

国际工程科技发展战略高端论坛

International Top-level Forum on Engineering Science
and Technology Development Strategy

中國工程院
CHINESE ACADEMY OF ENGINEERING

实现生物质废弃物的 循环经济技术途径

shixian shengwuzhi feiqiwu de xunhuan jingji jishu tujing

APPROACH FOR
ACHIEVEMENT OF
RECYCLING ECONOMY
OF BIOMASS WASTE



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内容提要

本论坛集是中国工程院国际工程科技发展战略高端论坛系列出版物的第一本——实现生物质废弃物的循环经济技术途径。在当前能源日益紧缺及温室气体造成气候变迁的背景下，该论坛的主题是实现生物质废弃物资源的循环经济技术途径。议题包括从宏观政策角度阐述生物质循环经济在大气环境的影响及在可持续发展中的地位与作用，从技术角度论证开展生物质化学加工及生物加工等循环经济技术的可行性及方案，以及从生物质循环经济产业链形成角度讨论生物质循环利用效率等问题。本论坛集凝练了工程科学领域国际顶尖专家与学者的智慧与经验，在战略高度综合评估了发展生物质循环经济的必要性，为国家政策制订提供了依据，为生物质循环经济的发展方向给出了指导原则。本论坛集适合工程科技领域的一线技术人员、科技研究者、战略研究者和研究生阅读与参考。

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第一部分

综 述

综 述

2012年7月7~9日,由中国工程院主办、化工冶金与材料工程学部、北京化工大学联合承办的“国际工程科技发展战略高端论坛—实现生物质废弃物的循环经济技术途径”在北京召开。大会由中国工程院化工、冶金材料学部主任曹湘洪院士主持并致欢迎词,科技部农村技术开发中心贾敬敦主任、发改委能源局刘群处长分别致贺辞。

科技部农村技术开发中心贾敬敦主任、发改委能源局刘群处长、加拿大皇家学会院士 Moo-Young 教授、德国化学工程和生物技术协会理事长 Wagemann 教授、中国化工学会名誉理事长曹湘洪院士、石油化工科学研究院汪燮卿院士、总参某研究所吴慰祖院士、北京有色金属研究总院屠海令院士、中石化北京设计院杨启业院士、中国石化工程建设公司徐承恩院士、石油化工科学研究院舒兴田院士、清华大学化工系陈丙珍院士、北京化工大学校长谭天伟院士,以及包括6位973首席科学家在内的多位知名学者和企业家受邀出席会议。

本次国际工程科技发展战略高端论坛的主题是实现生物质废弃物的循环经济技术途径。讨论议题包括从宏观政策角度阐述生物质循环经济的地位与作用,从技术角度论证开展生物加工包括生物质化学加工等循环经济技术的可行性及方案,以及从生物质循环经济产业链形成角度讨论生物质循环利用效率等问题。国内外相关领域的专家学者也分别做了高水平的大会报告,加拿大皇家学会院士 Moo-Young、南京工业大学的郑涛教授代表校长欧阳平凯院士、德国化学工程和生物技术协会理事长 Wagemann 教授、国际工业生态学学会执行理事、英国萨里大学环境策略中心 Clift 教授、北京化工大学校长谭天伟院士、德国鲁奇集团可再生能源部研发主任 Guenther 博士等和与会的专家学者一起共同分享了生物质能转化的最新研究成果,并共同探讨了实现生物质废弃物循环经济的技术途径和创新思路。

此次论坛的成功举行广泛汇集了来自政府、企业、和学术的各个层面上关于发展生物炼制,利用生物质生产运输燃料、化学品和高分子材料的不同观点和意见,将有助于确定生物质循环经济的地位、作用、技术发展方向,为国家政策、战略的制订提供参考依据。

与会专家交流并得出了以下结论和前瞻性建议:

1. 生物质能相对于其它可再生能源是一种稳定的能源供给,是未来可再生能源的主导能源。我国农业大国和人口大国的国情决定了其生物质资源十分丰富,而且品种多样,包括各种作物秸秆、林业废弃物、城市有机垃圾、工业有机废水及餐所废油、厨余垃圾等;同时生物炼制的产品也是多样化的,所以在利用生物质做下游产品时要根据资源状况和市场做出恰当选择。

2. 生物炼制是未来推动世界经济发展的生物经济的重要基础,虽然生物炼制目前还处于技术开发阶段,部分产品刚刚开始产业化,总体上还不具有经济性,但是其发展潜力很大。

3. 生物炼制要解决好以下两个问题:

一是原料分散和生产集中的矛盾。生物质原料非常分散而且能量密度低,但是在转化时又希望形成较大生产规模以降低单位产品的投资和运行成本,因而在设计规划时需要兼顾原料收集运输成本和生产集中度,综合平衡,科学确定集中生产的规模。

二是提高转化效率,实现能量产出与投入之比的最大化,只有能量产出大于能量的投入,生物质能源利用才有发展前途。

4. 我国是农业大国,广大农村有大量人畜粪便等低劣生物质资源,大力发展生物甲烷是其有效利用途径,生物甲烷既可以作为燃料供农村使用,还可以提纯后通过管道运输用作工业燃料和运输燃料。

5. 生物转化技术和热化学转化技术是生物炼制的两大关键技术平台,互有优势。其产品既可以是生物燃料,也可以是生物基化学品或材料,要因地制宜找到合适的生物质转化的技术路线和产品方案。

6. 对于生物炼制,从国家层面要组织专家研究制定技术路线图和相关的产业发展支持政策,实现生物炼制产业的健康发展。

7. 开展生物质能源利用,不同技术路线和产品方案的生命周期能效分析和CO₂排放分析是一项重要的基础性工作,尽管难度很大,但应组织力量开展工作。

8. 目前来看,与利用生物质生产生物运输燃料相比,生产生物基化学品、生物基材料等在经济性问题上可能比较容易解决,而且这也是一种石油替代;因而通过选取部分有代表性的生物炼制生产化学品或生物基材料的产业示范,验证其经济性,有利于增强社会对发展生物炼制的信心,应予重视。

第二部分

参会专家名单

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第三部分

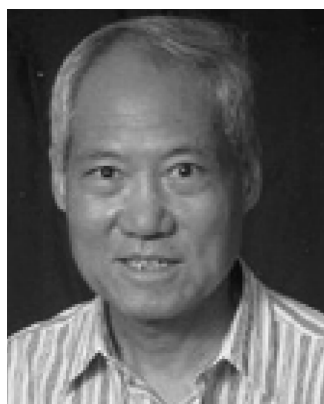
实现生物质废弃物的循环经济
技术途径(国际高端论坛)

生物质能源的生态—社会经济学评估综述

Murray Moo-Young

加拿大滑铁卢大学

关于环境污染和能源短缺的生态—社会经济问题越来越多地出现在公众媒体的头条上,与此同时,在全世界范围内都十分丰富的可再生生物质材料的数量也在不断增长,虽然通常被认为是垃圾,但通过生物技术手段可以利用这些生物质材料来减轻潜在的环境危害,并且生产生物燃料和其他具有经济价值的产品。在本综述中,将介绍针对几种不同产品生产的生物技术:目前占主导的生物乙醇燃料、未来具有吸引力的生物丁醇燃料、农业废物经过厌氧分解的生物甲烷气和通过生物转化方法将纤维素塑料变成的富含蛋白质的食品。基因工程和代谢工程方法是未来改善上述策略应用性的重要手段。



Murray Moo-Young 是加拿大滑铁卢大学杰出的荣誉教授。一直专注于生物技术和生物过程工艺研究,包括环境生物修复技术和生物制药、生物燃料的生产工艺。在进入学术界前,曾是英国工业部的一名过程工程师。作为一名牙买加出生的华裔加拿大人,Moo-Young 拥有伦敦大学的化学理学士学位、生物化工博士学位、及多伦多大学的化学工程和应用化学硕士学位。曾在英国爱丁堡大学作有关过程生物技术的

博士后研究。Moo-Young 有丰富的国际学术经历,一直担任几所知名大学的客座教授,包括麻省理工学院、加州大学伯克利分校、牛津大学、剑桥大学、苏黎世联邦理工学院、大连理工大学等。经常被国际会议邀请作大会发言。

截至目前,Moo-Young 已出版了 13 本书,获得了 10 项专利授权,并发表了

365 多篇论文(过去的五年有 7 篇)。在全球多个工业和政府部门担任顾问,包括杜邦、辉瑞、联合国开发计划署、联合国粮农组织、美洲国家组织。Moo-Young 是《Biotechnology Advances》杂志的主编(IF 7.60, www.elsevier.com/locate/biotechadv)和《Comprehensive Biotechnology》([www. Elsevier. com](http://www.Elsevier.com), 共六大卷)2011 年第 2 版的主编。Moo-Young 获得了很多荣誉,包括加拿大化学工程协会奖(CSChE)、安大略专业工程师协会奖(PEO)和美国化学学会(ACS)生物化学奖。当选为生物工程界最高荣誉的美国医学和生物工程研究院(FAIMBE)院士和加拿大学者最高荣誉的加拿大皇家学会(FRSC)院士。

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集中利用分散式生物质资源的高效生物甲烷能源体系发展策略

欧阳平凯

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一、我国分散的农村低劣生物质资源总量巨大,通过建立农工一体化的高效生物甲烷体系可实现其有效利用

以低劣生物质生产沼气作为生活能源在我国农村已取得很好的成效。但是传统的农村户用沼气工程的缺点也很明显:生物转化效率较低、发酵原料单一、以人畜粪便为主等。然而新时代下养殖业和种植业的集中化和规模化使生物质资源更加集中。与此同时,新农村、乡镇的现代化发展也对能源的质量有了更高层次的要求。因此,传统的分散式、低效率的户用沼气能源体系已经越来越不适应新时代农业和村镇的发展需求。

基于我国在生物甲烷产业方面积累的经验,为了高效利用我国农村每年产生的巨大的分散的生物质资源(见表1),克服传统户用沼气效率低下、无法适应高端用户需求的特点,可依据原料来源合理布局,利用现代生物技术和工程技术,建设批量的小规模沼气工程,实现高效的、工业化的沼气发酵,进而通过构建管网替代车辆运输,将各工程所产沼气利用大规模净化装置进行集中净化提质,生产高纯度生物甲烷,用作农村管道燃气、车用燃气和化工原料,建成分散集中式的农工一体化的高效生物甲烷体系。

表1 我国低劣生物质总量

资源类型	畜禽粪便	作物秸秆	林业废弃物	农产品加工废弃物	污水污泥	城乡生活垃圾	有机污水	合计
总量/ (亿吨/年)	25	7	2.7	2	1.5	2	20	60.2

生物甲烷作为一种前景广阔的可再生的绿色能源,与天然气的成分、热值非常接近,在我国拥有巨大的资源潜力(见表2)。通过发展农工一体化的高效生物甲烷体系,能替代化石能源用作汽车动力燃料,也可通过管道输送用作农村燃料,还可用作化工原料。

表2 中国低劣生物质生产生物甲烷资源潜力

总资源量			目前可利用资源量		
原料总量/ (亿吨/年)	沼气产量/ 亿立方	生物甲烷产量/ 亿立方	原料总量/ (亿吨/年)	沼气产量/ 亿立方	生物甲烷产量/ 亿立方
57.8	6220	3732	37.61	1990	1200

二、建立农工一体化高效生物甲烷体系是我国可再生能源的重要组成部分,也是节能减排的重要方式

随着能源危机的加剧,我国对可再生能源的需求将急剧增长。到2015年,我国天然气消费占比将从目前的3.9%提高至8.3%,达到2600亿立方,其中进口900亿立方以上。生物甲烷由于其在降低温室气体排放方面的巨大潜能,正成为最有希望的可再生绿色能源,可在保障能源供应安全方面做出巨大贡献,并将有效地减少温室气体排放。

由于生物甲烷是通过废弃生物质生产的能源,与化石能源相比,它的使用过程将没有CO₂净排放。以年产气1.5亿立方生物甲烷工程为例,每年可减排COD75万吨,温室气体275万吨,氮氧化物32.5吨,年节约用水约90万立方米,带来巨大的社会效益和生态效益。

三、农工一体化的高效生物甲烷体系尤其适合在我国南方地区实施推广

我国南方许多地区的典型特点是化石能源资源相对匮乏,而生物质资源丰富,因此,生物甲烷尤其适合在我国南方地区进行推广。以江苏省为例,2015年江苏省天然气需求达270亿立方,该省的油田产量仅为0.55亿立方,其余都需要通过管道输送以及进口气源海上运输补充,预计在2015年的天然气供应缺口会达到36亿立方。另一方面,江苏省每年农业秸秆量约4000万吨,禽畜粪便约3000万吨,可产生物甲烷约70亿立方,可完全满足即将面临的天然气供应缺口。为保障能源供应,调整能源结构,生物质资源丰富的南方地区理应把生物甲烷作

为可再生资源的重要组成部分进行发展。

按照农工一体化的生物甲烷体系建设思路,我们对在南方地区建立县级行政区生物甲烷体系工程进行了方案设计及投资成本分析。南方地区一个县级行政区的平均生物质资源量(主要有秸秆 100 万吨以及其他人禽粪便)完全足够支撑 1 亿立方生物甲烷工程。年产 1 亿立方生物甲烷工程项目总投资约 7 亿元人民币。生物甲烷作为运输燃料销售额可达到 4.6 亿元(交通运输用天然气价格:4.6 元/立方);年产沼渣 50 万吨用于做肥料,按照价格在 300 元/吨计,肥料年销售额为 1.5 亿元。两项总的销售额为 6.1 亿元,测算年总生产成本 4.3 亿元,预计年利润 1.8 亿元。表 3 对天然气管道输送与利用当地低劣生物质制造生物甲烷这两种能源产业方式进行了综合比较。

表 3 生物甲烷制造与天然气管道运输

	总投资 (亿元)	甲烷成本 (元)	能源性质	附带效益	带动产业
天然气 管道输送	1500 ^①	4(进口天然 气价格)	不可再生	/	钢铁、建材、 石化、电力
生物甲烷制造	840 ^②	2.86	可再生	减少碳排放, 治理环境	钢铁、建材、石化、 电力、环保、农业

① 以年输气能力 120 亿立方米计算(西气东输工程数据)。

② 年产 1 亿立方米生物甲烷工程造价约为 7 亿,120 亿立方米总投资 840 亿元。

四、建立农工一体化的高效生物甲烷体系仍需解决的问题

在国家政策的鼓励和扶持下,经过多年的科学研究和工程实践,我国在生物甲烷产业积累了一定的经验,正在逐步缩小和国外的技术差距。目前,已建设大中型沼气工程 4700 多处,部分实现了并网发电。尽管如此,在一些共性关键技术、系统集成化、标准化以及能源终端应用体系建设方面,仍然存在一些问题需要解决和完善。

低劣生物质收集方面:应因地制宜,物质收集(如秸秆)体系需要在政策引导下进一步完善。

生物转化过程方面:发酵原料由低浓度向高浓度、由单一原料发酵向多元原料共发酵转变;发酵温度由常温发酵向中温或高温发酵转变;过程装备标准化和成套化。

生物甲烷及副产品提质方面:净化工程装备实现设计标准化和制造成套化,

满足不同规模工业化生物甲烷工程的需求。

生物甲烷应用方面:需要在国家政策的引导下,明确生物甲烷在能源战略中的定位,建立能源终端应用体系,更好地融入现有的能源体系。

政策扶持方面:参照现有燃料乙醇体系,将沼气工程建设补贴变为生物甲烷销售补贴,改变现有沼气工程建成后难以正常运行的现状。



欧阳平凯,1945年8月出生,湖南湘潭人。南京工业大学校长,教授,博士生导师。现为中国工程院院士,973项目首席科学家,“十二五”863计划专家委员会委员。1981年毕业于清华大学化工系,获硕士学位。1985—1987年作为高级访问学者赴加拿大滑铁卢大学和美国普渡大学进修生物化工。2010年获滑铁卢大学“荣誉博士”学位。

欧阳平凯长期致力于生物化学工程领域的研究。

作为我国生物化工工程研究和工程教育领域的先行者,在南京工业大学创建生物化工、制药工程等专业,创建生物化工、发酵工程等硕士点,生物化工博士点,国家生化工程技术研究中心,是南京工业大学生物技术学科的创始人和主持人。先后主持了包括国家“973”项目2项、国家自然科学基金重点项目2项等多项国家和省部级项目。90年代以来共计发表论文300余篇,申请专利70余项,出版专著5部,培养博士、硕士100余名。欧阳平凯教授是我国生物化工学科知名的带头人,其研究成果先后获得国家科技进步一等奖1项,国家技术发明二等奖1项,杜邦科技创新奖1项,省部级一等奖3项,并荣获何梁何利科技进步奖、国家有突出贡献中青年专家、“全国杰出专业技术人才”称号。欧阳平凯现任中国生物工程学会理事长、中国石油和化学工业联合会副会长、江苏省科学与技术协会主席、江苏省生物技术协会理事长、江苏省化学化工学会理事长等职。1991年起享受政府特殊津贴,2001年获“全国模范教师”称号,2007被评为江苏省“教学名师”。

生物炼制对未来生物经济的贡献

Kurt Wagemann

德国化学工程和生物技术协会

生物质用于生产食品、饲料、燃料、化学品和材料的重要性已经凸显,而且在未来将会越来越重要。这种趋势是由多种因素共同促成的:化石资源是有限的;化石燃料产生的二氧化碳排放出于环境保护的要求也应该进行限制;另外,世界人口数量持续地增长,居民生活水平的提高进一步增加了对原材料的需求。

生物质作为能源的来源和化学品生产的碳源是可再生的,但同时也是有限的,这是由狭小的农业种植地区所决定的,用于生产食品和能源的土地竞争,种类繁多的工业品生产存在竞争关系,同样十分重要的一点是保护生物多样性的要求,这些因素都要求对有限的生物质资源高效利用并制定出方案。

