Various thermal conversion technologies have been successfully applied to upgrade heavy fraction of bio-oil (HB). However, all technical conversion routes involve thermal treatment process. In this work, the physicochemical properties of HB were characterized by Nuclear magnetic resonance (NMR) spectroscopy and gas chromatography/mass (GC/MS) spectrometer. Integrated results showed that slow heating rate had a negligible effect on the physicochemical properties of HB from 400 to 800°C. By contrast, decomposition, radical recombination and polymerization reactions could occur at fast heating rate. A clear trend of increasing tar yields was monitored from 300-500°C. However, a significant decrease was observed at high temperature (600-800°C). Through elemental analyzer, C content in tar expanded with the temperature increasing, whereas N content remained unchanged. NMR results indicated that the carboxyl functional groups would be destroyed at high temperature. Furthermore, the concentrations of aromatics showed a trend to increase accompanied by a simultaneous decrease in phenols with the temperature rising according to GC/MS analysis.

Keywords: Heavy fraction of bio-oil; Pyrolysis; Heating rates; Evolution

乙酸乙酯球形膨胀火焰的胞化特征

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摘　要：乙酸乙酯是一种典型的生物燃料，其具有成为内燃机内化石燃料替代品以及燃料添加剂的巨大潜力。乙酸乙酯在内燃机内燃烧的过程中，当其预混火焰表面由平滑转换褶皱状态后，会产生火焰自加速现象。因此有必要对乙酸乙酯预混火焰的动力学尤其是胞化不稳定性的进行研究。本文利用图像处理技术结合三维重构算法对图像中火焰表面的裂纹长度、火焰表面“细胞”数量、面积以及长度尺度等数据进行了提取与重构操作。此外，根据不同半径下“细胞”长度尺度本文推导出其波数，并将拟合所得的波数-帕克雷数曲线与理论曲线对比，本文发现实验所得曲线基本处于理论范围之内。

关键词：乙酸乙酯；生物燃料；内燃机；预混火焰；图像处理

Cellularization characteristics of ethyl acetate spherical expanding flame

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Abstract: Ethyl acetate is a typical biofuel, which has great potential as a fossil fuel substitute and fuel additive in internal combustion engines. During the combustion of ethyl acetate in an internal combustion engine, when the surface of the pre-mixed flame changes from smooth to a wrinkled state, flame self-acceleration will occur. Therefore, it is necessary to study the kinetics of ethyl acetate premixed flame, especially the instability of cellularization. This paper uses image processing technology combined with three-dimensional reconstruction algorithm to extract and reconstruct the data of the flame surface crack length, the number of cellular area and cellular length scale in the image. In addition, according to the cellular length scale under different radii, the wavenumber is derived in this paper, and the wavenumber-Parker number curve obtained by fitting is compared with the theoretical curve. This paper finds that the experimental curve is basically within the theoretical range.

Keywords: Ethyl acetate; Biofuel; Internal combustion engines; Premixed flame；Image process

供氢溶剂中不同木质素微波辅助氢解制备液体燃料研究

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摘　要:

在供氢溶剂中，研究了基于 CuNiAl 催化的微波辅助降解碱性木质素、脱碱性碱木质素和木质素磺酸盐。通过对不同木质素、溶剂和催化剂等实验参数的研究，发现在基于 CuNiAl 催化的甲醇体系中，木质素降解效率最佳且生物质油得率最高。进而研究了催化剂中金属协同作用以及溶剂作用对木质氢解的影响，发现随着催化剂中铜元素含量的增加，生物油的得率提高，且产物分子量降低，这表明木质素解聚过程中铜起到促进作用。结果表明，CuNiAl 基催化剂表现出高效的木质素解聚能力，成功地将木质素转化为具有较高 HHV 值和较低分子量的生物油，证实了 CuNiAl 基催化剂在微波辅助氢解过程中的氢化/加氢脱氧作用。

关键词：木质素；微波辅助；供氢溶剂；液体燃料

Insights into catalytic valorization of different lignin feedstocks into liquid fuels with microwave heating in hydrogen-donor solvents

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Abstract:

Microwave assisted valorization of alkaline lignin, dealkaline lignin and lignosulfonate over CuNiAl based catalysts were investigated in hydrogen donor solvents. The effect of lignin structures, solvents and catalysts were investigated concerning the bio-oil yields and properties. A common phenomenon was observed that the highest bio-oil yields were all obtained in methanol over CuNiAl based oxides under mild conditions. The synergistic and promotional effect of catalyst and solvent was discussed in detail, considering the elemental composition, HHV and molecular weights of bio-oil. The bio-oil yields improved and the molecular weights decreased with the increased Cu content in the catalysts, indicating the promotional effect of Cu during the lignin depolymerization. CuNiAl based catalysts exhibited to be effective to convert lignin to bio-oil with higher HHV and decreased molecular weights, confirming the hydrogenation/hydrodeoxygenation during microwave assisted hydrogenolysis.

