Structure & reactivity: application to biomass valorization

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Chinese Abstract

摘要

人类正面临两大主要问题：气候改变和不可再生资源的利用，如石油。化学和化学工业应该加入这场解决问题的全球的努力中。未来的化学工业及其他相关行业（如油脂，化妆品，食品，肥料等）发展趋势将是如何以更少的能量和二氧化碳的释放量以及更多的可再生原材料进行生产。

生物质产品属于可再生材料，可以被应用于也应该被用于工业中。而这些材料的一个主要的缺点是它们的复杂化学结构在实际的工业应用中会产生多个反应的多相反应系统。但是，生物质通常是由相似的基质构成。该项目拟研究生物质化学反应结构与反应活性之间的关系。生物质大分子具有复杂的化学结构，但是它们的组成基质是以一样的，例如植物油的基本组成是脂肪酸。那么，能否根据相应的基质的反应动力学规律和热动力学特性来预测生物质大分子的这些规律和特性呢？此外，生物质可以采用不同的醇溶剂将纤维素转化为乙酰丙酸或乙酰丙酸烷基酯。这些溶剂的自由基（如乙醇的自由基是乙基）与反应动力学和热动力学之间是否存在一定的关系呢？该项目针对这两个问题拟通过建立相应的动力学模型和热力学模型进行探讨。

1. 研究内容

如果下一代的化学工业考虑并采用绿色化学的十二条原则，那么未来的化学工业发展将是可持续的。采用生物质产品替代石油工业衍生品就是十二条原则之一。

法国鲁昂国立应用科学学院 LSPC 实验室（EA 4704）目前已经开展了不同的生物质增值利用研究体系，例如聚氨酯的合成[1]，植物油的碳酸酯化[2]和环氧化[3]研究以及乙酰丙酸的氢化[4]。

该实验室距离法国巴黎 1.5 个小时火车车程。在这里，共有约 25 名来自不同国家（多米尼加共和国，中国，法国，摩洛哥等）的研究人员。该实验室致力于研究化工过程强化和过程安全。化工过程强化的研究主要集中在微波辐射，二氧化碳捕获和利用。化工过程安全的研究主要是通过反应热和量热测量来进行安全评估。此外，该实验室与本单位的分析实验室合力确保该项目顺利进行。

该项目将会同芬兰奥博学术大学（Åbo Akademi University）的工业化学与反应工程实验室的 Salmi 教授课题组研究团队密切合作。该实验室隶属芬兰著名的 Johan Gadolin 过程化学中心。与此同时，Sébastien Leveneur 为该大学讲师。

该项目的研究目标是研究生物质在增值利用过程中，其化学结构与反应活性之间的关系，如植物油或木质素的环氧化反应，碳酸酯化反应和氨化反应。

我们实验室已具备相应的知识贮备和技能，包括环氧化植物油的合成（ZHENG Junliu 的博士论文课题），碳酸酯化植物油的合成（CAI Xiaoshuang 的博士论文课题，CSC 公派），非异氰酸酯聚氨酯的氨化合成（Wander PEREZ SENA 的博士论文课题）和乙酰丙酸及其酯类的氢化（WANG Yanjun 的博士论文课题，CSC 公派）。

2. 研究背景

生物质产品属于可再生材料，可以被应用于也应该被用于工业中。而这些材料的一个主要的缺点是它们的复杂化学结构在实际的工业应用中会产生多个反应的多相反应系统。但是，生物质通常是由相似的基质构成，比如，蛋白质的基本组成是氨基酸，多糖的基本组成是单糖，木质素的基本组成是芳香族化合物，油脂的基本组成是脂肪酸。一个生物质大分子（如植物油）的动力学和热动力学规律能否通过其基本组成单元（如脂肪酸）的动力学和热动力学规律进行预测呢？同样，在纤维素生物质的预处理过程中，采用不同的溶剂如甲醇，乙醇或丁醇会对应的形成具有不同取代基的乙酰丙酸，乙酰丙酸乙酯，乙酰丙酸甲酯或乙酰丙酸丁酯。这些溶剂和取代基团之间是否存在一定的动力学关系？该项目的研究针对这两个问题，结合其理化特性的变化和传质现象估算内在动力学和热力学常数。该方法对确定一个化学反应的关键影响因素和优化反应条件是必不可少的。此外，在对传质和理化性质研究的同时，应当考虑不同实验条件下存在的副反应。