生物炼制是同时实现经济效益和资源保护以及对生物质资源高效利用的关键。为了达到零排放和可持续利用可再生原料的目的,生物炼制耦合了不同的分离和转化过程。不同行业都将扮演重要的角色:农业和林木业—生物质生产,化学工业—开发新型转化过程、新的生物基产品,以及设备和厂房建设部门。这些行业之间的整合将成为建立以生物炼制为基础的经济的关键,在欧洲我们称之为“生物经济”。

德国政府已经决定由来自工业界和学术界的独立专家小组制定一个路线图(图1)。该路线图系统性地描述了不同的生物炼制的概念、现状和发展前景。它兼顾经济因素和生态保护,并分析了对研发(R&D)的需求(图2)。

以下是生物炼制的定义及分析的基础:“生物炼制是一种专门的、经过整合的综合方法,通过尽可能完全地利用生物质各种成分作为各种原材料,可持续性地生产一系列不同的中间产物和商业产品(化学品、材料、生物能源和食品/饲料)。”

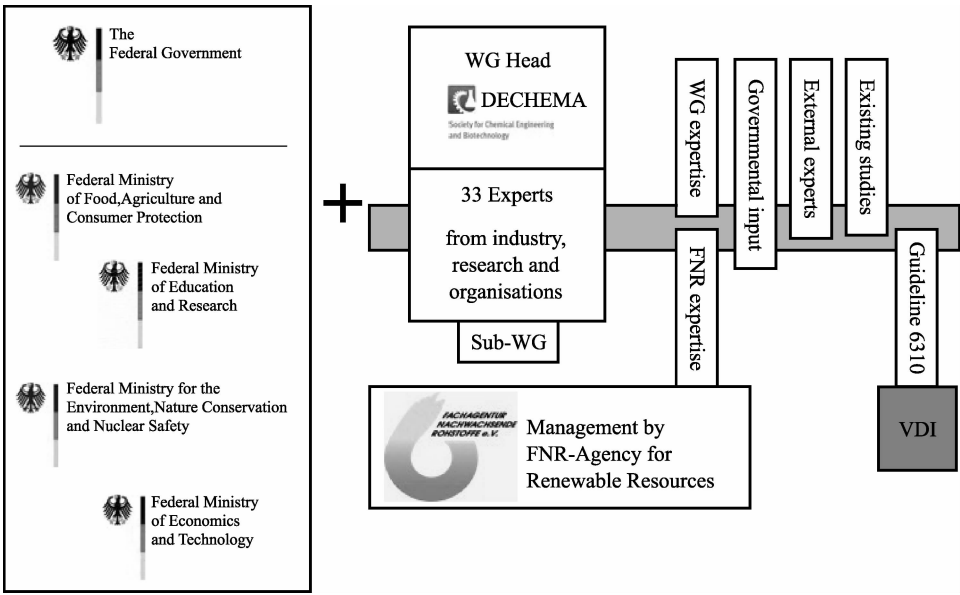


图 1 德国生物炼制项目路线图基本概况

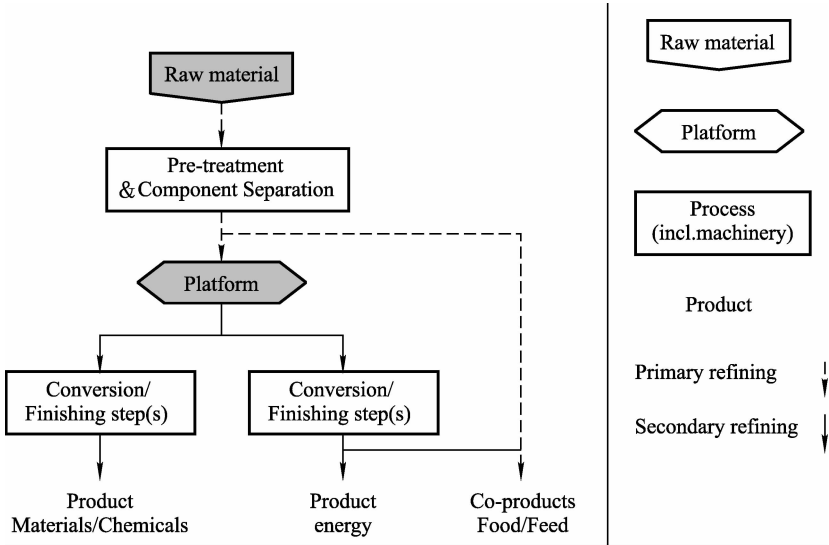


图 2 德国生物炼制项目路线图

生物炼制分析包括以下几个非常有前景的概念：

(1) 糖和淀粉生物炼制（图 3）：

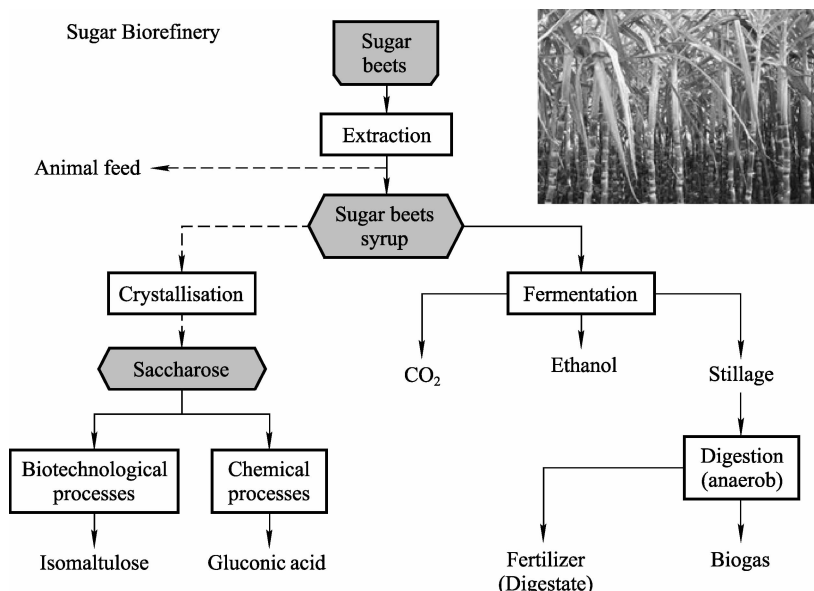


图 3 糖和淀粉的生物炼制基本工艺流程图

(2) 植物油生物炼制(包括藻类脂质炼制)(图 4 和 5):

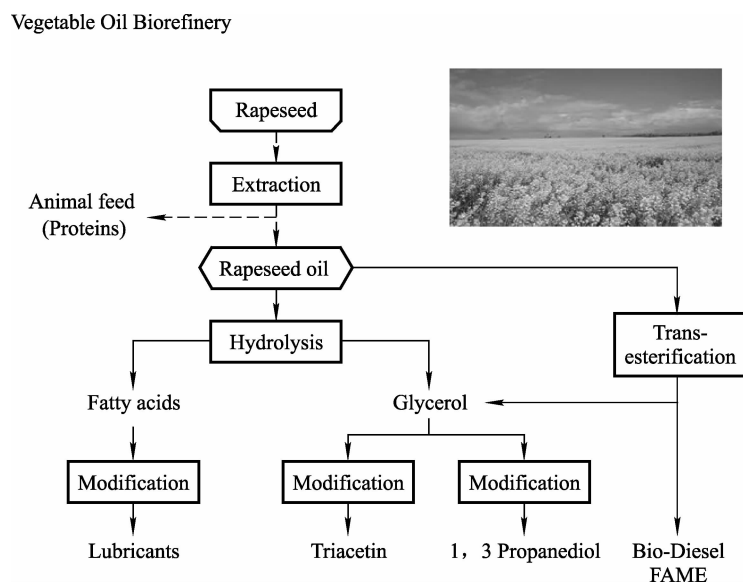


图 4 植物油生物炼制基本工艺流程图

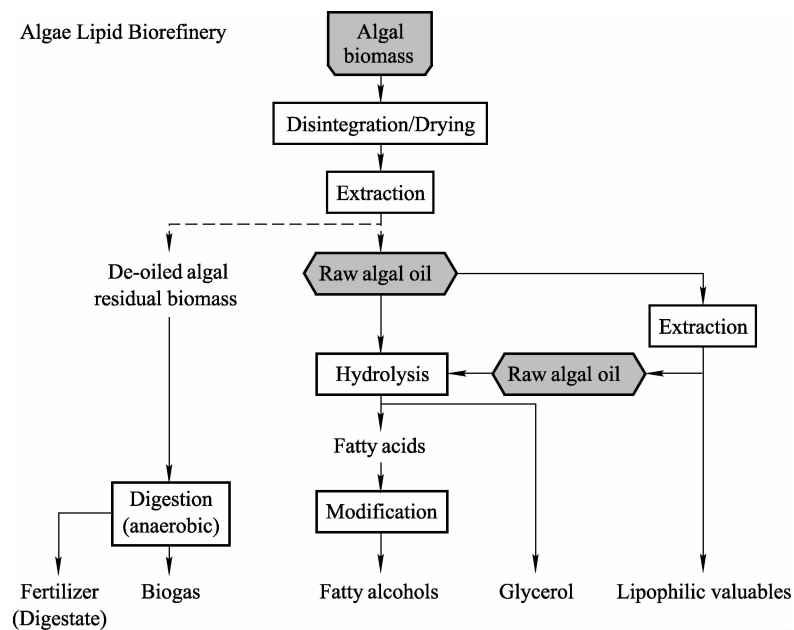


图 5 藻类脂质生物炼制基本工艺流程图

(3.1) 木质纤维素(纤维素/半纤维素/木质素)生物炼制(图 6 和 7):

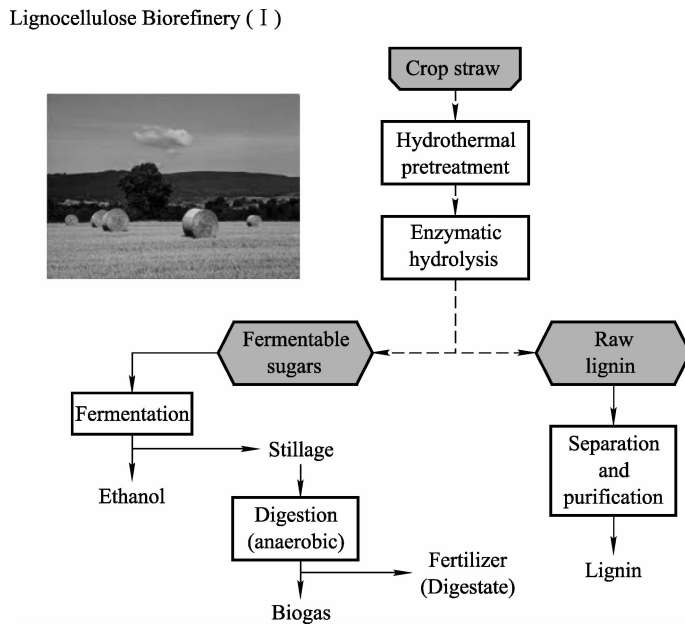


图 6 木质纤维素生物炼制基本工艺流程图 I (以农作物秸秆为原料)

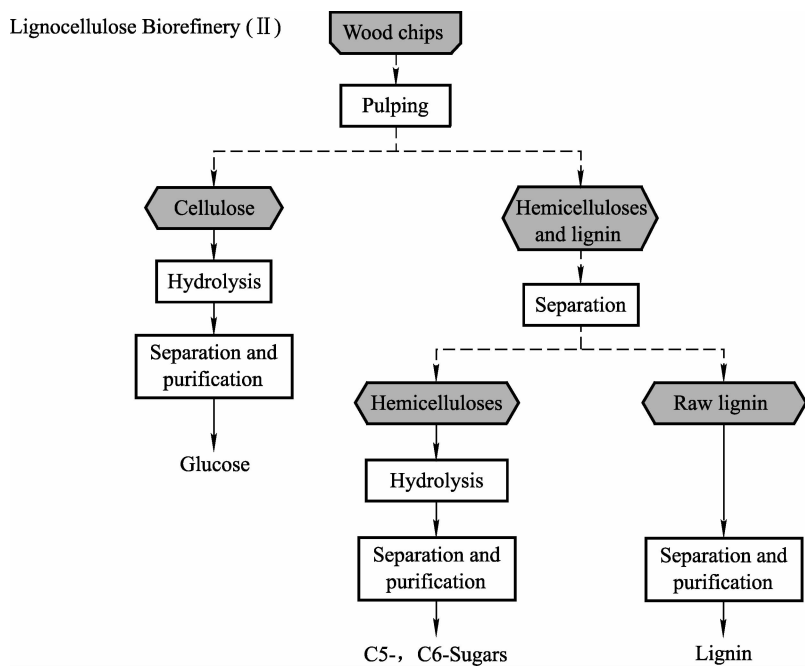


图7 木质纤维素生物炼制基本工艺流程图 II (以木屑为原料)

(3.2) 绿色生物炼制(绿色纤维/绿汁)(图8):

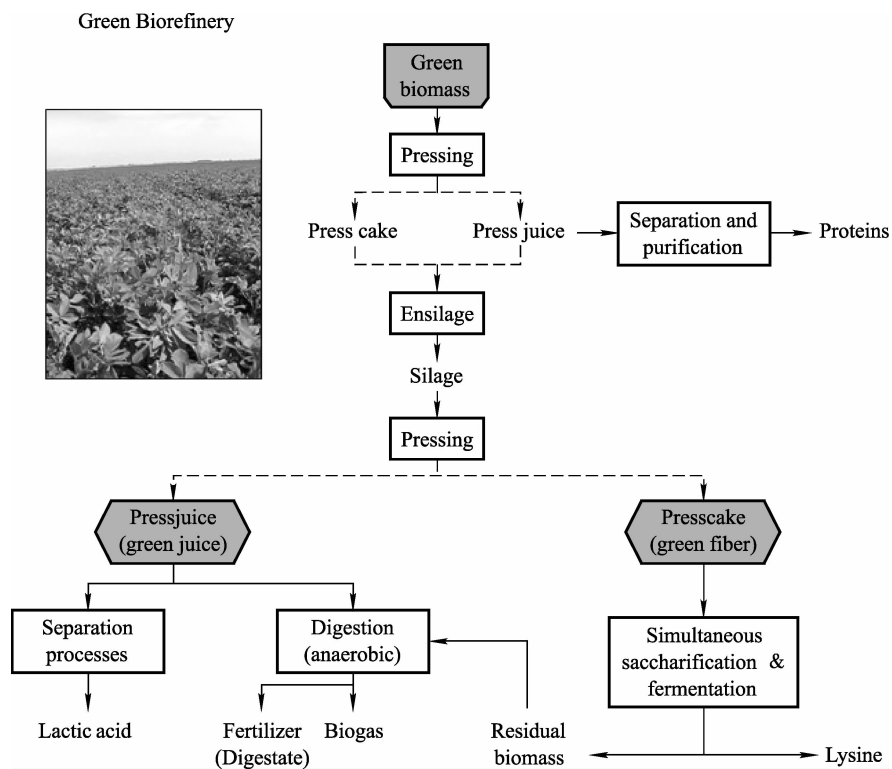


图8 绿色生物炼制(绿色纤维/绿汁)基本工艺流程图

(4) 合成气生物炼制(图 9):

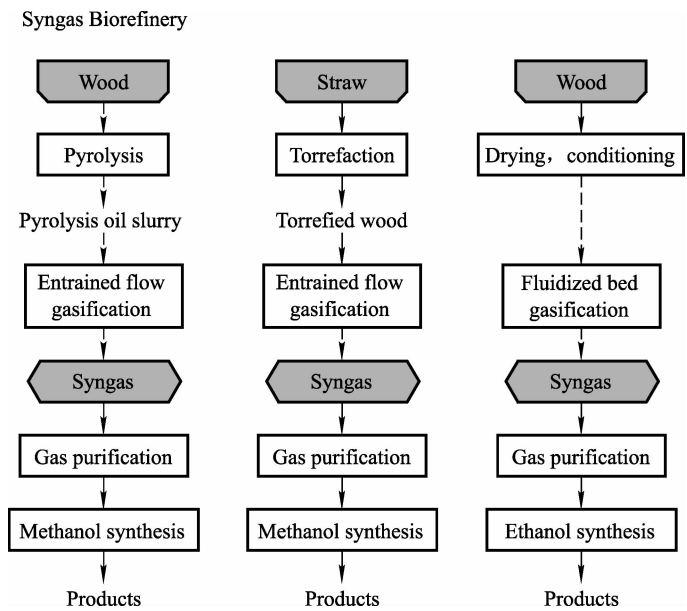


图 9 合成气生物炼制基本工艺流程图

(5) 沼气生物炼制(图 10):

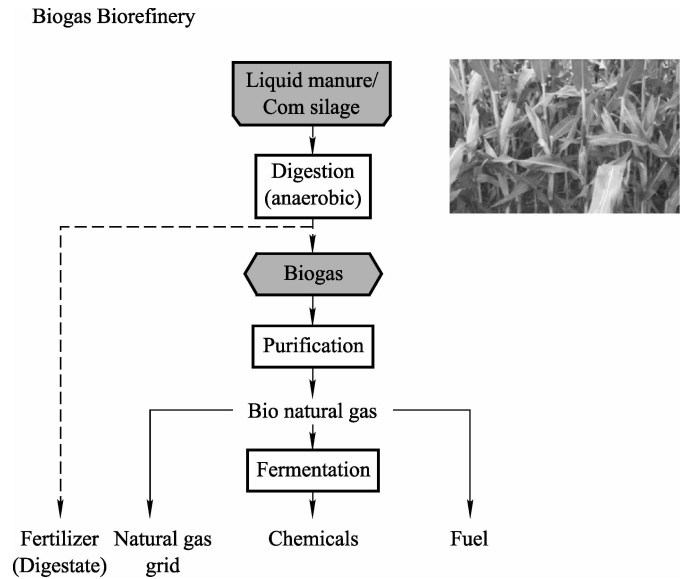


图 10 沼气生物炼制基本工艺流程图



Kurt Wagemann 教授,1959 年出生于慕尼黑,1989 年在马克斯-普朗克量子光学研究所获得博士学位。自 1989 年以来,他在 DECHEMA(德国化学工程和生物技术协会)的数个大型科研机构担任研究规划、会议和科研管理工作。