Keywords: lignin; microwave assisted valorization; hydrogen donor solvents; liquid fuel

玉米芯水热解聚制取航煤组分过程模拟的㶲分析及生命周期评价

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摘要:

利用 Aspen Plus 软件建立了 2t/d 玉米芯水热解聚制取航煤组分的仿真流程，得到整个系统的物流、能流数据。对整个系统进行了㶲分析以及全生命周期评价，研究了仿真流程中各个子系统的㶲效率和㶲损失分布，探究了流程全生命周期的环境影响。结果表明：以输入湿生物质 100 kg 计，可得到航煤组分 10.1 kg；系统的总㶲效率为 33.04%，固体缩合加氢子系统具有最高的㶲效率，乙酰丙酸制备子系统具有最大的㶲损失，占全部㶲损的 53.28%，其次是糠醛制备子系统占 39.52%；航煤在全生命周期内的化石资源消耗潜值(FDP)为 72.70MJ/kg 航煤，一次资源消耗主要集中在航煤的使用过程；全球变暖潜值(GWP)为 1170.63g CO_2-eq/kg 航煤，酸化潜值(AP)为 8.86gSO_2eq/MJ 航煤，富营养化潜值(EP)为 1.32gPO_4^{3-}eq/MJ。航煤制备生产阶段中用于缩合的反应物制备过程是航煤全生命周期内的主要污染源，提高糠醛和乙酰丙酸浓缩过程中的热量利用有利于减少玉米芯水解制备航煤系统的环境影响。

关键词：航煤；水热解聚；㶲分析；生命周期评价

Exergy analysis and life cycle assessment of jet fuel production by hydrothermal decomposition of corncob

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Abstract:

The process of jet fuel production by hydrothermal depolymerization of 2t/d rice core was simulated using Aspen Plus software; and the flow data of the whole system was obtained. Exergy analysisand life cycle assessment (LCA) of the whole system was performed. The exergy efficiency and exergy loss distribution were conducted in each subsystem, and the environmental impact was explored of the simulation process. The results showed that, based on 100 kg wet biomass input , 10.1 kg of jet fuel was obtained. The whole exergy efficiency of the system was

33.04%; the solid condensation and hydrogenation subsystem had the highest exergy efficiency; Levulinic acid production subsystem had the largest exergy loss, accounting for 53.28% of the total exergy loss, followed by furfural production subsystem 39.52%. The fossil resource consumption potential (FDP) of jet fuel in its entire life cycle is 72.70 MJ/kg jet fuel, and the resource consumption is mainly concentrated in the use of jet fuel. The greenhouse gas emissions of life cycle are 27.87 gCO_2-eq/MJ, the acidification potential (AP) is 8.86 gSO_2eq/MJ jet fuel and the eutrophication potential (EP) is 1.32 gPO_4^{3-}eq/MJ. Reactants productions for condensation was the main source of pollution in the life cycle of jet fuel. The further reduction of the environmental impact in hydrothermal depolymerization should focus on the heat utilization of both furfural and levulinic acid concentration.

Keywords:jet fuel; hydrothermal depolymerization; Exergy analysis; life cycle assessment

醋酸梭菌的代谢工程改造用于合成气制备丙酮的研究

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摘　要：摘要—黑体/小五；摘要内容—宋体/小五；行距为 1.25 行

丙酮是化工生产中的重要原料。本课题拟借助微生物细胞工厂利用合成气生物制备丙酮。醋酸梭菌（*Clostridium aceticum*）是一种严格厌氧的革兰氏阳性细菌，它可以通过 Wood-Ljungdahl 途径将 H_2 和 CO_2 转化为乙酰辅酶 A，并进一步代谢产生乙酸。本研究利用丙丁梭菌（Clostridium *acetobutylicum*）来源的 *thlA*，*ctfB* 和 *adc* 基因，打通醋酸梭菌中从乙酰辅酶 A 到丙酮的代谢途径，实现合成气到丙酮的生物合成。

关键词：代谢工程；生物合成；伍德-永达尔途径；细胞工厂

Metabolic Engineering of *Clostridium aceticum* for producing acetone from syngas

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Abstract:

Acetone is an important raw material in chemical production. Our research objective is to use of a cell factory for acetone production from syngas. Clostridium aceticum is an anaerobic Gram-positive bacterium that can convert H_2 and CO_2 to acetyl-CoA via the Wood-Ljungdahl pathway and further metabolizes to produce acetic acid. In this study, we use the thlA, ctfB and adc genes cloned from Clostridium acetobutylicum to construct a metabolic pathway from acetyl-CoA to acetone in Clostridium aceticum, aiming to achieve the biosynthesis of acetone from syngas.