从工业化层角度讲，生物质具有以下缺点：其化学组成多样且变化各异，需要重新研究其动力学和热力学规律，确定最佳的工艺条件。尽管如此，生物质是基本组成是相似的，如果我们能够根据其基本组成基质的动力学和热动力学规律预测生物质本身的动力学和热动力学规律，将会节省大量的时间和成本。

将该方法应用于生物质的增值利用过程中的相关研究非常匮乏。目前还没有动力学或热力学和化学结构之间的相关性的研究报道。这种方法学的建立通过研究不同生物质大分子的结构来预测其动力学行为，将有助于过程模拟（成本分析，设计等）。

化学结构-反应活性研究将分为两个方向：

-化学结构-反应活性研究 1：研究不同取代基之间的化学反应动力学和热动力学关系。将通过建立线性自由能关系[4]，研究结构和反应活性之间的定量关系。

-化学结构-反应活性研究 2：建立生物质大分子与其对应组成基质之间的动力学和热动力学关系。不同品种的植物油和相应的脂肪酸甲酯[5]的不同化学反应将被作为研究对象。

这两方面的研究均采用非均相催化剂，以解决产物分离的问题。对于这方面的研究，我们也将同时与奥博学术大学展开密切的合作，博士研究生将有机会前往该大学进行研究访问。

申请者应具备扎实的化学工程背景和化学分析，热力学和反应动力学的相关知识。要求申请者能够说流利的英语。

English Abstract

Humanity is facing two major problems: climate change and use of non-renewable raw materials such as petroleum. Chemistry and its industry should participate to the global effort to tackle these problems. The future of chemical and related industries (oil, cosmetics, food, fertilizers...) is how to produce with less energy and CO_2 emission and with more renewable raw materials.

Biomass products are renewable materials, which are and could be used in industry. One of the main drawbacks of these materials is their complex chemical structure leading to multiphase reaction systems with several reactions. This project proposes to study the relationship between structure and reactivity of chemicals for biomass valorization. Biomass macromolecules have complex structure but have the same building-blocks, e.g., fatty acids for vegetable oils. Would it be possible to predict the kinetics and thermodynamics of biomass molecules by knowing the ones of their building-blocks? Besides, biomass can be treated by different alcohol solvents for the conversion of cellulose to levulinic acid or alkyl levulinates. Is there a relationship between the substituents of these solvents (e.g., ethyl for ethanol) and the kinetics and thermodynamics of the reaction? This project replies to these 2 questions by building intrinsic kinetic and thermodynamic models.

1. Context

Chemical industry will be sustainable if the future of the next generation is taking into account and by using the twelve principle of green chemistry. Substitution of molecules derived from petroleum industry by molecules from biomass is one of the principles.

At LSPC laboratory, we have studied different biomass valorization system such as production of polyurethanes [1]; carbonation of vegetable oils [2]; epoxidation of vegetable oils [3] or hydrogenation of levulinic acid [4].

LSPC laboratory (EA 4704) is located at 1.5 hours by train from Paris. There are around 25 researchers of different nationalities (Dominican, Chinese, French, Moroccan…). Research activities of our laboratory are process intensification and process safety. Process intensification activity is mainly focused on microwave irradiation and CO2 capture and valorization. Further, process safety is focused on thermal and calorimetric measurements thus addressing the safety assessment. This project will benefit from the expertise of these two research activities. Furthermore, our laboratory is close to an analytical laboratory, essential to the success of this effort.