除此之外,Kurt Wagemann 还是得累斯顿 fms e. V. 和法兰克福 ProcessNet 的执行董事。2010 年担任 DECHEMA 的执行董事。

自 2006 年以来,Kurt Wagemann 教授一直在斯图加特大学任教。2011 年 2 月被任命为斯图加特大学名誉教授。

生物质废弃物处理的工业生态研究

Roland Clift

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评价废弃物的综合处理,包括生物质的利用,需要对整个过程进行分析:包括废物是如何产生的,废物是如何转化为材料和能源的。这就是全生命周期评价(Life Cycle Assessment, LCA)以及其他更易受环境影响的评估方法研究的内容。全生命周期评价方法的基本框架在近几年已经有了良好的发展,并已经设计了许多可以用来比较不同废弃物综合处理对环境影响的软件包。

全生命周期分析的过程如图1所示,“前台”(Foreground)阶段为之后的废弃物处理做充分的准备。它需要用到背景经济系统提供物质和能量包括运输燃料。同时,废物转化的物质和能量,也可以回收到背景经济系统中加以利用。对整个系统的分析必须包含这种物质和能量的交换。通常,我们假设背景系统的其他功能输出是不变的,因此,废弃物处理中物质和能量的回收代表着附加的经济行为,并且回收的物质和能源取代了背景经济活动。因此,总清单(inventory)——即资源投入和环境排放——就由废弃物处理时的直接经济负担,加上废弃物处理中产生物质和能源的间接经济负担,减去在背景系统中因物质能量回收而避免流失的经济负担组成。

生命周期应用关键点是辨别哪些经济行为会被废弃物的物质以及能量回收代替,尤其是评估是否应该建立在边界成本和平均活动上。对这一论点的讨论已经持续了近20年,对生命周期示踪的标准化方法的引入,特别是对产品进行“碳足迹”的计算,终于使这一争论有了方法论上的统一。然而,关于何时使用“归因”(accounting),何时使用“结果”(prospective)分析的讨论仍在继续。理解这两种分析在方法和实际运用上的差别,以及何种场合运用何种分析,对评价循环策略是极其重要的。

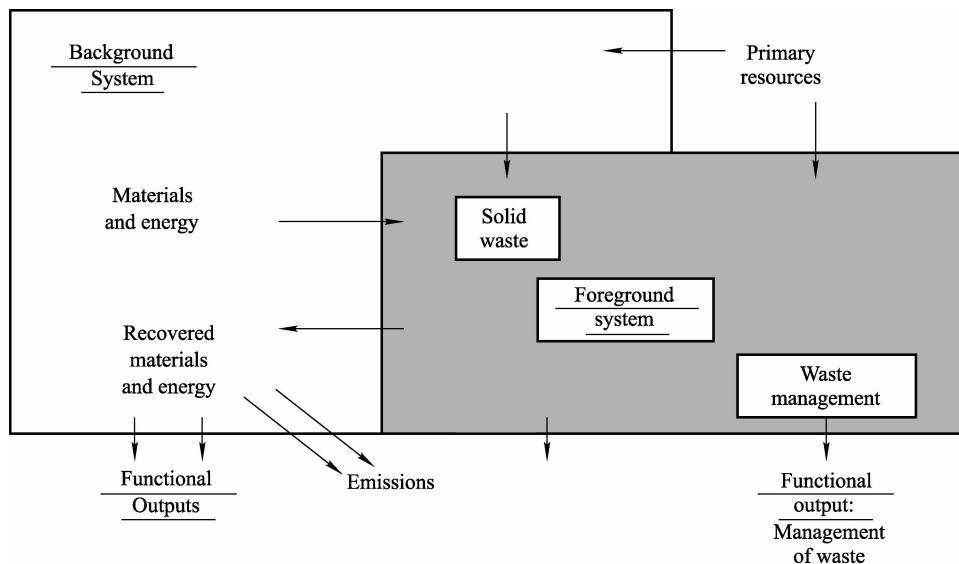


图1 废弃物综合处理全生命周期分析 (from Clift, R. ,Doig, A. , & Finnveden, G. (2000) The Application of Life Cycle Assessment to Integrated Solid Waste Management: Part 1—Methodology. *Trans IChemE (Process Safety and Environmental Protection)*, Special Issue: *Sustainable Development*,78:279 – 287.)

废弃物管理系统的运作背景,包含废弃物回收时造成的流失以及废弃物处理量等,随时间而变化,尤其在经济快速转型时期。因此,详尽且系统地分析未来可能发生的情况是对生命周期评价的重要补充。

对于废弃物综合处理,首先要问的问题是“这种资源利用的最佳方案是什么?”而不是“这个资源怎样应用于某一特定体系?”。在如今要求碳约束的世界里,生物质的利用必须达到最大能量回收的效益,或者减少温室效应(相对于化石燃料)。这两个目标是不同的,但很多情况下殊途同归。在这样的目标要求下,也更强调了生物质不论作为能源或材料,应当恰当地利用的重要性。

图2是热力学简图,解释了为何要最简化生物质过程的原因。生物质作为能源,无论其应用途径是什么,最终都将被转化成燃烧产物。如果是简单地燃烧,如图中上部分路径所示,能源产量用生物质的热值表示,即扣除任何能量输入,如种植、收割、运输,可得出生物质小规模生产开发的结论,即最小的运输路程,低密度物质。图中下部分显示:假如将生物质转化为液体燃料,为了达到规模经济的目的,处理工艺设置相对较大,生物质必然来自更大面积的搜集地。因而,运输路途以及相应的运输能耗就增大了。更重要的,将生物质转化成精制的产品,需要能量投入,同时根据热动力学原理,这个过程不可避免会有能量损耗(有效能 exergy)。因此,精制产品燃烧时,例如在一个内置的燃油发动机,其净释放能量将

远远小于未处理的生物质的燃烧值。

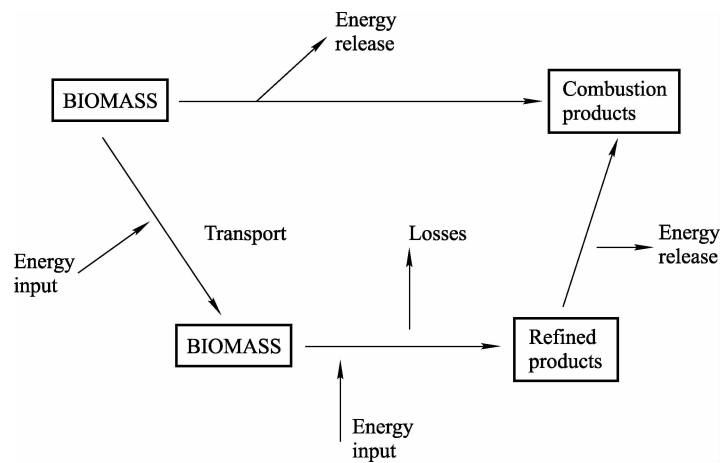


图 2 生物质利用路径

因此可以得出结论:将生物质转化成液体运输燃料不是最优策略。如果将生物质进一步处理,应该是转化成更高值的产品。另外,页岩气的日益普及,正在改变能源部门的看法;将天然气转化成液体燃料的可能性对整个生物运输燃料的发展提出了疑问。因此,这个过程虽然在技术上是可行的,但是政策上不够周全。当今世界更需要的,不是第二或第三代生物燃料技术,而是小规模依靠生物质燃料的热电联产技术。



Roland Clift 是英国萨里大学环境技术荣誉教授、环境策略中心创会理事;化学与加工过程学院前任院长;瑞典查尔姆斯大学环境系统分析访问教授;加拿大英属哥伦比亚大学化学与生物工程兼职教授;国际工业生态学学会执行理事及前任会长;英国皇家环境污染委员会以往委员;英国环境、食品和农村事务部生态标签委员会和科学咨询委员会委员;英国环境保护部副部长。研究领域包括环境管理系统方法以及工业生态,包括全生命周期评价以及能量系统研究。

利用生物转化技术实现低值生物质 生产生物燃料

谭天伟

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全球石油化工巨头埃克森美孚近日发布的《全球能源展望 2012》报告中提到,受经济增长和人口因素影响,到 2040 年全球能源需求将比 2010 年高出 30%。自 1993 年起,中国由能源净出口国变成净进口国,能源总消费已大于总供给,能源需求的对外依存度迅速增大。2011 年中国原油进口数量达 25 378 万吨,同比增长率 6.00%。进口金额为 1966.64 亿美元,同比增长率为 45.30%。石油需求量的大增以及由此引起的结构性矛盾日益成为中国能源安全所面临的最大难题。

能源危机已经触动每个人的神经,也激起了人们寻找可替代能源的强烈愿望。目前国际上生产、利用的低值生物质有哪些?生产的生物燃料种类有哪些?利用生物转化技术的方向主要包括什么?都有什么优缺点?我国发展生物质燃料的前景如何?这些问题都需要我国从事生物燃料开发的工作人员一一解答。

一、生物质原料

(一) 低值生物质种类

低值生物质主要包括农作物秸秆和农业加工剩余物、薪材及林业加工剩余物、禽畜粪便、工业有机废水和废渣、城市生活垃圾和能源植物。可转换为多种终端能源如电力、气体燃料、固体燃料和液体燃料,其中受到最多关注的是生物质液体燃料(生物燃油)。世界不少国家已经开始发展生物燃油产业(包括生物燃油加工业及其相关产业,如能源农业和能源林业),其共同的目的在于保障石油安全。

木质纤维素是地球上最丰富的可再生资源,据测算年总产量高达 1500 亿吨,蕴藏着巨大的生物质能(6.9×10^{15} 千卡)。我国是一个农业大国,作物秸秆(如稻

草、麦秆等)的年产量巨大(年产可达7亿吨左右,相当于5亿吨标煤)。据统计,目前的秸秆利用率为33%,但经过一定技术处理后利用的仅占2.6%,其余大部分只是作为燃料等直接利用,开发前景非常广阔。

随着社会的进步和生活水平的不断提高,我国城市生活垃圾的产生量也快速增长。据统计,全国城市生活垃圾年清运量已接近1.7亿吨。以北京为例,生活垃圾中的有机成分已由上世纪70年代的20%,迅速提高到60%左右。而造成生活垃圾中有机组分上升的主要原因即大量餐厨垃圾混入了城市生活垃圾清运系统。中国城市每年产生餐厨垃圾不低于6000万吨,其中北京市每天产生约2000吨餐厨垃圾,在城市垃圾中所占比例为37%。

事实上,我国已经逐渐形成了一个以卫生填埋为主,焚烧、堆肥为辅的生活垃圾处理处置技术体系。到目前为止,在全国661个设市城市中建有各类填埋场479座、堆肥厂46座、焚烧厂66座。填埋、焚烧和堆肥按处理能力的比例分别为85%、10%、和5%。而由于缺乏对餐厨垃圾的妥善处置,国内普遍将餐厨垃圾混入普通生活垃圾统一处理,而正是由于生活垃圾有机物含量及含水率的提高,导致传统“三大生活垃圾处理处置方法”逐渐凸显了系列问题。与其他垃圾相比,餐厨垃圾具有含水量、有机物含量、油脂含量及盐分含量高,营养丰富等特点,具有很大的回收利用价值,而且随着人们环境保护意识的提高,以及餐厨垃圾便于单独收集的特点,完全可以逐步实现餐厨垃圾单独收集与处置,从而能够减轻城市生活垃圾的处理难度。

(二) 中国生物质原料情况

(1) 利用废糖蜜、食品加工业和饮食业废油、棉籽油等废弃糖油类资源,估计可满足年产80万吨燃料乙醇和200万吨以上生物柴油的原料需求;

(2) 可能源化利用的农作物秸秆和林业剩余物年产量目前约2.5亿吨,且可望继续增加,在中长期可满足年产3000~5000万吨第二代生物燃料的原料需求;

(3) 我国现有3200~7600万公顷边际性土地,可通过推广良种良法、品种替换、开发劣质边际土地等途径发展能源植物,例如甜高粱、木薯、麻风树等。

总体估算,(1)我国以非食用粮糖类农作物为原料的燃料乙醇生产潜力近中期约为1500万吨;(2)以废油为原料的生物柴油生产潜力近中期约200万吨;(3)以油料林为原料的生物柴油生产潜力在中长期约为数百万吨;(4)以纤维素和藻类生物质为原料的先进生物燃料生产潜力在长期可达每年数千万吨。

二、生物能源情况

(一) 生物能源主要种类

目前国内外研究、应用较多的几种生物能源主要有燃料乙醇和丁醇、生物制氢、生物油脂、生物柴油等。很多东西可以替代汽油,我国发展生物质燃料的前景非常广阔。我国燃料乙醇生产企业的发展主要是两个方向:一是木薯乙醇;二是纤维素乙醇。两者都属于非粮食作物,其中,木薯乙醇已处于规模化生产阶段,技术发展已相对完善;而纤维素乙醇在我国还处在试验阶段,技术还有待完善。

(二) 中国生物燃料研究进度

(1) 我国利用薯类、甜高粱、小桐子等非粮作物/植物生产燃料乙醇和生物柴油的技术已进入示范阶段。木薯和甘薯乙醇技术也可实现商业化应用,例如:广西于 2007 年建成年产 20 万吨木薯乙醇项目;

(2) 木质纤维素乙醇在原料预处理、纤维素转化以及酶制剂生产成本等方面均取得实质性进展,例如:黑龙江、河南等地建成了年产数百吨和数千吨乙醇的示范生产装置;

(3) 生物柴油产业化示范工作的时机也已基本成熟,但受废油资源收集利用量、油料植物种植基地建设进度的限制,目前只有少数生物柴油企业实现规模化持续生产,也没有正式进入车用成品油的主要流通使用体系;

(4) 其他第二代生物燃料(如合成燃料技术)目前仍处于实验室研究和小规模中试阶段。

三、低值生物质利用方面的研究

(一) 甜高粱联产乙醇、丁醇和木塑材料新工艺

甜高粱被公认为是生产燃料乙醇的能源植物。开发了新型甜高粱联产乙醇、丁醇和木塑材料新工艺。可以利用甜高粱中糖汁生产乙醇,采用固定化酵母细胞发酵,乙醇得率为理论值的 93% 以上;榨汁后的甜高粱秸秆经过酸预处理,以纤维素水解液作为发酵原料(总糖在 55 g/L 左右),利用梭菌发酵后可得到 19.21 g/L 的产物浓度(其中丁醇 9.34 g,乙醇 2.5 g 和丙酮 7.36 g);剩余甜高粱渣经过预处理可以生产木塑材料,其拉伸强度可达 49.5 Mpa,弯曲强度为 65 Mpa,该产品作为可生物降解材料。现已建成甜高粱 1000 吨/年燃料乙醇中试

工艺和 200 吨/年丁醇中试工艺。

(二) 含糖工业废水生产油脂

针对目前生物柴油原料短缺问题,开发了工业含糖废水发酵生产微生物油脂工艺,对于高浓度淀粉废水,采用气升式发酵池,建成了每天处理 2000 吨淀粉废水生产生物油脂的示范工程,发酵液不经灭菌和调节 pH 值,发酵 35 h 后,生物量达 28 g/L ~ 33 g/L,油脂含量为 28% ~ 37%,COD 降解率达 80% 以上,每立方米废水可获得 7 公斤以上的油脂。该工艺已获得国家发明专利,并于 2008 年通过了石油化工协会组织的中试工艺技术鉴定,鉴定意见“总体技术水平达到国际先进水平”。

(三) 餐厨垃圾资源化利用

建成 80 吨级餐厨垃圾发酵产沼气中试基地,成套装备主要由餐厨垃圾分选、固液分离、油水分离、垃圾破碎、酸化调配、厌氧发酵等构件组成。该成套装备利用北京化工大学昌平校区食堂餐厨垃圾、学校蔬菜市场果蔬垃圾为原料,集中进行厌氧消化,提取油脂用于制取生物柴油,产生的沼气净化后转化为热能,主要用于中试基地实验及生产过程用能,发酵剩余液经改性处理后作为绿色有机肥料回用至基地草坪、花园等,整体实现了废物的能源化及资源物质的良性循环。

利用自主研发生产脂肪酶催化生物柴油技术,以城市废油为原料,开发了新型酶固定化方法,在上海建成了国内第一套年产万吨的废弃油脂酶法生产生物柴油示范装置。目前,该企业利用地沟油所生产的生物柴油产品已经在上海市出租车中得到应用。



谭天伟,博士,中国工程院院士,国家教学名师。现任北京化工大学校长,教授,博士生导师。

1986 年 7 月毕业于清华大学化工系,同年考取清华大学硕士研究生,1987 年 9 月直接攻读清华大学博士研究生。1990 年 2 月 ~ 1992 年 10 月公派到德国生物技术研究所以及瑞典伦德大学攻读联合博士研究生,1993 年 3 月获得清华大学化学工程专业博士学位。1993 年 5 月 ~ 1995 年 5 月在北京化工大学生物

化工专业做博士后。1997 年 3 ~ 8 月及 1998 年 1 ~ 4 月在瑞典 Uppsala 大学做访

问学者。

谭天伟教授长期从事生物化工及工业生物技术等方面的教学、研究工作。2001 年获得教育部长江学者特聘教授。2003 年获得国家杰出青年基金。2006 年获得中国青年科技奖、何梁何利创新奖。2007 年担任“工业生物技术过程科学的基础研究”973 项目首席科学家。2011 年当选为中国工程院院士、中国化工学会副理事长、中国化工学会生物化工专业委员会副主任委员、中国酶工程学会理事、国家生物化工重点实验室学术委员会委员、国家生物反应器重点实验室学术委员会委员,并任多个中英文核心刊物编委。

作为项目负责人先后承担了国家攻关项目、863 项目、国家自然科学基金重点基金项目和 973 项目共 14 项,部委级项目 10 项;累计发表 SCI 论文 200 多篇, EI 论文 230 多篇。以第一获奖人获得国家技术发明二等奖 2 项,省部级一等奖 5 项,二等奖 5 项。