Keywords: Metabolic Engineering; Biosynthesis; Wood-Ljungdahl pathway; Cell factory

木质素定向解聚过程设计

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摘　要:

木质素是生物质的主要成分，也是天然芳烃来源。木质素优先炼制过程具备良好的前景，可深度解聚木质素得到高产木质素单体。本研究首先通过催化剂设计解决了木质素优先炼制过程半纤维素的保留和原料扩展两大难题。进一步通过催化剂在线投放装置，证明了木质素解聚单体及时稳定是高产木质素单体的重要前提，而且脱木质素和加氢稳定过程在一定条件下可实现分割。基于催化剂设计和过程分析结果，在半连续流动反应器中利用高沸点溶剂在典型造纸工业预处理条件下实现了木质素的半连续分离和解聚，为未来进一步探索直接串联模拟工业制浆的连续化装置实现木质素连续解聚过程奠定了基础。

关键词：木质素；木质素优先炼制；木质素单体；催化剂及过程设计;半连续过程

Design of Process on Lignin Depolymerization

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Abstract:

Lignin as a major component of biomass is a natural source of aromatics. Lignin-first biorefinery is a promising strategy that yields a deeply depolymerized lignin and high lignin monomers. Here, the important issues, hemicellulose retention and feedstock extension, in the lignin-first biorefinery are addressed. The development of lignin fractionation in flow is essential for the complete utilization of biomass. An on-line catalyst addition device was used to prove the immediate stabilization is indispensable for high lignin monomer, and the feasibility of splitting the delignification and stabilization/hydrogenation processes under specified condition. Based on this result, we used flowthrough reactors to semicontinuously extract and depolymerize lignin with high boiling point solvent under mild process condition, which is compatible with the continuous digestion process in paper industry. This study can provide a perspective on overcoming scale-up hurdles for the fractionation of biomass.

Keywords: Lignin, Lignin-first biorefinery, Semicontinuous process, Hemicellulose retention, Feedstock extension

基于酸碱萃取及柱层析的油品组分分离方法研究

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摘　要:

通过采用馏程切割、轻质油酸碱萃取以及中性组分柱层析等实验方法，将船用燃油分为酸性组分、碱性组分、六个中性亚组分，对各组分分子组成结构予以表征。经 GC-MS 定性，酸性组分主要为苯酚及羧酸类化合物，且低级酚含量明显高于高级酚含量。碱性组分主要为碱性氮化合物。选用合适的洗脱剂作为流动相，利用制备色谱完成中性组分柱层析分离，实现了脂肪烃、芳香烃、脂肪酮、脂肪腈等不同类型化合物的族组分分离。最终形成了一种集馏程分离、轻质油酸碱萃取及中性组分柱层析的油品分离新方法。

关键词：酸碱萃取；柱层析；分子组成

Study on separation method of oil products based on acidic/basic extraction and extrography

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Abstract:

In this study, a new method for oil products separation based on acidic/basic extraction and extrography of neutral fraction was developed. Hence, the acidic, basic and neutral sub-fractions were obtained, and the molecular structure was characterized by the most suitable characterization analysis method, respectively. The results showed that phenols and carboxylic acids were dominant in acidic fractions and the relative content of lower phenols was obvious higher than that in higher phenols. Moreover, basic nitrogen compounds were dominant in basic fraction. In addition, aliphatic hydrocarbons, aromatic hydrocarbons, aliphatic ketones, aliphatic nitriles and other different types of compounds were separated by using preparative chromatography. Finally, a new method of oil products separation was formed, which included distillation separation, acidic/basic extraction and extrography.