This work will be done in close collaboration with Åbo Akademi University (Finland) and particularly with Professor Salmi, who's research team is part of the well-known Johan Gadolin Process Chemistry Centre. Professor Salmi is a member of the Laboratory of Industrial Chemistry and Reaction Engineering, which also belongs to this Centre of excellence. Sébastien Leveneur is docent at Åbo Akademi University.

The objective of this project is to find some relationships between the reactant structure and their reactivity for reaction implying biomass valorization such as epoxidation, carbonation and aminolysis for vegetable oils or lignocellulosic biomass.

Our laboratory has acquired knowledge for the synthesis of epoxidized vegetable oil (Doctoral thesis of ZHENG Junliu), carbonation of epoxidized vegetable oils (Doctoral thesis of CAI Xiaoshuang, CSC thesis), aminolysis for the production of non-isocyanate polyurethane (Doctoral thesis of Wander PEREZ SENA) and hydrogenation of levulinic acid and its esters (doctoral thesis of WANG Yajun, CSC thesis).

2. Research activities

Biomass products are renewable materials, which are and could be used in industry. One of the main drawbacks of these materials is their complex chemical structure leading to multiphase reaction systems with several reactions. Biomass is usually composed of similar building-blocks: amino acids for proteins, simple sugars for polysaccharides, aromatic compounds for lignin, or fatty acids for oils. Would it be possible to estimate the kinetic and thermodynamic behavior of a biomass macromolecule, e.g., vegetable oil, conversion based on the knowledge of the kinetic and thermodynamic behavior of its building-blocks, e.g., free fatty acids? Also, during the pretreatment of lignocellulosic biomass, different solvents could be used such as methanol, ethanol or butanol leading to molecules with different substituent groups such as levulinic acid, ethyl levulinate, methyl levulinate or butyl levulinate. Is there a correlation between the kinetics of these solvents and their substituent groups? The goal of this project is to reply to these two questions by taking into account the evolution of physicochemical properties and mass transfer phenomena, to estimate intrinsic kinetic and thermodynamic constants. Such approach is essential to know which parameters to intensify and how to optimize production in a chemical reactor. Besides, mass transfer and physicochemical properties study, one should take into account the side reactions at different operating conditions.

From an industrial viewpoint, biomass presents the following flaws: diversity and variation of the chemical composition which implies the need to re-study the kinetics and thermodynamics to re-determine the optimal process conditions. Thus, if one could predict the behavior of biomass by knowing the kinetics and thermodynamics of their building-blocks, it would save time and money. Experimental data are needed to validate the different kinetic and thermodynamic models.

Such approach for biomass valorization is very scarce. Moreover, the current research has not included a methodology for finding the correlations between the kinetics or thermodynamics and the chemical structure. The development of such methodology will aid in process simulation (cost analysis, design…) by predicting the kinetic behavior of different biomass macromolecules by knowing their structure.

Two kinds of structure-reactivity studies will be investigated:

-Structure-Reactivity study 1: Kinetic and thermodynamic correlations between different chemical reactions involving different substituents, we will use the concept of Linear Free Energy Relationship [4].

-Structure-Reactivity study 2: Correlations between kinetics and thermodynamics and reactivity of biomass molecules and their building-blocks. For that, we will study different chemical reactions for vegetable oils and their corresponding fatty acid methyl esters [5].

In both studies, heterogeneous catalyst will be used to surmount the separation issue. For that, a close collaboration with Åbo Akademi will be done and the PhD candidate could make a research visit at this university. A close collaboration will be done with Prof. Held (TU Dortmund) on the development of thermodynamic models, which are important to evaluate the impact of physicochemical property evolution on kinetic constants [6].

The PhD student should have a solid background in chemical engineering but also some knowledge in chemical analysis, kinetics and thermodynamics. The candidate should be fluent in English.

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