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转换可再生原料生产第二代生物燃料和 产品:热化学路线

Armin Guenther

鲁奇集团可再生能源部

在未来的 50 年内,全球能源需求将大幅增长,可再生能源和替代能源仍有很大的潜在前景。但是,当只有粮食作物而不是整个植物用于第一代生物燃料的情况下,便会存在原材料的限制,在这种情况下,可能会出现燃料与粮食的竞争。

目前,大量的生物质和农业、林业残留物以及全植物利用的可能性,开启了一个远远高于第一代生物燃料、生物柴油和生物乙醇的大规模应用潜能。有很多不同的路线可以将生物质、煤炭、炼油残渣和天然气转化成 FT-合成油(FT-synfuels)、甲醇(MeOH)、二甲醚(DME)、合成天然气(SNG)和其他化工产品。

然而,考虑到生物质如秸秆、干草及其残渣作为热化学转化原料,具有能量密度低的特点,这些材料仅仅在短距离运输时才能实现经济可行性。

生物质液体燃料工艺(bioliq process)是在德国农业部、食品和消费者保护部资助下,由卡尔斯鲁厄理工学院与鲁奇公司合作开发,该工艺将大型工业规模的合成燃料的生产需求与经济的生物质物流联合起来。

首先通过气化,在附近的快速热解车间处理生物质,以增加能量密度。将快速热解所得到的产物:炭和浓缩汁液,混合后即形成一个稳定的并且便于运输的悬浊液体(生物合成原油)。

在中央车间,这种悬浊液体将进入气流床气化炉进行气化,这是一种内置冷却屏的由氧气吹动的结渣反应器。根据合成步骤的要求,合成气的转化需要高温和相当于 80 巴的高压。

昂贵并涉及高技术风险的气体临时压缩步骤是多余的。几乎所有的重要化工基础材料,如可再生能源产品(BTC)、清洁和环保的合成汽车燃料(BTL)都可由这种生物基合成气生产。

下面将概述这种联合开发的实际情况。



Armin Guenther 博士是德国鲁奇集团可再生能源部研发主任,毕业于法兰克福大学化学系,同时在意大利国家研究委员会(CNR,博洛尼亚)做在职培养,并取得学位。在法兰克福大学化学系取得博士学位,毕业后工作于法兰克福环境研究中心。

Guenther 博士作为一家工程公司的可再生能源部的项目经理,负责国内外传统能源项目、可再生能源以及生物柴油项目。在鲁奇集团,Guenther 博士在可再生能源部曾担任多种职务,例如生产销售经理以及可再生能源市场组主任。目前,Guenther 博士在鲁奇集团旗下液化空气集团的职务是“可再生能源研究与开发部主任”。

第四部分

生物燃料工业核心技术的发展、示范和应用

基于木质纤维素转化技术构建糖平台

岳国君

中粮集团有限公司

全世界生物质的产量巨大,据估计达到 1700 ~ 2000 亿吨/年,目前生物质大约可提供世界年能源消耗的 10%。可作为生物质糖化的原料来源广泛、形式多样,除去传统的农业作物,如粮食、糖类作物、油料作物外,生物质原料大概可以分为以下三大类:来自农业及林业废弃物的木质纤维素原料;专用能源作物如多年生牧草和树木;其他类型的废弃物如食品及造纸工业废弃物、城市固体废弃物等。基于这些原料的不同特质和地理分布,可采用多样的生物质转化技术来生产液体燃料、生物基化学品及其他有用途的产品。而木质纤维素的糖化技术是生物质转化最关键的步骤之一。

中国目前仍是农业大国。据 2010 年《全国农作物秸秆资源调查与评价报告》显示,我国农作物秸秆可收集资源量为 6.87 亿吨,其中玉米秸 2.65 亿吨、稻草约为 2.05 亿吨、麦秸 1.50 亿吨。到目前为止,中国农业秸秆利用率为 69%。主要用作饲料、固体燃料、及肥料。如何运输如此巨大的木质纤维素秸秆资源是其高效利用过程中的一个难题。目前国内以麦秆、棉秆、玉米秸秆为主的农业秸秆的物流运输采取的是专业经纪人向分散农户收购(包括打包及存储)再集中运送至加工厂的方式。

木质纤维素原料的利用可按其终端产品的用途分为三大类:产热和发电;作为生物液体燃料;用作合成精细化学品及聚合物产品。目前,后两大用途对于当今社会越来越重要和紧迫,因为我们过于依赖石油资源来生产这些产品,一旦原油价格波动,世界经济都会受到影响。人们用生物炼制这个概念来定义将生物质废弃物转化生产为有用的液体燃料和化学产品的过程。当提到这一概念的时候就会发现这两个过程有一共同之处,即在下游加工成燃料或化学品之前,都需要进行生物质的糖化过程。这是由木质纤维素原料的组成所决定的:绝大多数原料中都含有 30% ~ 40% 左右的纤维素和 15% ~ 20% 左右的半纤维素,而这两

者都是由单糖(葡萄糖、木糖、阿拉伯糖、甘露糖、半乳糖等)构成的聚合物,剩余20%~30%是几丁质聚合体。因此从这个意义上说,生物炼制生产燃料及化学品的重要前提就是木质纤维素糖平台的建立。

目前环境友好型的木质纤维素糖化平台,离不开预处理和酶解过程这两个重要步骤。预处理的目的是把耐酶水解的木质纤维素的结构破坏,打开半纤维素(木聚糖)、几丁质同纤维素间的交联,同时将纤维素(葡聚糖)暴露,增加其表面积和纤维素酶作用位点的可及性。预处理效果对于后续酶解糖化至关重要,影响到酶解过程的效率和成本。物理的、化学的以及物理化学结合的方法是常规的而且有效的预处理方法,其中中性蒸煮、稀酸气爆预处理方法在世界上多数纤维素乙醇示范工程中得到应用。

半纤维素水解得到的主要产物木糖和纤维素酶解得到的主要产物葡萄糖可以用作化学产品及能源产品。来源于淀粉质原料生产的化学产品和能源产品已经较为成熟,是中粮产业链条上的重要环节,如氨基酸、有机酸、多元糖醇、燃料乙醇等,也是生化能源事业部的主营产品。目前,因粮食深加工能力的增加和对粮食原料的过多消耗,已引发国际上对土地用途改变和粮食安全的担忧。而利用木质纤维素原料转化为葡萄糖,构建纤维素糖平台,替代淀粉资源,为淀粉质糖、有机酸、氨基酸等生化产业提供廉价糖原料,促进糖基下游产业延伸,创造新的利润增长点,意义凸显。这将是中粮生化能源事业今后战略方向之一,也是目前技术的难点。

燃料乙醇是中粮生化能源事业部的主营业务,历年产量稳居国内第一,占市场份额的46%。纤维素乙醇技术研发是中粮集团生化能源事业部、国家能源生物液体燃料研发(实验)中心及中粮营养健康研究院的重要业务。木质纤维素液体燃料作为一种方便易得的可再生能源,所用的各种生物质原料与粮食生产、加工密不可分,涉及的生物质加工理论与技术和中粮集团“生命、健康、可持续发展”理念息息相关。

中粮集团于2006年9月完成500吨纤维素乙醇中试装置建设。装置测试运行多年,至今不断优化改造,已基本具备长周期连续稳定运行条件。中试实现了全自动化备料,预处理设备已实现国产化,连续汽爆预处理固形物回收率大于90%,半纤维素转化率大于90%,酶解纤维素转化率大于80%,五碳、六碳糖共发酵,糖醇转化率大于80%,发酵醪终点乙醇浓度达到6%(v/v)以上,吨乙醇玉米秸秆单耗6吨,积累了大量基础实验运行数据,同时系统研究了秸秆资源分布,构建了原料收集物流体系,万吨级示范装置工艺包已经初步编制完成。目前工艺中酶制剂成本份额大幅减小,小于总成本20%,而原料成本和能耗是最大的

支出,下一步技术研发应重视提高资源利用率和能量耦合,降低公用工程消耗,以降低成本,加快示范装置建设进程。



岳国君,49岁,教授级高级工程师,2007年1月获委任为中国粮油控股有限公司执行董事兼副总经理,兼任生化能源事业部总经理。岳国君于2005年11月加入中粮集团,2007年2月起任中粮集团有限公司总裁助理。2007年11月至2011年11月任中粮生物化学(安徽)股份有限公司(一家于深圳证券交易所上市之公司)董事兼董事长。2007年2月获得国务院政府特殊津贴,2008年2月获选为中华人民共和国第十一届全国人民代表大会代表。

岳国君先后毕业于吉林化工学院、哈尔滨工业大学和北京化工大学,并分别获工学学士学位、环境工程学硕士学位和化学工程与技术专业工学博士学位,拥有逾20年的生物化学产品生产及销售经验,并于2011年11月当选中国淀粉工业协会会长。

浮萍在生物燃料生产和环境保护方面的作用

赵海

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随着全球经济的发展、人口的增长和人民生活水平的提高,能源短缺已成为制约世界经济的核心问题。中国正处于工业化加速发展的重要阶段,对能源需求巨大。2007 年中国成为煤炭净进口国,5 年后,一跃成为世界第一大煤炭进口国。2009 年石油对外依存度更是超过 50% 这一心理支撑线。石油供应紧张,油价飞涨,2004 年到 2012 年,汽油价格从 2.3 元/升一路飙升到 8 元/升。我国能源供应已经捉襟见肘,每当盛夏酷暑用电高峰,错峰用电、拉闸限电等现象越来越频繁。能源短缺已严重影响社会和经济的发展,未来的形势会更严峻,解决能源危机刻不容缓。

同时环境污染也日趋严峻。目前我国有 1 亿多辆汽车,约为全球的十分之一,CO₂ 排放全球第一。空气污染严重,北京、上海等城市上空的大气污染指数为发达国家的 2~5 倍。此外,相当匮乏的水资源也是污染不堪。2008 年我国总取水量为 5910 亿立方米,水资源使用率为 65%; 预计 2015 年为 7000 亿立方米,使用率约 80%,逼近极限。同时,由于污水处理率低,致使 70% 的河流受污染和富营养化,其中 47% 水体富磷化,44% 水体富氮化,形势严峻。

受能源、环保和全球气候变化的影响,发展清洁的可再生的生物燃料已经引起众多国家的重视。在中国,发展生物燃料不论是过去、现在还是将来都是至关重要的,它将有利的维持我国经济和社会的和谐、可持续发展。根据我国能源局规划,我国燃料乙醇和生物柴油“十二五”期间的年利用量规划目标分别为 500 万吨和 100 万吨。然而“十一五”规划提出生物燃料乙醇年利用量为 300 万吨,但是实际只达到 170 万吨左右。究其原因,我国人口众多、耕地匮乏,以粮食为原料生产燃料乙醇有限。因此,根据我国国情和国家发展生物能源战略原则,急需开发“不与人争粮、不与粮争地”环保经济的非粮生物燃料。

浮萍 (Duckweed) 是浮萍科 (Lemnaceae) 植物的统称, 为微小草本, 世界上最小的开花植物, 共有 5 个属 38 个种, 世界各地均有分布。浮萍能直接利用废水积累生物量, 同时吸收空气中的 CO_2 和 水体中的 N、P, 因此浮萍能源化利用对保障国家能源安全, 保护环境与生态, 促进 CO_2 减排, 建设和谐社会具有十分积极的作用。浮萍作为能源植物的战略意义已获得充分认识。2008 年, 美国能源部 (USDOE) 已将浮萍列为最具发展潜力的新型能源植物之一, 宣布对浮萍 (多根紫萍) 开展全基因测序工作。2010 年 12 月 2 日在美国华盛顿召开的中美先进生物燃料第五次工作组会议中, 美国能源部生物能源项目主任 Paul Bryan 先生认为“浮萍是 10 年内可实现产业化的能源植物”。

浮萍生产能源的优势: 浮萍基本不含木质素, 却富含可转化为发酵糖的淀粉 (最高可达干重的 75%)、纤维素等, 是极具潜力的新型第三代生物燃料原料植物 (表 1); 浮萍生长速度快, 可大规模工业化生产并开发为研究植物生长发育的模式生物; 可生产期长 (水温 5°C 以上即可生长), 解决原料季节性供应问题; 几乎不含木质素, 可最大程度地利用生物量; 可直接利用废水生长并可抑制藻类生长, 具有生态及环境价值; 积累高附加值活性成分, 具有综合开发价值。

表 1 浮萍生产能源的优势

特点	优势	对国家能源战略基本原则的满足			
		不争粮	3E 原则		
			能源	环境	经济
繁殖快 (2 天一代, 玉米 28 倍)	可工业化生产	+	+		+
可生长期长 (水温 5°C 以上即可生长)	可实现原料均衡供应	+	+		+
几乎不含木质素	能最大限度利用生物量	+	+	+	
直接利用废水生长	消除水体 N、P 污染	+		+	+
具有高附加值活性成分, 蛋白含量高	具有综合开发价值	+			+

在野外条件下, 实现 12 天内淀粉积累达到 40% 以上, 每平米浮萍干重达到 80 g (图 1)。在能量产出水平上, 即使与其他糖质或淀粉类能源作物比较, 浮萍也具有显著优势。以浮萍平均淀粉含量按 30% 计, 每公顷理论乙醇产量为 8.43 吨, 约为甘蔗的 2 倍、玉米的 5 倍; 若浮萍平均淀粉含量按 50% 计, 则每公顷理论乙醇产量为 14.05 吨, 为甘蔗的 3 倍、玉米的 8 倍。按覆盖中国淡水湖泊和池塘总面积的 1% 算, 种植浮萍年产乙醇 172 万吨, 直接产值 103 亿元; 同时, 可以减排 CO_2 1000 万吨, 占我国 CO_2 排放总量的 1.5%; 减排磷 1.2 万吨, 占农业磷排放的 4%; 减排氮 10.32 万吨。

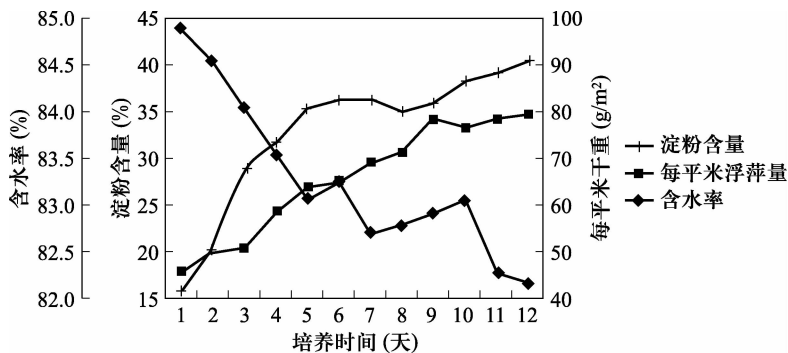


图1 浮萍生长及淀粉积累变化曲线

通过近5年的前期研究,本课题组初步整合了包括能源、生态、农业、天然产物领域在内的多学科优势力量与人员,并形成了国际合作平台与研究主导力量;开展了浮萍资源收集、保藏、评价、规模化培养,燃料乙醇、丁醇转化,以及副产物开发利用等领域的综合研究与开发。

建立全球最完善的浮萍种质资源库:已收集到浮萍样品400余份,并完成了初步鉴定;初步建立了近红外光谱模型,并对收集的浮萍样品进行了DNA条形码分析,利用DNA barcode标记扫描少根紫萍,采用3个非编码基因:atpF-atpH, trnH-psbA,和psbK-psbI用于DNA barcode分析浮萍资源。分析结果表明:3对引物扩增效果好,同时PCR片段长度多态性高,适合用于区分浮萍资源。利用DNA barcode标记扫描少根紫萍,结果发现17个居群可以分为3种类型,其中一种占绝对优势(图2)。利用DNA barcode标记扫描多根紫萍,发现17个居群可以分为4种类型,表明多根紫萍的多样性丰富,且有明显的分化。此外,首次开发了SSR引物分析浮萍群落。SSR可用于对种内浮萍的高效筛选,由于浮萍种内的变化差异较大,因此,利用SSR分析同种、不同居群浮萍可以获得较好结果。

建立直接利用废水规模化培养浮萍技术体系:在滇池建立了直接利用富含N、P生活废水规模化生产高品位生物质原料浮萍的试验基地。该基地占地5亩,分Y、A、B、C四个区,共15条跑道75个处理池,具有预处理、跑道式处理以及循环再处理等多个流程。建立了野外大规模培养条件下的测定方法,实现在保证能源产出的前提下,能够通过10~12天的处理,实现 $\text{COD} < 100 \text{ mg/L}$, $\text{NH}_4 - \text{N} < 20 \text{ mg/L}$, $\text{PO}_4 - \text{P} < 5 \text{ mg/L}$ 的农村生活污水(8%~10%的进水量)的出水水质达标,并至少积累生物量 $36.5 \text{ t}/(\text{ha} \cdot \text{a})^{-1}$ (干重),积累有机碳 $13.3 \text{ t}/(\text{ha} \cdot \text{a})^{-1}$ (即固定 $\text{CO}_2 48.9 \text{ t}/(\text{ha} \cdot \text{a})^{-1}$),积累全氮 $2.1 \text{ t}/(\text{ha} \cdot \text{a})^{-1}$,积累全磷 $0.55 \text{ t}/(\text{ha} \cdot \text{a})^{-1}$ 。