Keywords: Acidic/basic extraction; Extrography; Molecular composition

生物质热裂解制备可再生燃料和化学品研究进展

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摘　要:

废弃纤维素类生物质原料通过热裂解反应过程可以生产液体燃料和化工原料。但是纤维素类生物质种类多、结构复杂，较难降解，生成产物的化学性质不稳定、品质比较差，严重制约了热裂解技术的推广应用。选择合适的生物质原料和最佳反应器是提高产物品质和产率的两个关键性因素。本文对常用于热裂解研究的生物质原料的特性、生物质热裂解反应器的种类、热裂解产物的常见用途进行了研究，对生物质热裂解技术的发展现状及快速热解技术的未来发展方向进行了总结和展望，目标提高生物质快速热解的效率和热解产物的品质，促进热解技术的推广应用。

关键词：纤维素类生物质，快速热解反应器，可再生液体燃料，绿色化工产品

Review of biomass fast pyrolysis for renewable fuels and chemicals in China

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Abstract:

Renewable fuels and chemicals can be obtained from biomass through the fast pyrolysis process. However, the biomass recalcitrance, the drawbacks of the fast pyrolysis process/ reactor, and the poor properties of the end-products hinder the development of the relatively simple and effective conversion technology strongly. The choice of the optimum types of the biomass resources and the choice of the reactor are the two key factors for elevating the yield, content, and quality of the renewable end-products. In this review, the properties of biomass feedstocks as well as the main features of reactors and renewable fuels/ chemicals related to fast pyrolysis research in China are presented and discussed for the promotion of the biomass fast pyrolysis technology development in China. In addition, the current research status is presented and future development of fast pyrolysis technology is proposed. This paper aims to increase fast pyrolysis efficiency and promote the application of renewable fuels and chemicals from fast pyrolysis technology.

Keywords: Biomass; Fast pyrolysis reactor; Renewable fuels; Renewable chemicals

双层金属负载的核壳结构催化剂催化热解酶解木质素制取芳香烃的研究

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摘　要:

制备双层金属负载的核壳结构催化剂，通过 Py-GC/MS 微型联用热解仪进行酶解木质素的催化热解，以研究金属种类和负载位置对液体产物的影响。在微孔内核上负载 Fe，介孔层负载 Mg 时，得到了最佳的液体产物分布情况，表现为对单环芳烃（MAHs）的促进以及对酚类的抑制。在介孔层中引入 Mg 有助于产生碱性活性位，Fe 在微孔内核上的负载增加了强酸数量。这两种金属引入到核壳结构催化剂各自层中的协同作用可以抑制 MAHs 的过度芳构化和聚合形成 PAHs，并加速脱氧反应的发生。

关键词：酶解木质素；催化热解；核壳结构；双金属改性；强酸位；单环芳烃

Preparation of aromatics from catalytic pyrolysis of enzymatic lignin over double-layer metal supported core-shell catalyst

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Abstract:

Double-layer metal supported core-shell catalysts were prepared for catalytic fast pyrolysis of enzymatic lignin via Py-GC/MS, in order to investigate the influence of metal types and loading positions on liquid products. The optimal liquid product distribution was obtained when loading Fe species on the microporous core and Mg on the mesoporous layer of core-shell catalysts, manifested in the promotion of monocyclic aromatic hydrocarbons (MAHs) and inhibition of phenols. The incorporation of Mg into the mesoporous layer probably generated the basic sites and the loading of Fe on the microporous core increased the strong acid sites. The synergistic effect of the two metals incorporated into the respective layers of core-shell catalyst could inhibit the immoderate aromatization and polymerization of MAHs to form polycyclic aromatic hydrocarbons (PAHs), and accelerate the deoxygenation reaction.

Keywords: Enzymatic lignin; Catalytic fast pyrolysis; Core-shell catalysts; Double-layer metal modification; Strong acid sites; Monocyclic aromatic hydrocarbons

EPR 检测木质素单体热解焦化过程中的关键自由基

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摘　要：木质素热解是一种可持续生产液体燃料的有效途径。但是，当前的研究缺少有关此过程中的自由基反应，及其在焦化过程中影响的详细机理解释。本文中，我们研究了愈创木酚，一种重要的木质素单体，在惰性气体和氢气条件下，在 600℃的高温下的热解。在热解过程中，通过两种改进的电子顺磁共振光谱法检测生成的活性自由基。在愈创木酚的热解过程中，成功地观测到了邻苯半醌自由基阴离子，环戊二烯基自由基，甲基自由基，羟基自由基，甲氧基自由基，苯基自由基，苯氧基自由基等，以及不同热解阶段相关自由基的变化情况。发现邻苯半醌自由基阴离子和环戊二烯基自由基是热解过程中，参与焦炭和焦油生成的关键自由基。并通过加氢热解实验，证实了通过添加供氢源，可以降低反应生成的邻苯半醌自由基阴离子和固体焦炭的相对含量。我们的结果表明，通过定向调控热解焦化过程中的关键自由基的反应路径，可以抑制焦炭的形成，并提高转化效率。