建立高效燃料乙醇、丁醇生物转化体系:浮萍富含可转化为发酵糖的淀粉,最

Genus	Population name	atpF-atpH	psbK-psbI	imH-psbA
<i>Landoltia</i>	ZH0005-S-0	683	501	273
	ZH0173-S-3	682	501	...
	ZH0125-S-10	683	501	273
	ZH0106-S-8	683	501	273
	ZH0160-S-2	683	501	273
	ZH0161-S-1	683	501	273
	ZH0168-S-3	683	501	...
	ZH0170-S-3	683	501	273
	ZH0044-S-5	683	501	273
	ZH0115-S-8	683	501	273
	ZH0118-S-8	683	501	273
	ZH0011-S-0	683	501	273
	ZH0001-S-0	683	501	273
	ZH0069-S-5	683	501	273
	ZH0175-S-3	683	501	273
	ZH0041-S-5	683	529	273
	ZH0029-S-0	683	531	273
<i>Spirodela</i>	ZH0022-D-0	662	522	484
	ZH0023-D-0	662	522	484
	ZH0075-D-5	662	522	484
	ZH0109-D-8	662	522	484
	ZH0032-D-0	662	522	484
	ZH0136-D-10	662	522	484
	ZH0043-D-5	662	522	484
	ZH0094-D-7	662	522	484
	ZH0171-D-3	662	522	484
	ZH0123-D-9	662	522	484
	ZH0102-D-7	662	522	484
	ZH0013-D-0	662	522	273
	ZH0003-D-0	662	522	273
	ZH0095-D-7	662	522	273
	ZH0090-D-6	662	501	273

图 2 DNA barcode 标记扫描浮萍

高可达干重的 75%。图 3 为扫描电镜下浮萍淀粉形态,与马铃薯淀粉相比,浮萍淀粉较小,形态较不均匀,并有片状淀粉颗粒。X 射线衍射图根据特征峰鉴定浮萍淀粉属于更为稳定的 A 型结构。

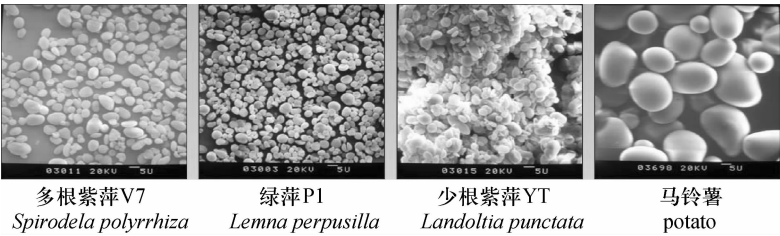


图 3 扫描电镜下浮萍淀粉形态 (×1000)

由于鲜浮萍具有粘度大的特点,传统液化糖化处理很难在短时间内充分糖化原料;高粘度的醪液也难以进行管道输送,容易堵塞管路;同时,也会降低后续的乙醇发酵效率。通过复合降粘酶系优化试验,确定降粘效果好、成本低、操作简便、适应性强的预处理降粘酶系和预处理工艺(见图4)。

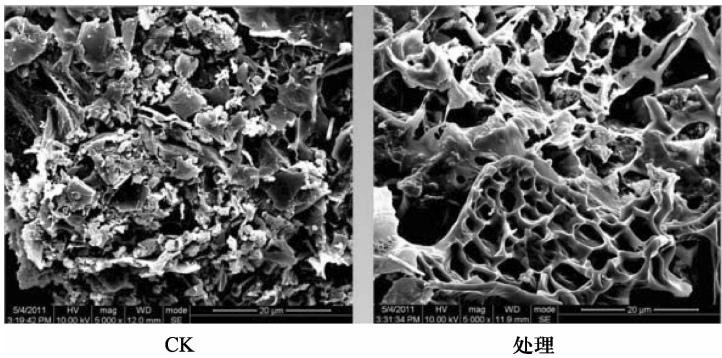


图4 浮萍降粘处理

高淀粉少根紫萍 zh0051 发酵醪在最优预处理下发酵效果如图5所示。浮萍淀粉含量43.11%,料水比1:2.5时发酵乙醇浓度可达7.52%,发酵效率达92.54%。以浮萍为原料,经64小时发酵,丁醇浓度可达11.65 g/L,已接近玉米丁醇发酵的水平(玉米对照组丁醇产量为11.85 g/L~12.50 g/L)。实验结果说明,以浮萍为原料发酵燃料乙醇和丁醇是完全可行的。

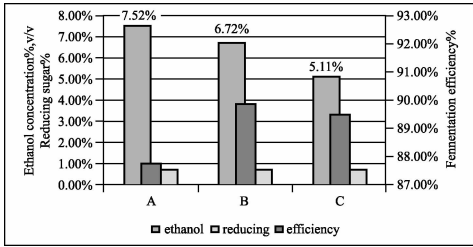
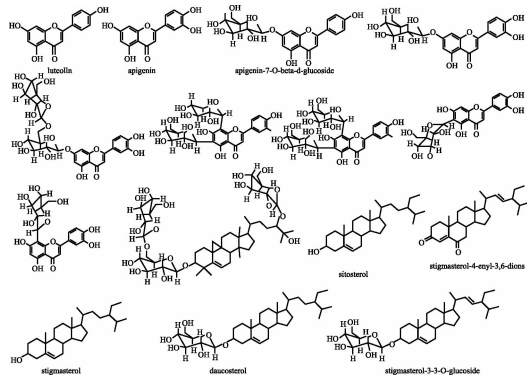


图5 少根紫萍 zh0051 发酵醪在最优预处理下发酵效果

A - 淀粉含量43.11%,料水比1:2.5; B - 淀粉含量43.11%,料水比1:3;
C - 淀粉含量33.80%,料水比1:3。

开展有价值化合物的发现与综合开发:对浮萍中黄酮、环阿尔廷三萜皂苷、神经酰胺、甾体类化合物进行分离鉴定和生物活性研究。系统阐明了多根紫萍的黄酮类化学成分,分离鉴定出16种成分;建立了四个属的黄酮指纹图谱,能够准确区分各个不同的属。

鉴定出16种多根紫萍的黄酮类化学成分:



建立浮萍研究领域的国际合作平台与机制:已初步建立了浮萍生物能源研究领域的国际合作平台和机制,与国际上浮萍研究的主要机构建立了合作关系并进行了人员和浮萍资源的交流。与美国罗格斯新泽西州立大学签订了浮萍研究全面合作的双边合作协议;与丹麦奥尔堡大学、美国北卡罗来纳州立大学、德国耶拿大学以及瑞士环境科学研究所进行了人员与浮萍资源的交流;与丹麦哥本哈根大学、奥尔堡大学共同申请 2012 年丹麦科技部的国际科技合作项目;牵头组织了“第一届国际浮萍研究与应用研讨会”,来自美国、澳大利亚、丹麦、德国、日本等国的专家学者共计六十余人参加了会议。会议形成“成都宣言”,达成了国际浮萍研讨会每 2 年召开一届的常态化机制,并决定在成都生物研究所建立全球浮萍种质资源收集和保藏中心,以实现浮萍资源全球范围内的交流与共享。

目前正在进行的工作:(1)资源收集与活体保藏新技术研究;(2)多维信息与指纹图谱数据库及系统评价体系开发;(3)适于生活废水生长的生物能源专用品系选育;(4)规模化培养技术及病虫害研究;(5)浮萍能源转化利用研究。

沼气:利用高生物量浮萍原料,开展沼气发酵技术研究。

燃料乙醇、丁醇:利用高淀粉浮萍原料,开展生物质液体燃料乙醇、丁醇发酵技术研究。

期待交流与合作:欢迎对浮萍研究感兴趣的研究机构、企业及个人与我们互相交流,资源共享,项目合作。



赵海,研究员,博士生导师。1987年获四川大学微生物学学士,1990年获中国科学院成都生物研究所微生物学硕士。1990年至1996年作为助理研究员在中国科学院成都生物研究所从事纤维素发酵产乙醇和产甲烷研究。1996年至2002年在中国科学院成都生物研究所负责地奥公司“脂必妥原料的发酵技术及规模化工艺研究”项目,并于1998年任副研究员。

2002年至2003年作为中方合作者在法国科学院图卢兹应用技术研究所进行中国科学院院级合作项目“微生物次生代谢产物研究”。2003年至今作为研究员在中国科学院成都生物研究所从事能源生物技术研究,主要研究领域是非粮原料的燃料乙醇关键技术开发,已取得多项成果。2000年以来承担国家、省部级生物能源科研项目17项,国际合作项目1项。发表论文60余篇,申请发明专利4项,获得授权1项,培养博士、硕士研究生20人。

主要研究方向:非粮原料燃料乙醇的系统研究与开发,在浮萍和甘薯原料的能源评价体系、原料储存与均衡供应、高效快速发酵及发酵副产物综合利用等领域进行深入的研究。

突破生物质转化利用的抗降解屏障： 目前的挑战、机遇和策略

孙建中

江苏大学生物质能源研究所

目前,全球能源系统主要是依赖像石油、天然气、煤碳等碳氢类资源的一次性能源,并且由此奠定了我们当前能源和化学基原料的主要物质基础,其中,有超过90%的有机化学产品均来自于对石油的各种加工。然而,全球的石油储量却非常有限,并且其需求量还在以前所未有的规模和速度增加。有研究表明,全球未来20年的主要能源需求将会以年均1.6%的速度增加,仅中国和印度经济发展对能源需求的增加速度就超过了世界年均增加速度的一半。由于这些传统能源的大量使用,对环境的负面影响越来越严重。因此,为了实现经济发展的可持续性和对全球环境的有效保护,近年来,纤维素生物燃料的可再生特性等优点受到了全球越来越多的企业和科学界的极大兴趣和密切关注,许多国家的政府也逐渐形成这样一个共识:即我们需要持续不断地减少对石油资源的依赖,建立以可再生能源为基础的经济发展模式。可以预见,发展生物能源的好处是可以直接形成一个新的能源工业技术领域,以及带来一个全新的能源农业的发展机遇,这将有助于大力发展和振兴我国传统的农业和林业,改变农村经济的单一发展模式、促进社会的稳定、并最终达到维护我们国家能源安全的目的。

农作物秸秆或其他木质纤维素类生物质的利用与开发具有许多其他可再生能源所不具备的独特优点,可用来制备成液体、气体或固体形式的各种能源,可用于发电、交通能源或制备后石油时代的各种生物基材料。近年来,大部分的燃料乙醇和生物柴油这类通过生物质的转化所产生的生物能源主要是来自于对玉米淀粉和油脂类植物原料的转化。但是,研究人员和投资家们现今却越来越关注另一类更有前途的生物质资源—木质纤维素类生物质的转化和利用,它是我们地球上最为丰富的可再生生物质资源。人们已经认识到:生物质能源的稳定原料来源和工业规模的可持续发展,将越来越依赖于专用能源作物、农作物废弃秸秆以及

森林枝桠材的高效转化和利用,它们未来的资源总量供给潜力和能源的转化利用潜力将有可能满足我国 2050 年能源需求总量的一半左右。毫无疑问,以木质纤维素的转化利用为代表的所谓第二代生物质能源将有能力改变我们对石油资源的过度依赖,显著地减少目前的能源消费方式对全球气候的诸多负面影响。然而,尽管我们大家都认同燃料乙醇等其它生物质能源可以很好地替代目前以石油为主导的交通能源,但这些新型的可再生能源目前仍然处于一个微不足道的影响地位。究其原因,由于生物质细胞壁的抗降解屏障,极大地制约了木质纤维素的转化效率和转化过程中的经济成本,在生物炼制等相关重大关键技术方面仍期待着理论和工艺技术等方面的突破。

目前,木质纤维素类生物质转化利用的产业化技术正朝向高效、低成本的方向发展,生物质的预处理技术是实现高效生物转化和降低成本的首要核心技术,其次还包括制约我们多年的另外两个关键因素:即木质纤维素酶制剂的价格成本以及有限的发酵微生物转化能力等方面。然而,在过去的 20 多年中,木质纤维素的生物催化转化过程主要依赖于一些有限的细菌和木腐真菌等少量几类工业微生物资源,虽然通过现代生物技术,如分子遗传改造、酶工程、代谢工程等组学技术的应用,使得目前的纤维素燃料乙醇的研究与开发有了相当程度的进展或突破。但是,生物质高效催化转化的产业化关键核心技术仍然没有实现真正意义上的突破,其所谓的转化过程工艺与技术,对于如何巧妙地打开或经济有效地分解结构复杂的植物细胞壁,人类目前的知识还非常有限,现有的生物质转化利用还显得不成熟,其技术途径仍然值得置疑。为了切实解决这一重大科学技术挑战,我们需要重新审视当前所采用的主要技术策略和技术途径。因此,寻找对生物质中的纤维素、半纤维素、甚至木质素,能够迅速转化又能高效利用的自然生物系统,如食木白蚁或其他以木质纤维素为原料的自然生物转化催化系统,代表了目前的重要研究方向和解决问题的有效途径。这些自然生物系统经过了亿万年生物进化的过程和演变,其独特的生物转化系统显示了高效生物转化木质纤维素的超凡能力(如白蚁生物转化系统 24 小时内,在常温条件下可转化 90% 以上的纤维素,50% ~ 80% 左右的半纤维素,25% ~ 30% 木质素)。初步研究结果证明,白蚁高效转化利用生物质的主要作用机制,是其自身进化形成了一个对付植物木质纤维素抗降解屏障的独特生物转化系统。在其独特的肠道理化微环境条件下,通过巧妙的生物质预处理过程设计及其肠道木质纤维素酶系的配合,使得生物质的高效糖化过程得以连续性地维持。因此,自然生物系统过程仿生工程研究的突破,将为实现生物质的高效转化提供全新的科学理论、产业化利用的有效途径以及获得高效催化资源的物质条件。近年来,通过采用各种现代生物技术和系统生

物学的研究手段所获得的一系列科学新发现表明:研究和利用自然高效生物转化系统是解决生物质高效转化这一重大科学问题最具潜力的有效途径之一,值得我们重视。

该综述将针对不同的自然生物转化系统,阐明它们在建立现代生物炼制技术系统中的潜在科学价值以及构建仿生过程工程系统中所存在的各种主要科学技术挑战与突破生物质抗降解屏障的重要途径。文章的重点将主要包括:1) 生物质自然高效转化系统的重要科学和工业应用价值;2) 来自自然生物转化系统中的新型高效催化转化酶系统的工程化应用途径;3) 采用现代“组学”生物技术,发现、改造并实现高效共生微生物菌系的产业化利用;4) 新型仿生生物反应器的系统构建与结构创新;5) 新型专用纤维素类能源植物的研究方向和发展潜力。作者期望通过这一讨论能够带来近年来国际国内在攻克生物质抗降解屏障发展木质纤维素燃料方面的最新进展、最新感受和突破关键科学技术问题的不同途径。



孙建中,美国路易斯安那州立大学博士。现任江苏大学特聘教授、环境学院副院长、江苏大学生物质能源研究所所长、及美国华盛顿州立大学系统生物工程系兼职教授。

孙建中曾任美国密西西比州立大学昆虫系/海岸研究与推广中心助理教授/副教授、博士生导师,昆虫生物过程仿生与生物能源专家;曾主持美国农业部、能源部、交通部等多个研究项目;受邀担任美国农业部重大研究项目评审专家、中国国家自然科学基金评审委员会重大项目海外评审专家;并担任15种国际SCI专业杂志审稿人及部分刊物编委、特邀主编。孙建中教授是国际上将白蚁高效生物降解植物木质纤维素特性引入到生物质能源研究中的少数科学家之一。共发表各类研究论文、研究报告80多篇,其中有30多篇第一作者研究论文在同行业国际顶尖或主流SCI专业刊物上发表。在生物质能源研究领域,主编第一本生物过程仿生SCI杂志研究特刊(《Insects and Biofuels, Insect Science》, Wiley - Blackwell 2010),并主编关于自然生物系统过程仿生与能源植物改造英文专著一本《Biological conversion of biomass for fuels and chemicals—Explorations from natural biomass utilization systems》,英国皇家化学

协会 RSC,2012 出版),另参与 4 部著作章节撰写(中文 2 部、英文 2 部)。应邀做过 20 多次国际性学术会议大会发言和 40 多次国际会议报告。作为大会执行主席之一,2011 年成功申请召开第 395 次国家香山科学会议“高效降解生物质的自然生物系统资源利用与仿生”。目前的主要研究领域和兴趣,详见英文版部分。

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玉米秸秆固体碱制浆分离组分 及其酶水解

林鹿

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生物质组分清洁分离及其高效水解是生物质炼制的重要步骤。本文提出一种新型和环境友好型的蒸煮脱木素工艺分离得到纤维素、半纤维素和木质素,并进行工艺条件的探索和优化,得出了较佳的工艺条件;另外,还研究了浆料纤维的表面特性并发现其与碱法蒸煮的不同之处,探索了固体碱在蒸煮过程的变化及固体碱的蒸煮分离和对纤维素的保护机制;最后,还论述了玉米秸秆分离组分的酶解过程及其机制。



林鹿,厦门大学能源研究院副院长/生物能源研究所所长,教授/博士生导师、中国生物质能专业委员会委员、中国能源学会常务理事;国家自然科学基金委员会项目评审二审专家,教育部重大项目评审专家;美国《BioResources》杂志编委、美国《Journal of Bio-Based Materials and Biofuels》和美国《Journal of Bioprocessing and Bioenergy》杂志编委。

近5年来,承担了10多项包括973计划课题、科技支撑计划课题、863计划项目、国家自然科学基金-广东联合基金重点项目等研究工作;在国内外有关刊物上发表论文170多篇,其中被SCI收录论文近70篇;获省部级以上奖5项;出版专著《生物质基乙酰丙酸化学与技术》(2009)。

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我国餐厨垃圾收集、处理利用现状 与未来发展

李秀金

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一、餐厨垃圾的产生与危害

餐厨垃圾俗称泔水、泔脚或泔水,是指居民日常生活所产生的食物残渣。餐厨垃圾主要来源于三大部分:家庭饮食产生的食物残渣、企事业单位高校等内部食堂产生的食物残渣、餐饮行业产生的食物残渣。

随着我国经济的快速发展、城镇规模的迅速扩大和城镇人口的快速增加,城镇餐厨垃圾的产生量越来越大。北京市 2011 年餐厨垃圾日产量达到 1700 t,而北京市现有的餐厨垃圾处理站点能处理的餐厨垃圾每天仅有 600 t~800 t,每天还有将近 1000 t 的餐厨垃圾没有被处理。全国餐厨垃圾的年产生量约为 6000 万吨。

餐厨垃圾主要有以下几方面的特性:

(1) 有机物含量高。有机物占干物质重量 93% 以上,主要包括食物纤维素、淀粉、动植物脂肪、蛋白质等。

(2) 含水率高,在 85% 以上。因此,收集、运输、处理处置餐厨垃圾都比较困难。因为餐厨垃圾有机物含量高,含水率高,所以很容易腐败,滋生病菌,产生恶臭。

(3) 有机物含量高、营养价值高,氮、磷、钾等含量也比较丰富,具有较高的利用价值。

(4) 含油量、含盐量高。会对餐厨垃圾处理产生抑制。

目前,我国餐厨垃圾很大一部分被用来喂猪,或者提炼地沟油,对环境和人们的身体健康造成严重危害。这些危害包括:

(1) 因为餐厨垃圾含水率和有机物含量都很高,餐厨垃圾极容易酸化腐败,产生恶臭,对人们视觉嗅觉都有污染,也会污染人们的生活环境。

(2) 餐厨垃圾腐败后,很容易滋生病菌,一些家畜以及宠物等乱食后容易传播疾病。

(3) 餐厨垃圾含油较高,一些商贩便收集餐厨垃圾提炼地沟油,冒充正规生产的食用油出售,地沟油中含有大量致癌物质,严重威胁人类健康。

可见餐厨垃圾的危害是广泛且严重的,但是餐厨垃圾本身的特性又决定了餐厨垃圾具有很大的利用价值。合理的利用不仅可以减少环境污染,还可以获得相应的利用价值。

二、收集、处理与利用现状

从 20 世纪 90 年代开始,发达国家就开始了餐厨垃圾处理处置技术的研究。尤其是德国、日本、韩国等国家餐厨垃圾处理处置技术已经非常成熟,获得了很多经验。比如日本在 2000 年就制定了餐厨垃圾排放减量标准以及饲料化堆肥化标准。截至 2007 年末,通过鼓励民间投资,韩国已经投产并正式运营 300 多条各类餐厨垃圾资源化处理,民间投资占 60% 以上。美国通过堆肥,将产品出售给农场,也得到了很好的处理效果和经济效益。德国主要采用的方法是与其他废物一起厌氧消化或堆肥化。

直接饲喂动物:这是最普遍的利用方式,我国大部分餐厨垃圾都流向了一些小的饲养场,直接用于饲喂动物,生产所谓的“垃圾猪”。

生产蛋白饲料:通过生物发酵法获得蛋白饲料。生物法是通过微生物的新陈代谢活动来分解转化餐厨垃圾获得有机饲料,这种方法效率高、周期短、能耗低、售价高,是经济效益最好的一种利用途径。但存在安全隐患,国家也没有相关标准。青海洁神、北京嘉博文 200 t/d 采用这种技术,发酵料可以做饲料,在要求严格时,也可作肥料使用。

堆肥:通过微生物的好氧发酵,使餐厨垃圾稳定化,获得有机肥料。北京南宫堆肥厂采用主要车库式好氧发酵技术(200 t/d),把餐厨垃圾和分选后的厨余垃圾一起进行堆肥化处理,生产出的肥料用于林木绿化等。

厌氧发酵:厌氧发酵技术是指在严格无氧或者厌氧环境下,微生物通过自身的新陈代谢作用,将餐厨垃圾中的有机成分,逐步分解成 CH_4 和 CO_2 的一种技术。厌氧发酵的主要产物,甲烷,可以用作发电、作汽车燃料等,利用价值高,沼渣沼液也可以用作有机肥料。从餐厨垃圾到甲烷和肥料,实现资源的完全利用。但是目前国内在餐厨垃圾厌氧发酵这方面做的还不够成熟。厌氧发酵技术对前处理要求较苛刻,分选难度大。餐厨垃圾也易酸化,沼渣沼液无害化处理技术也有待发展。该技术几年来在国内发展比较快,如北京董村 200 t/d、重庆、上海、深圳

等地都建有餐厨垃圾厌氧发酵处理厂。

三、未来发展

(1) 研究适合高分散源餐厨垃圾的基于物联网的信息化收运系统,解决餐厨垃圾收集不上来、非法收集和流向不明等问题。

(2) 开发适合我国餐厨垃圾理化和生物学特性的预处理设备,解决餐厨垃圾成分复杂,高含油盐、含有大量塑料、陶瓷、金属等废弃物,提高后端处理系统处理效率和运行稳定性。

(3) 研究高温湿式厌氧消化工艺技术,解决餐厨垃圾能源化转化和卫生安全问题。

(4) 研究餐厨垃圾与其它原料协同干法厌氧消化技术,解决餐厨垃圾单一处理时,油盐抑制、产品油盐含量高、沼液无法处理利用等问题。

(5) 研究适用于餐厨垃圾厌氧发酵的高效微生物制剂,解决现有餐厨垃圾厌氧消化周期长、速度慢及成本高等问题。

(6) 研制高效反应器与相关装备,解决缺乏装备问题,包括厌氧消化反应器、搅动、输送、换热、保温、数据采集和安全监控等设备。



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1994 至 1998 年分别就读于中国农业大学和美国加州大学(UCDAVIS),并于 1998 年获博士学位,之后在美国加州大学(UCDAVIS)生物环境与能源工程实验室做博士后研究工作,至 2000 年底回国工作。主要从事生物质废物处理、能源化与高值化转化利用方面的教学和研究工作。

曾主持和参与了包括国家“863”、“十一五”科技支撑计划、环保部、教育部、农业部和北京市的 30 多项科研课题。曾获国家科技进步三等奖、农业部科技进步二等奖、中国石化联合会技术发明三等奖各一项,在国内外重要学术期刊发表论文 140 多篇,申报和获国家授权发明专利 10 多项,主编国家“十一五”规划教材《固体废物工程》一部。

社会兼职包括中国环境科学学会固废分会副主任委员、中国沼气学会副理事长、科技部“城市生物质燃气化技术创新战略联盟”副理事长、《农业工程学报》、《北京化工大学学报》、《Journal of Chinese Chemical Engineering》编委,以及《Bioresource Technology》、《Energy & Fuels》、《Biochemistry & Bioengineering》等国际著名期刊特约审稿人等。

生物质水相催化合成生物汽油和航空燃油技术

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众所周知,我国是一个能源消耗大国,仅 2009 年一次能源消费总量就达到 30.66 亿吨标准煤,占全世界总能耗的 17.5%。而我国又是一个石油资源相对匮乏的国家,2010 年我国原油进口量达到了 2.39 亿吨,进口依存度再超 50%;从长远考虑,这些石油资源短缺会对我国的国家能源安全造成一定的影响,同时大规模使用这些化石能源也会造成环境的严重污染。因而,寻求和开发新型能源,特别是环境友好的可再生能源已迫在眉睫。

生物质是唯一可制备液体燃料的可再生碳源,具有清洁无污染、碳活性高等优点。我国的农林废弃物储量十分丰富,每年储量达到 9.2 亿吨左右,如果其中 40% 被充分利用的话,可替代石油约 4000 万吨。所以,生物质能被认为是一种重要的石油补充能源。传统利用生物质转化成液体燃料的方式,主要是通过将其先水解成相应糖,经过发酵获取乙醇和丁醇,但是这种工艺存在糖利用率低、能耗高等缺点。我们的策略是:通过对木质纤维素进行预处理酸水解,得到相应的单糖类,对这些糖进行水相催化重整,可以获取以 C5 ~ C8 烷烃为主的生物汽油组分;通过对碳链的增长,可得到以 C8 ~ C15 烷烃为主的航空燃油组分。采用水相催化重整技术,由于反应均在液相中进行,反应速度快,避免了原料的汽化,利用产物烷烃与水相自动分离,大大简化反应工艺和降低系统能耗,同时也可实现水解液中单糖或低聚糖的全利用。因此,以非粮的木质纤维素类生物质资源经高效水解、水解液催化合成生物汽油和航空燃油具有明显的技术优势和应用前景。

其次,我们对生物质水相催化制取生物汽油和航空燃油的技术路线进行简要地介绍。该生产工艺中,木质纤维素首先经过水解处理,其中容易水解的半纤维素首先转变成五碳糖,然后纤维素水解生成六碳糖,对富含五碳糖、六碳糖类的水解液通过两种途径将其转化:一是对水解液进行加氢处理,获取相应的多元醇,采

用新型的水相催化重整方法,并结合加氢异构方式对烷烃异构化,利用烷烃与水不相溶的特性,实现烷烃与水相的自动分离,获取以 C5 ~ C8 烷烃为主的生物汽油组分。二是水解液中糖类首先在酸性条件下进行脱水处理,生成糠醛和 5-羟甲基糠醛,引入丙酮与其发生羟醛缩合反应,控制航空燃油中间体碳链的长度,并结合脱水、加氢和异构工艺,最终可获取以 C8 ~ C15 烷烃为主的航空燃油。

接下来,我们对工艺中涉及的一些关键技术,如生物质水解技术、水相加氢重整技术及航空燃油合成关键技术与工艺进行介绍。在研究过程中,我们利用了高温液态水、超低酸-酶水解与酸酸耦合水解的方式进行生物质水解工艺研究,实现生物质中半纤维素和纤维素的分级解聚,整个过程中能耗较低、功能单体收率和选择性均较高。我们还对水解工艺和金属盐助水解工艺进行了详细的探索研究。

对水解液中糖的转化利用,通过两种途径实现其高效转化。首先,采用 Ru/C 催化剂对糖进行加氢转变成相应的多元醇,并在水相重整镍基催化剂上进行多元醇加氢异构生成相应的以 C5 ~ C8 为主要成分的生物汽油组分。这个工艺中主要的技术难点在于水相催化重整催化剂的设计与制备、水相加氢工艺的耦合及催化剂的稳定性研究。通过对催化剂的结构与性能关联研究,我们自主研发了一种高性能镍基分子筛催化剂,多元醇转化率达到 80% 以上,C5 ~ C6 烷烃收率接近 90%,避免了贵金属催化剂的使用,降低了生产成本,提高了原料的转化效率。我们并对产物烷烃的异构性能进行了研究,异构化程度达到 45.6%。中科院广州能源研究所已于 2010 年建成了国内首套年产 150 吨生物汽油中试示范系统,系统连续运行稳定。其次,利用糖进行酸脱水生成糠醛类,通过引入丙酮与其发生羟醛缩合反应,调节原料之间的摩尔比例,即可控制缩合产物中碳链的长度。对这些缩合中间体进行低温加氢和高温加氢与异构研究,可获得以 C8 ~ C15 为主要成分的航空燃油组分。本工艺中主要技术难点为缩合催化剂设计、加氢催化剂与反应器设计。利用自主制备的 MgO/NaY 催化剂具有优异的缩合催化性能,反应 8 h 后糠醛转化率和总选择性均可达到 98%。在实验室中,采用固定床反应器,C13 烷烃收率可达 90% 左右,催化剂连续使用 120 小时,性能稳定,具有较广阔的应用前景。目前正在筹建百吨级生物航空燃油示范系统。

最后,简要地对生物液体燃料产业化过程中可能面临的问题进行归纳,并提出几点解决措施。其问题主要体现在以下几个层次:(1) 缺乏专用的生物汽油/航油燃料的相关评价体系;(2) 原料地域性和季节性强,难以满足全年生产;(3) 一些关键生产技术有待完善;(4) 原料综合利用还有待进一步加强。针对上述问题,试图通过几种途径得以解决:(1) 编制相应的评价标准和规范,确定生物

液体燃料组成范围;(2) 选择性培育草本能源植物,发展原料多元化;(3) 突破复杂原料高效预处理共性技术;(4) 寻找糖类衍生物多途径转化;(5) 水解残渣木质素的充分利用,获取高价值的芳烃产品,实现生物质全组分利用。



马隆龙 研究员,973 项目首席科学家,中国科学院广州能源研究所副所长,生物质能源产业技术创新战略联盟副理事长兼秘书长,“十二五”863 计划“农林生物质高效转化技术”主题专家组专家,中国可再生能源学会理事;生物质能专业委员会副主任委员。

主要研究方向:生物质高效转化与综合利用,包括以下几个方向:生物燃料高效制备与利用,生物质热解、气化及发电,生物质全组分高效转化与利用,能源技术评估与经济性分析。

主持完成了 973、国家自然科学基金、863、科技攻关、重大国际合作项目和广东省研究项目等 30 余项科研项目,取得了较高水平的科研成果和较大的经济效益。共发表论文 70 余篇,专著 7 部。

木质纤维素生物炼制技术

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随着我国石油进口率超过 50% 和温室气体排放跃居全球首位,资源、环境问题已经成为我国经济社会可持续发展的最主要瓶颈。利用年产量巨大、可持续再生的非粮木质纤维素资源来部分替代日益紧缺的石油资源,生产国家急需的液体燃料和各种化学品,是突破上述瓶颈,实现经济社会可持续发展的重要途径之一。其核心技术是实现金融危机后经济体制转变、发展新兴产业的重要关键技术。其中,纤维素乙醇生产技术是国内外长期以来力求实现的第一个突破点。然而,由于木质纤维素材料是植物长期进化形成的支撑和保护组织,非常难以直接被微生物及其酶系降解转化,以致工艺过程复杂,加上乙醇作为燃料的过低产品价格,导致纤维素乙醇生产一直无法同石化产品和粮食加工产品在经济上竞争。

总体来看,目前国内外多数研究机构和企业均试图以秸秆等原料单纯生产乙醇一种产品,使得原料、预处理所占的成本在总成本中的比例过高,而原料中的各种成分未能被充分利用,最终价值也没有最大化。这是纤维素乙醇工艺尚未能产业化的主要原因之一。特别是我国在酶生产技术、戊糖发酵菌株构建等方面还没有取得根本性突破,如只能生产廉价的燃料乙醇一种产品,因此预计的生产成本都明显高于当前粮食乙醇的成本。在各单位中试研究中,每吨纤维素乙醇的原料消耗都在 6 吨以上,成本估算多半都在 8000 元/吨乙醇以上,实际运行可能还要更高些,因而无法实现大规模工业化生产。因此,急需引入新的研究思路和技术。生物炼制概念的引进和实践是解决上述矛盾的根本途径之一。

现代石油化工成功的一个重要经验是,通过分馏和催化转化等技术,把复杂的底物(如原油)中的每一种组分都分别变成不同的产品,即使是工业加工中的残渣(如沥青),也转化成适当的产品,从而最大限度的开拓产品总价值。这就是所谓的“炼制(refinery)”。这一概念已经被引入生物质资源开发领域,提出了“生物炼制(biorefinery)”的新概念:以生物质为基础的化学工业也必需打破原来用复

杂的生物质只单纯生产单一产品的传统观念,充分地利用原料中的每一种主要组分,将其分别转化为不同的产品,实现原料充分利用、产品价值最大化和土地利用效率最大化。

木质纤维素类生物质可以通过精炼的方式转化成人类社会需要的食品、饲料、化学品、材料和燃料等。要实现精炼,首先,要把复杂的生物质分离成其组成成分,进而加工转化。构成植物细胞壁的木质纤维类生物质含有纤维素、半纤维素和木质素等复杂的组成成分。三类主要组分能够分别衍生出不同的化学品:纤维素断开为葡萄糖,葡萄糖发酵制乙醇、有机酸或溶剂;半纤维素可水解成木糖等单糖或寡糖,木糖及其衍生物可以生产各种功能食品,也是糠醛和呋喃树脂的前体;木质素是苯丙烷衍生物的聚合物,热值很高,是优质的固体燃料,也可以用作混凝土、沥青等建筑材料或聚氨酯等塑料的添加剂,或用于生产高值的芳香族化合物(如香草素)。通过同时生产多种产品,我们可以充分利用各种木质纤维素组分和中间体在性能上的差异,从木质纤维素材料中获得最大价值。

在山东大学长期从事纤维素酶基础和应用研究而获得大量成果、山东禹城龙力公司已建立起玉米芯生产木糖系列产品技术并实现大规模产业化的基础上,我们提出了利用玉米芯木糖加工废渣生产纤维素酶和燃料乙醇的新技术路线,成功地利用木糖醇、低聚木糖等高附加值产品的生产过程,将玉米芯中纤维素、半纤维素、木质素相互束缚的坚固结构变得松散,既可将原料和预处理成本转移到高附加值产品的生产成本中,又在保障预处理效果的前提下,为下一步的酶解工艺提供了易酶解的原料,提高了纤维素乙醇生产的经济性。同时,通过在预处理阶段将玉米芯的半纤维素部分转化为低聚木糖、木糖醇等高附加值产品,解决了生物质资源中的半纤维素部分转化乙醇效率低的难题。剩余的木质素也可以生产较高值的化工产品,从而形成产品多元化的合理产业结构,提高了生产工艺的整体经济效益(图1)。

在新工艺中,通过利用有自主知识产权的斜卧青霉工业菌株、使用木糖渣等工业废料作为主要培养基成分、现场就地生产出粗纤维素酶发酵液以避免酶制剂加工、运输的较大成本增加,我们大幅度降低了纤维素乙醇生产的用酶成本。同时,采用基因组重组、蛋白质分泌组学分析、同步糖化发酵、补料分批发酵、pH分段控制等新技术,克服由于木糖渣作为新工业原料而带来的培养基营养成分欠缺、发酵液粘度大、易喷料或挂壁、发酵过程pH不稳定、产品乙醇浓度低等一系列技术难题,集成发明了成套生产工艺技术。