关键词：EPR；热解；自由基；愈创木酚；焦炭

EPR Detection of Key Radicals During Coking Process of Lignin Monomer Pyrolysis

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Abstract: Lignin pyrolysis is an effective way to sustainably produce liquid fuels. However, detailed knowledge about the radicals involved in this process and their influence during the coking is missing. Herein, we report on the pyrolysis of guaiacol, a lignin monomer at 600°C under inert and hydrogen gas conditions. During the pyrolysis process, the formed radicals were detected by two improved electron paramagnetic resonance spectroscopy methods. Successfully observed o-phenyl semiquinone radical anion, cyclopentadienyl radical, methyl radical, hydroxyl radical, methoxy radical, phenyl radical, phenoxy radical, etc. during the pyrolysis of guaiacol, as well as the changes of related radicals in different pyrolysis stages. It was found that o-semiquinone radical anions and cyclopentadienyl radicals were the key free radicals in the generation of coke and tar during the pyrolysis process. And through hydrogenation pyrolysis experiments, it was verified that the relative content of o-semiquinone radical and the solid coke were reduced with a hydrogen supply source. Our results showed that by controlling the key free radicals in the coking process, the formation of coke can be suppressed and the conversion efficiency can be improved.

Keywords: EPR; pyrolysis; radical; guaiacol; coke

木质纤维素类生物质转化为液体燃料的能源-环境-经济综合评价研究

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摘　要:

从能源-环境-经济三个维度，选择技术相对成熟的三条路线作为研究对象：生物化学转化制取纤维素乙醇、快速热解超临界乙醇提质制取生物油、气化费托合成制取生物航空燃料。在 Aspen plus 软件上分别建立对应的工艺仿真模型，获得相应的物流、能流和热力学数据，根据这些数据采用可用能的分析方法对三条路线进行能量评价，采用全生命周期的方法对系统进行环境评价，同时对三条路线的资本投资以及燃料的生产成本进行计算，结果表：系统外部㶲损较小，主要㶲损来自系统内部不可逆因素。三者的能量转化率分别是 42.40%、47.37%和 37.44%，㶲效率分别是 45.09%、59.02%、40.74%。三条路线相对于化石汽油均有较好的环境表现，其中生物航煤环境性最优。 此外，用可再生氢和生物乙醇替代化石源能略微改善总体环境影响。经济性方面，应用技术经济分析方法，计算了各路线的固定资产投资和总生产成本。 纤维素乙醇、生物油、生物航煤的总生产成本分别约为 8600、 6600、 11000 元/吨。三者暂时都不具备市场竞争力，其中热解提质生物油的经济性相对最好。

关键词：木质纤维素类生物质；生物燃料；㶲分析；生命周期评价；技术经济分析；

Energy-Environment-Economic Comprehensive Evaluation Research on the Conversion of Lignocellulose Biomass into Liquid Fuel

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Abstract:

From the three dimensions of energy-environment-economy, three routes with relatively mature technology are selected as the research objects: biochemical conversion to produce cellulosic ethanol, rapid pyrolysis to produce bio-oil from supercritical ethanol, and gasification Fischer-Tropsch synthesis to produce Bio-aviation fuel. Establish corresponding process simulation models on Aspen plus software to obtain corresponding logistics, energy flow and thermodynamic data. According to these data, use the available energy analysis method to evaluate the energy of the three routes, and use the whole life cycle method to carry out the environment of the system Evaluation and calculation of the capital investment and fuel production cost of the three routes at the same time, the result table: The external exergy loss of the system is small, and the main exergy loss comes from irreversible factors inside the system. The energy conversion rates of the three are 42.40%, 47.37%, and 37.44%, respectively, and the exergy efficiencies are 45.09%, 59.02%, and 40.74%, respectively. Compared with fossil gasoline, the three routes have better environmental performance, among which bio-jet fuel has the best environmental performance. In addition, replacing fossil sources with renewable hydrogen and bioethanol can slightly improve the overall environmental impact. In terms of economy, technical and economic analysis methods are applied to calculate the fixed asset investment and total production cost of each route. The total production costs of cellulosic ethanol, bio-oil, and bio-jet fuel are approximately RMB 8,600, 6,600, and 11,000 per ton, respectively. None of the three have market competitiveness for the time being, and the economics of pyrolysis-improved bio-oil are relatively best.

Keywords: Lignocellulosic biomass; Biofuels; exergy analysis;Life cycle assessment; Technical and economic analysis;