在这些技术发明的基础上,我们率先在国际上先后建成了用玉米芯年产3000吨纤维素乙醇的中试生产装置和万吨级的生产示范装置,并实现了新工艺

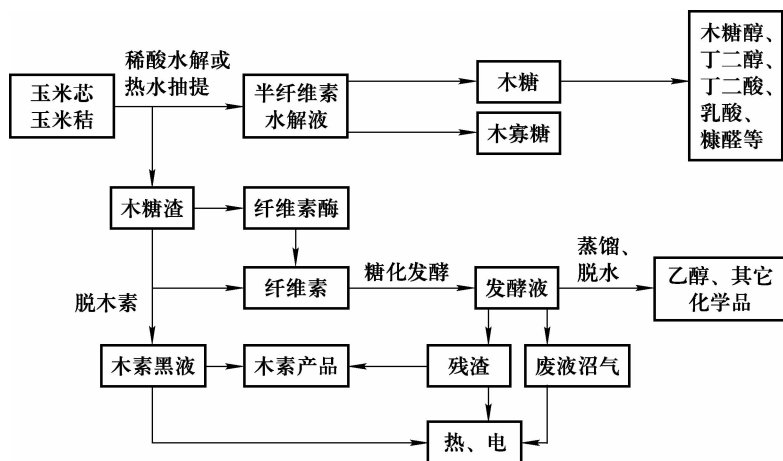


图 1 玉米芯或玉米秸生物炼制技术过程示意图

在较大规模上的试生产,生产成本接近粮食乙醇生产水平。相关技术成功获得了国家发明专利,并先后获得了2009年山东省技术发明一等奖、2011年国家技术发明二等奖。新技术成功通过了中石化委托中咨公司进行的规划评估及国家环保部的环境技术评估。最近,山东龙力生物科技股份有限公司5万吨/年纤维燃料乙醇项目又成功地获得国家发展改革委核准,成为国内首家获得国家正式批准的纤维素乙醇生产厂。

木质纤维素生物炼制新技术一经提出,就迅速扩展开来。济南圣泉集团开发出的新能源-新材料一体化(糠醛-乙醇-木素发电联产)工艺已完成工业规模装置的建设,即将进入生产调试阶段。中科院过程工程研究所等科研单位与吉林省松原市吉安生化丁醇有限公司等企业合作完成了“秸秆半纤维素发酵丁醇及其综合利用技术与示范”项目,开发出的用玉米秸秆生物炼制联产丁醇-纤维素衍生物-多元醇技术也已进入产业化发展阶段。

通过艰苦努力,我们希望最终实现生物质原料(淀粉、糖类、纤维素、木素等)全部利用,产品(燃料、大宗化学品和精细化学品、药品、饲料、塑料等)多元化,形成生物质炼制巨型行业,部分替代不可再生的一次性矿产资源,实现以碳水化合物为基础的经济社会可持续发展。



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长期从事纤维素酶和可再生资源微生物转化技术研究。先后主持或参加了 20 余项国家或省部级以上科研项目。与同事合作,在国内外学术期刊上发表论文 270 余篇,其中 SCI 收录刊物 100 余篇。编(译)《微生物技术开发原理》、《木质纤维素降解酶与生物炼制》等著作 10 余部。选育出的青霉抗降解物阻遏突变株,产酶能力达到了国际先进水平,已用于投资建厂生产工业用酶。提出了新的植物纤维原料生物炼制技术路线,新技术已进入产业化开发阶段。“玉米芯废渣制备纤维素乙醇技术与应用”获 2011 年国家技术发明二等奖;“麦草浆的生物漂白和酶法改性”获 2005 年国家科学技术进步奖二等奖,获其它省部级科技奖励一等奖 3 项、二等奖 5 项,国家发明专利 12 项。

生物质废弃物制备航空生物 燃油技术进展

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一、背景与需求分析

目前,航空运输业在经济全球化进程中扮演的角色越来越重要,人员空运与货物空运的数量分别以每年 4.9% 和 5.3% 的速率增长,航空燃油的用量也占到整个石油产品产量的 8%。据统计,当前全球航空运输业每年消耗 15 亿~17 亿桶航空煤油(相当于 2500 亿升),2008 年全球航空运输业排放的二氧化碳高达 6.77 亿吨,占全球总排放量的 2%。国际航空运输协会(IATA)致力于减少航空排放对环境的影响提出了三大减排目标承诺:到 2020 年,每年燃烧效率提高 1.5%;从 2020 年起,实现碳中和增长,稳定碳排放量;在 2050 年,碳的净排放量比 2005 年减少 50%。欧盟计划于 2012 年起对所有抵离欧盟的商业航班实施碳排放权配额制度,2000 多家航空公司将被纳入欧盟排放交易体系,其中包括 35 家中国公司。届时,全球航空公司每年成本将增加 35 亿欧元,中国民航业仅 2012 年一年就将向欧盟支付约 8 亿元人民币。在航空燃料价格急剧上涨和航空碳减排的双重压力下,包括中国在内的世界各国航空公司都开始积极寻求解决方案。然而,仅凭飞机燃烧效率和航空公司营运效率的提高,无法从根本上实现碳排放减少。因此,开发第二代可再生航空生物替代燃料是航空业减排和降低燃油成本的一大出路。国际航空运输协会报告称,第二代生物燃料有望于 2012 年开始在航空运输业正式商用,可以减少最高达 96% 的温室气体排放。

二、航空生物燃油技术概述

(一) 费托合成技术

费托合成是一种把含碳物质经合成气转化为液体燃料的工业技术。将合成气经过催化剂作用转化为液态烃的方法是 1923 年由德国科学家 Frans - Fischer 和 Hans Tropsch 发明的,简称 F - T 合成。费托合成技术可分为高温费托合成 (HTFT) 和低温费托合成 (LTFT) 两种。前者一般使用铁基催化剂生成轻质合成油和烯烃为主,合成产品经加工可以得到环境友好的汽油、柴油、溶剂油和烯烃等。后者使用钴基催化剂生成重质合成油、石蜡为主,合成的主产品石蜡原料可以加工成特种蜡或经加氢裂化/异构化生产优质柴油、润滑油基础油、石脑油馏分(理想的裂解原料),产品既无硫也无芳烃。费托合成技术按照原材料的不同可以分为三种类型:煤炭为原料的煤制油工艺 (CTL)、天然气为原料的天然气合成油工艺 (GTL)、以及生物质为原料的生物质合成油工艺 (BTL)。为了解决当地的石油需求问题,南非于 1951 年建成了第一座由煤生产液体运输燃料的 SASOL - I 厂。荷兰皇家 Shell 石油公司一直在进行从煤或天然气基合成气制取发动机燃料的研究开发工作,尤其对一氧化碳加氢反应的 Schulz - Flory 聚合动力学的规律性进行了深入的研究。在 1985 年第五次合成燃料研讨会上,该公司宣布已成功开发 F - T 合成两段法的新技术—SMDS (Shell Middle Distillate Synthesis),并通过中试装置的长期运转。基于费托合成的生物质合成油工艺可以适用于各种不同的生物质原料,包括森林和农业废弃物、木质加工业底料、能源作物、以及城市固体废弃物等。

(二) 氢化处理技术

第二代生物燃料,包括非粮作物乙醇、纤维素乙醇和生物柴油等,其原料主要使用秸秆、枯草、甘蔗渣、稻壳、木屑和藻类等非粮作物,因其“不与人争粮”、“不与粮争地”被认为是未来生物燃料的发展方向。而用作航空燃料的第二代航空生物燃料,业界对其提出了更高的要求,要求必须具备极高的燃烧品质、可以直接替代传统的航空煤油,而且无需飞机制造商重新设计引擎或飞机,不需要航空公司和机场开发新的燃料运输系统。此外,考虑到环境的可持续发展,业界还要求生物燃料的原料种植不能砍伐森林或破坏环境,同时不会影响粮食生产和淡水资源,并在其整个生命周期可以减少碳排放。目前,比较典型的第二代航空生物燃料技术包括 UOPTM 工艺和 Bio - Synfining 工艺。UOP 工艺主要包括加氢脱氧和加氢裂化/异构化两个部分。首先通过加氢脱除动植物油中的氧,该部分是强放

热过程,加氢脱氧之后的物料再通过加氢进行选择裂解和异构化反应获得石蜡基航空油组分。另外,UOP 公司还开发了 RTPTM 工艺,通过生物质的快速裂解和加氢精制来提取芳烃,作为航空生物燃料的调和组分。在 Bio - Synfining 工艺中,脂肪酸和脂肪酸甘油酯通过三个工艺过程转化为航空燃油。首先,要去除原料油中的杂质和水,98% 的金属杂质和磷脂组分将会被选择性脱除。处理后的脂肪酸通过加氢催化转化成长碳链饱和烷烃,最后再通过加氢裂化/异构化过程制得含有支链的短链饱和烷烃。2008 年 Syntroleum 公司已经以废弃动物油脂和皂脚为原料,采用 Bio - Synfining 工艺生产了 600 加仑航空燃油用于美国空军的飞行计划。Honeywell's UOP 公司也计划为美国海军和空军分别提供 190,000 加仑和 400,000 加仑的航空生物燃油,该计划将采用动物油脂,第一代能源作物大豆油和棕榈油,以及第二代可再生能源植物麻风树、亚麻和微藻作为原料。

(三) 生物合成烃技术

Virent 能源公司的 BioForming 工艺组合了专有的水相重整 (APR) 技术与石油炼制中常规的催化加工技术,如催化加氢处理和催化缩合工艺 (包括 ZSM - 5 酸缩合、碱催化缩合、酸催化脱水和烷基化),从植物的糖类、淀粉或纤维素制取喷气燃料。首先,水溶性碳水化合物被催化加氢处理。然后在水相重整过程中,得到的糖醇类与水借助于专有的多相金属催化剂,生成氢气和化学品中间体。最后,通过碱催化的缩合途径,将这些化学品转化为喷气燃料组分。这一技术也产出汽油、柴油、烷烃燃料气体和其它化学品。从 Virent 能源公司的工艺得到的烃类生物燃料与石油产品可以互换使用,在组成、性能和功能方面均能与之匹配,可在现有的发动机、燃料泵和管道中使用。初步分析表明,Virent 能源公司的 BioForming 工艺在原油价格 60 美元/bbl (1 bbl $\approx$ 159 L) 时,在经济上完全可与石油基燃料相竞争。与发酵法不同,该工艺可采用混合糖类物流、多糖类和从纤维素生物质衍生的 C5 和 C6 糖类。Virent 能源公司生产的能量密集的生物燃料可从水中自然地分离出来,为此,该工艺无需其它技术所需的能量密集的蒸馏去分离和收集生物燃料,仅需要很少量的外部能源。研究表明,由该工艺衍生的燃料与乙醇相比,单位热值的生产成本要低 20% ~ 30%。

三、原料资源分析

(一) 麻风籽

麻风树土生土长在中美洲,是一种高约 3 米的植物,在热带和亚热带具有良

好的适应性。树中包含的不可食用的油脂可用于生产燃料,每颗种子可产出30%~40%的油份。麻风树耐旱,抗虫害和疾病,不与粮食资源竞争。麻风树2~3年后达到成熟,可以活40年,并能达到超过4米的高度。麻风树从大气中吸收的二氧化碳可能超过其所释放的二氧化碳;另外,这种神奇的树种还可以稳定和恢复已经退化的土壤。正因为如此,2007年,《科学美国人》(*Scientific American*)杂志将麻风树称为“灌木中的绿色黄金”。

世界上第一架装备第二代可持续生物燃料的商业飞机试飞于2008年12月3日,新西兰航空公司的一架747—400承担试飞工作,其中一台劳斯莱斯RB211发动机由麻风籽油混合燃料驱动。这种基于麻风籽油的燃料按1:1的比例与Jet A1混合,并经劳斯莱斯认证为适宜燃料。生物燃料测试飞行结果显示:按照50:50比例混合而成的麻风籽油燃料和标准喷气式燃料在B747上节省了12%的燃油,并减少了60%~75%的二氧化碳排放量。

(二) 海藻

美国大陆航空公司试飞的波音737—800飞机采用了包含海藻与麻风树提取物的混合生物燃料,海藻油由Sapphire能源公司提供,而麻风树油则由Terrasol公司提供。这是第一次采用包含部分藻类提取物的燃料提供动力的商用飞机飞行。相比于麻风树来说,海藻似乎是一种更为物美价廉的替代品。海藻藻类即使是在贫瘠的地区,诸如在地下水成涩的沙漠地区也能生长,即使是利用已污染或含盐分的水也可以生长,这样就避免了占用良好的土地资源和清洁的水资源。同时,这种单细胞有机体仅需要阳光、水和二氧化碳就能生长。在仅仅一天的时间里它的数量就能够翻两番,而且还能大量吸收碳。美国新罕布什尔州立大学在2004年的报告中就指出,3000万英亩沙漠中生长的藻类转换为藻类燃料可满足美国所有的运输用燃料需求,而这块面积仅占全美种植农作物和养殖牲畜土地面积的3%。

2010年5月26日,中国科学院青岛生物能源与过程研究所(青能所)与美国波音公司研发中心共同签署了推进藻类可持续航空生物燃料合作备忘录,将在青岛组建可持续航空生物燃料联合实验室,启动微藻航空生物燃油这一能源技术的大规模研发。青能所将于2010年底在山东平度百亩中试基地建成2000平米微藻规模培养中试系统,计划到2015年建成1座产量为5 kt/a的微藻生物柴油产业化示范系统装置。

(三) 亚麻荠

亚麻荠又被称作“快乐的黄金”或假亚麻,含油量高(通常包含35%~38%的

油),并且能够与小麦和其它谷物交替种植。亚麻荠最早来自北欧和中亚,主要生长在气候比较温和的地区,如美国和加拿大的北部平原。

日本航空公司试飞的波音 747—300 飞机首次在普惠发动机上测试三种第二代生物燃料混合而成的燃油,其成分分别是亚麻荠油(84%)、麻风树油(低于16%)以及海藻油(低于1%)。

美国密歇根理工大学的研究人员对以亚麻荠为原料生产的航空燃油整个生命周期的温室气体排放进行了测定。研究结果表明:由于亚麻荠的一些独特属性,如对肥料的需求量低、产油量高等,其副产品还可高附加值利用。亚麻荠航空燃油是所有以农作物为生产原料的生物燃料中温室气体排放量最少的,比化石燃料的温室气体排放量减少 84%。

(四) 生物质废弃物

用上述原料生产航空生物燃料,因为原料易于集中且原料油结构与组分适合制备航空燃油,因此被特别关注,但是成本是个瓶颈问题,估计需要很长的时间来解决。

现阶段,从环保与节能减排角度,同时结合经济性,利用生物质废弃物制备航空燃料更有优势。生物质废弃物包括农业废弃物,如秸秆、玉米芯、稻壳;林业废弃物,如园林绿化修剪物、木屑、刨花、树枝等;果蔬剩余物;生活垃圾;畜禽粪便;污泥和工业生物质废弃物等。这些废弃物从可获得量角度分析,折合标准煤近 5 亿吨/年。

四、航空生物燃油技术进展

长期以来,民航业一直受国际油价制约,经营业绩波动较大,如果能开发一种性能好、价格低、安全性又达标的新型生物燃料,无疑将开启世界民航绿色发展的新纪元。随着费托合成技术在南非 Sasol 公司及 Shell 公司的大规模应用,越来越多的能源工业开始考虑应用该技术来解决由于石油资源匮乏和国内石油供应不足带来的一系列问题。1993 年 Shell 公司的 SMDS 工艺在马来西亚实现了 50 万 t/a 规模的工业生产,Exxon 公司开发了以 $\text{Co}-\text{TiO}_2$ 催化剂和浆态床反应器为特征的 AGC21 新工艺,已完成规模 200 bbls/d 的中试。20 世纪 80 年代初,中国科学院山西煤炭化学研究所开始 F-T 合成的技术与开发,提出将传统的 F-T 合成与形选分子筛相结合的固定床两段法合成工艺技术(MFT),该工艺先后被国家列为“七·五”与“985”重点攻关项目。

越来越多的航空公司开始研发新型的可替代能源,并将第二代可再生燃料应

用于试航飞行,为未来的航空业带来新的曙光。英国维珍大西洋航空公司成为世界上第一家完成生物燃料试飞的航空公司,一架波音 747 客机进行了由生物燃料提供部分动力的飞行试验。客机从英国伦敦希思罗机场起飞,大约 1 个半小时后安全降落于荷兰阿姆斯特丹的斯希普霍尔机场。这架客机共有 4 个主燃料箱,其中之一使用了由普通航空燃料和生物燃料组成的混合燃料。飞行中试用的生物燃料由椰子油和棕榈油制成。另外,各大国际航空公司如:空客公司、新西兰航空公司、巴西蔚蓝航空公司、美国大陆航空公司、日本航空公司也相继使用第二代可再生资源燃料完成了生物燃料的试航测试(见表 1)。

表 1 全球航空公司生物燃料试飞汇总表

航空公司名称	试飞机型	燃料组成
英国维珍大西洋航空公司	波音 747 - 400	椰子油、棕榈油
美国大陆航空公司	波音 737 - 800	海藻、麻风树
日本航空公司	波音 747 - 300	亚麻荠油(84%)、麻风树油(16%)、海藻(1%)
新西兰航空公司	波音 747 - 400	青桐木油(50%)、喷气机燃油 Jet A1(50%)
荷兰皇家空军	波音 AH - 64D	藻类、废弃食用油
荷兰皇家航空公司	波音 747	亚麻荠油(50%)、传统煤油(50%)
欧洲民航飞机制造公司	新一代钻石 DA42	100% 的海藻生物燃料
空中客车公司	空客 A380 - 841	40% 液化燃气和 60% 标准航空燃料
德国汉莎航空公司	空客 sasa321	来自植物油提炼的煤油占一半
中国国际航空公司	波音 747	麻风树油
卡塔尔航空公司 + 空客	空客 A340 - 600	48.5% 的天然气合成油与常规喷气机燃料混合
巴西塔姆航空公司	空客 A320	麻风树生物燃油和传统航空燃油

五、天津大学航空生物燃油研究进展

从 2009 年开始,天津大学开展了航空生物燃油技术与开发工作。该技术路线主要包括两部分内容(图 2):一是从废弃油脂转化制得生物柴油后经电解脱氧技术获得直链烷烃,然后经加氢异构化获得航空生物燃料的烷烃组分。二是从秸秆类生物质资源经过热解气化制取生物油,然后经过生物法处理、多级萃取提取出芳烃成分,最后经加氢重整制得航空生物燃料的芳烃组分,该组成不超过总含量的 20%。

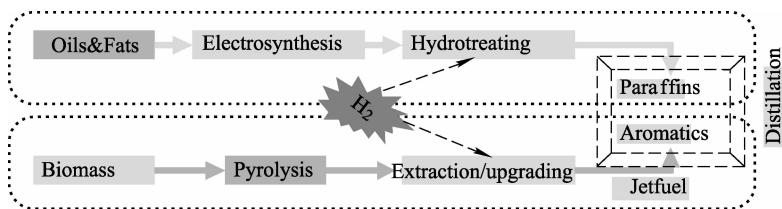


图2 航空生物燃油技术路线

（一）废弃油脂资源制取航空生物燃料支链烷烃组分

连续化生产过程中高活性酯化催化剂的研究制备。该催化剂必须具有较高的催化活性,以及良好的使用寿命。

高效能固体酸碱催化剂的均匀性、稳定性、对复杂原料的适应性及再生重复使用问题。

高转化率的连续化酯化生产工艺过程的优化耦合技术、生物柴油连续化生产过程中生物柴油与甘油的连续分离设备的开发和工艺条件的控制。连续化生产过程的工程放大中设备和工艺条件的确定。这里面涉及连续化管式反应器高效传热、传质、温度及物料浓度分布问题。

催化氢化及异构化催化剂的研发与制备。异构化催化剂主要用于航油组分的异构化转换,用于提高航空燃料的低温特性。

电解脱氧工艺参数的优化与控制。

（二）生物质热裂解后提质制取航空生物燃料芳环组分

生物油制取生物质柴油的精制过程中采用介孔分子筛催化剂,以提高生物油的稳定性和产物分布,改善生物油蒸馏过程中的变质问题。

通过极端微生物制取极端催化酶,通过酶对生物油进行提升品质。

极端微生物选取与有效催化酶的制取,介孔分子筛催化剂在生物油中的失活研究。

（三）航空生物燃料不同组分均匀调和技术

航空燃料的组成包括烷烃、环烷烃、以及芳烃。但是芳烃含量具有严格的规范限制,使用量不高于20%。因此,不同组分的均匀调和技术会较大地提升航空燃料的使用性能。

(四) 航空生物燃料生命周期评价体系的建立

航空生物燃料生命周期评价体系的建立,可以有效地预测航空燃料在整个生命周期中对环境的影响,并能合理对比不同技术对于环境的影响程度,以利于在有效环节合理降低环境污染。

六、结论与展望

对能源安全性的强烈需求是对采用合成方法生产费托合成燃料的主要驱动力,这些费托合成燃料尤其以化石能源如煤炭和天然气生产最受关注。然而,以煤炭和天然气为原料的费托合成燃料炼油厂建设费用是常规炼油厂的2倍,合成过程中 CO_2 排放较多,需解决 CO_2 的捕集和封存问题。发展以生物质为原料的费托合成技术,可以有效减少 CO_2 排放量达90%以上。同样,以第二代可再生能源作物为原料的氢化处理合成技术已经成功应用于航空飞行测试。从长远看,该技术可以使航空运输业有效减少油料依赖、降低成本和实现减排。生物合成烃技术目前仍处于试验研究阶段,相关信息的报道比较少。虽然该技术也可以应用于生物质以及糖类、淀粉类等原料,能够有效降低 CO_2 排放,但是该技术主要用于合成汽油基航空燃料。航空汽油用在活塞式航空发动机,该类型发动机目前只用于一些辅助机种,如直升机、通讯机、气象机等,所以相应的航空汽油的用量也大大减少。综上所述,发展以生物质和第二代可再生能源油料作物为原料的航空燃料新技术将会成为航空运输业可持续发展的新希望。



陈冠益,博士、教授,天津大学环境学院院长。科研成果:围绕有机废物的生物能利用开展创新研究。先后负责了国家自然科学基金重点项目、863和973课题、国家重大基础研究计划前期项目、科技部国际合作重点项目、天津市科技发展计划重点项目、欧盟项目、中荷政府合作项目等。2011年获天津市科技进步奖一等奖(排名第一)、2005年入选教育部新世纪优秀人才资助计划并获霍英东优秀青年教师基金;2011年入选天津131创新型人才工程第一层次人选。

近五年被国家基金委邀请并资助参加中泰、中丹、中芬、中日、中欧学术研讨会并作特邀发言。学术会议做大会/特邀报告 16 次;组织或参与组织国际学术会议 5 次。发表学术论文 70 多篇。担任国家可持续发展实验区专家委员会委员(科技部聘)、生物质能源产业技术创新战略联盟副秘书长、固体废物产业技术创新战略联盟秘书长;中国农业生态环境保护协会理事、天津市环境科学学会副理事长、天津市可再生能源学会副理事长、天津市能源研究会副理事长;《工程热物理学报》、《太阳能学报》、《天津大学学报》和《Transactions of Tianjin University》等编委;参编专著 3 部。

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自固定化酵母细胞发酵技术生产 第二代燃料乙醇

白凤武

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恒化条件下的连续细胞培养和发酵技术不仅可以节省辅助操作时间,而且系统运行平稳均衡,是生物炼制生产燃料和生物基产品的发展方向。然而,对于通常的各类游离细胞,受生长和流失自平衡条件制约,生物反应器中难以获得高细胞密度。利用载体材料以包埋、吸附和交联等方式实现细胞固定化预期可以解决这一问题。自上世纪七十年代以来,国内外开展了大量的研究工作,但遗憾的是,几乎未见工业化成功应用的实例,特别是以燃料乙醇为代表的生物燃料生产,其原因剖析如下:1) 载体材料固定化细胞,特别是广泛研究开发的凝胶类材料包埋固定化技术,严重制约细胞生长,因此在理论上不适宜于与细胞生长密切偶联的乙醇等初级代谢产物生产;2) 载体固定化细胞大规模制备的附加成本,及使用过程中控制杂菌污染风险的增加,使其在经济上无法与游离细胞连续培养和发酵技术竞争;3) 工业生产过程一般均联产副产品,载体材料对副产品(如乙醇发酵过程副产的酵母)品质的污染,使载体固定化细胞无法满足工业化生产的要求。

某些细胞在培养和发酵过程中具有自絮凝的特点,但这种自絮凝过程一般不稳定。如果能够改造生产菌株,对细胞自絮凝过程进行调控,获得适宜的尺度分布,就可以使其在生物反应器中实现固定化。这种自固定化细胞不消耗任何载体材料,因此能够克服载体固定化细胞普遍存在的技术和经济缺陷。基于此,我们以酵母细胞乙醇发酵为模式体系:1) 以乙醇生产性能优良但不具有自絮凝特征的酿酒酵母(*Saccharomyces cerevisiae*)工业菌株和具有自絮凝特性但乙醇发酵性能较差的粟酒裂殖酵母(*Schizosaccharomyces pombe*)为亲株,采用原生质体融合技术成功选育了乙醇发酵性能优良且具有自絮凝特征的工程菌株;2) 研究开发了适宜于自絮凝颗粒酵母固定化连续发酵生产乙醇的悬浮床生物反应器;3) 基于自絮凝颗粒酵母生长和乙醇发酵表观动力学优化了发酵过程,开发了多级反应器

串联系统并建立了万吨级规模中试装置,对技术经济指标进行验证,取得的技术成果在国家燃料乙醇试点工程建设中得到实际应用。

最新研究进展表明,细胞从游离状态微米尺度自絮凝形成毫米尺度颗粒这一明显的形态改变,可以显著提高其对环境胁迫的耐受性,其理论依据在于细胞间接触导致群体效应和协同作用增强。因此,对自絮凝酵母菌株进行代谢工程改造,赋予其五碳糖代谢途径,可以获得对秸秆类生物质预处理过程产生毒性副产物耐受性好的工程菌株,提高第二代燃料乙醇生产的技术经济指标。这一研究工作对农业生产过程秸秆类生物质的开发利用,促进经济和社会可持续发展,具有重要意义。



白凤武教授在大连理工大学获得学士和硕士学位,在加拿大滑铁卢大学获得博士学位,专业均为化学工程。自1999年起,在大连理工大学生命科学与生物技术学院担任教授。其研究方向是生物化工,重点是生物燃料、生物能源和生物基化学品的高效生产。已发表学术论文120多篇,应邀撰写学术专著章节4个,出版学术专著3部,授权专利3项。

白凤武教授担任国际纯粹与应用化学会(IUPAC)生物技术专业委员会委员,亚洲生物技术联盟(AFOB)执行委员,Elsevier出版的生物技术期刊《Biotechnology Advances》副主编,及重要生物技术学术期刊包括《Biotechnology for Biofuels》,《Biotechnology and Bioengineering》,《Journal of Biotechnology》及《生物工程学报》的编委。作为主要组织者之一,成功在大连组织了IUPAC发起的第13届国际生物技术大会(IBS2008)。应邀在欧美和日韩等国家召开的重要生物技术国际会议上作包括大会报告在内的各类学术报告,获得UNESCO-ASM MIRCEN奖和教育部科技进步二等奖,并在包括麻省理工学院(MIT)在内的世界一流大学担任访问教授。

基于“系列培养新模式”的集“高附加值微藻产品、微藻能源与生物固碳一体化”的产业化技术研究

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随着传统化石能源的日益减少及实现低碳经济的迫切需要,微藻能源与微藻固碳已成为国内外的热点研究方向。微藻能源与微藻固碳集农业和工业于一体,其开发过程涉及多个学科,是一个典型的生物产品工程。高成本和各种资源的匹配问题(如 CO_2 气源、水、土地等)是制约微藻能源与微藻固碳产业化的瓶颈,亟待突破。由于目前能源产品价格不高,因此在近期,若要实现微藻能源与微藻固碳技术的产业化,则该技术必须可同时生产高附加值的微藻产品,即在微藻能源与微藻固碳这一战略性新兴产业的发展过程中,必须涉及已有微藻产业的技术升级与应用范围的拓展。

微藻种类繁多,但目前可户外大规模光自养培养的藻种很少,其中既可积累大量油脂又已实现户外大规模培养的仅有小球藻。

笔者所在实验室通过长期研究,利用在国内外首创的微藻培养领域的一项崭新的平台技术—异养—稀释—光诱导串联培养,实现了小球藻的高密度高品质培养,不仅可实现封闭式培养而且可大幅度降低成本,有望取代现有的小球藻大规模光自养培养。此外,通过培养基和培养工艺的优化,小球藻也可高产叶黄素和油脂,用来生产高附加值产品及生物柴油,以降低微藻能源的成本。此外,利用该技术还可实现高附加值微藻产品—雨生红球藻的高密度高品质培养。

为了解决能源微藻大规模光自养培养所需大量藻种的及时制备问题,笔者所在实验室成功地开发了利用异养培养的小球藻细胞作为能源微藻光自养培养的藻种这一新技术,并对该技术进行了初步的放大。此外,还初步建立了基于计算流体力学(CFD)的光生物反应器的优化方法,获得了可用于光生物反应器优化与

放大的敏感性参数。

利用小球藻异养培养过程排放的发酵尾气和锅炉废气,作为以高油脂产率为目标的小球藻光自养培养的 CO_2 气源,实现生物固碳的同时又可降低能源微藻培养的碳源成本;这样不仅可实现整个工厂 CO_2 的低排放甚至零排放,还可解决微藻能源产业化时受 CO_2 气源配置制约这一问题。

基于上述培养新技术的集“高附加值微藻产品、微藻能源与生物固碳一体化”的开发策略,有望加快微藻能源与微藻固碳的产业化进程。目前正在嘉兴泽元生物制品有限责任公司对此进行中试研究,以期在国内外率先实现“异养-稀释-光诱导串联培养技术”的产业化并生产高品质的小球藻和雨生红球藻系列产品、微藻能源的产业化、微藻固碳的产业化,同时实现工厂 CO_2 的低排放甚至零排放。本文将对已有的中试研究结果进行系统的介绍并对其产业化进程进行展望。



李元 1966 年出生于安徽省,教授,博士生导师。1994 年 3 月于清华大学化工系生物化工与食品化工研究所获得博士学位。2011 年启动的 973 计划能源领域“微藻能源规模化制备的科学基础”项目首席科学家。现为生物反应器工程国家重点实验室海洋生化工程研究室主任。

主要研究方向有:以生化工程技术为基础,将其广泛应用于生物技术的相关领域,针对所涉及领域的特点,以“生物产品工程”为主线,对其中存在的生化工程及相关的生物学问题进行基础研究、应用基础研究、产品开发及其产业化,积极探索生物高科技产业化的有效机制。具体包括:微藻生物技术领域:微藻能源与 CO_2 固定产业化技术开发、微藻培养及光生物反应器开发与产业化、微藻产品开发与产业化、微藻分子生物学。生物农药领域:微生物农药、农用抗生素的创制与产业化;海洋生物技术领域:海洋微生物发酵及活性物质分离提取;发酵工程领域:微生物发酵工艺优化与放大。

主要成果有“封闭式光生物反应器及微藻高密度培养与养殖过程在线检测技术”被认定为国家“九五”科技攻关成果,研制出我国第一台全自动封闭式光生物反应器;在国内外首创微藻培养领域的一项崭新的平台技术:异养-稀释-光诱导串联培养,目前已完成小球藻及雨生红球藻培养的中试,即将实现产业化以取

代现有的小球藻与雨生红球藻大规模光自养培养技术;国内外首次利用类芽孢杆菌属菌株为生防菌成功创制出防治土传病害的新型、高效微生物农药—0.1 亿 CFU/克多粘类芽孢杆菌细粒剂(商品名:康地蕾得)、多粘类芽孢杆菌原药及 10 亿 CFU/克多粘类芽孢杆菌可湿性粉剂等系列产品;康地蕾得是国内外唯一的一个以类芽孢杆菌属菌株为生防菌的微生物农药,于 2004 年 9 月实现产业化,2009 年获得正式登记,已在国内外进行推广;多粘类芽孢杆菌原药及可湿性粉剂已于 2011 年获得农药登记证,已实现产业化;成功创制并获得农药田间实验批准证书且已完成中试的国内外首个以海洋微生物为生防菌的微生物农药 10 亿 CFU/克海洋芽孢杆菌可湿性粉剂,即将实现产业化;申请国内外发明专利 28 项,发表学术论文 80 余篇。

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利用生物质生产生物能源和原料

H. J. Leimkuehler

德国 拜耳技术服务公司

拜耳是在保健、营养和高科技材料领域拥有核心竞争力的全球性企业。作为一家以创新为核心的公司,拜耳确定着研究密集型领域的趋势。拜耳公司的产品和服务旨在造福人类,提高生活质量。同时,通过创新、不断增长和提高盈利能力创造价值。拜耳致力于可持续发展的原则,秉持做社会和道德上负责任的企业公民。在 2011 财年,本集团雇用约 112,000 名员工,获得 365 亿欧元的销售额。资本性支出为 17 亿欧元,研发费用为 29 亿欧元。

拜耳在大中华区有:拜耳医药保健、拜耳作物科学、和拜耳材料科技三家子公司,以及拜耳技术服务公司,并设有几个不同的生产设施。本地生产产品在大中华区的销售比例越来越大。随着重大投资正在进行,拜耳被定位为中国发展的一个关键合作伙伴。

我们深信,只有平衡经济增长与生态保护和社会责任,拜耳才能取得长期的商业成功。作为社会的一员,我们认为只有得到社会长期的接受,拜耳才能不断开拓进取。在这种长期价值观的指导下,我们实施可持续发展的战略。我们秉持可持续发展,这可以由以下几方面体现:我们的使命宣言“拜耳:科技使生活更美好”;我们坚守联合国全球契约的 10 项原则;我们参与 2011 年新推出的联合国全球契约的“企业可持续发展先行者——领导”的倡议以及化工行业的责任关怀的倡议。

拜耳还希望承担起其在气候变化问题上的义务。我们认真对待气候变化所带来的环境和经济的挑战,它会影响我们商业活动的基础。一方面,拜耳在环保领域的努力必须得到加强。另一方面,我们要更加重视创新型的解决方案,以应对气候变化的后果。拜耳计划在这两方面都作出具体的贡献。

我们打算进一步加大力度,并制订了以下的气候目标:

1. 加强在提高能源效率和减少排放方面的努力:我们正在不断地提供市场

化的解决方案以提高运营效率,从而减少我们及客户的碳排放量。我们减少温室气体排放的措施涵盖在所有的操作环节中。比如在生产基地,我们已经取得了很大进展:1990年至2005年间,我们减少了三分之一以上的温室气体排放,主要是通过技术改进、新的化学工艺、和一些方法诸如拜耳气候检查、创新的能源管理系统 STRUCTese 的应用,从而提高了能源效率。作为生产活动的补充,采取了配套的销售措施(例如,改善车队)和管理(例如,视频会议替代商务旅行、拜耳绿色办公和绿色数据中心等举措)。2005—2020年,我们制定了一个新的雄心勃勃的目标:我们要进一步减少温室气体排放量,实现每吨出售的产品碳排放量减少35%。

2. 开发市场解决方案:我们的产品以各种不同的方式发挥了它们在节约能源和保护资源方面的作用。比如,我们的聚氨酯保温材料和我们用在机动车中的超轻聚碳酸酯产品。依据拜耳的环保型商用建筑方案,拜耳集成了在建筑施工方面的所有成员,并促进了减排建筑材料的使用。作为一个创新型公司,我们已经启动了各种研发项目,以得到新的解决方案。在我们的项目组合中,包括了减缓气候变化的解决方案,例如,我们开发了一种技术使氯气生产的能源利用效率提高了30%~50%);以及适应气候变化的解决方案,例如,开发应激耐受植物,它们可以更好地适应不断变化的气候条件。

3. 扩大伙伴关系:气候变化是一个巨大的挑战,没有人可以单独解决。我们相信,高影响力的伙伴关系会(给社会)带来更有益的影响。故此,我们已经加入了一些机构,如联合国环境计划署(环境署)以提升环保意识;菲律宾国际水稻研究所(IRRI),以开发从环境上来说可持续生产的水稻;和创新病媒控制联盟(Innovative Vector Control Consortium),以提高病媒控制的力量。我们同时也与领先的学术机构和私营公司建立了研发伙伴关系,研究进一步减缓气候变化和适应气候的解决方案。

中国政府已经清楚地表达了在第12个五年计划期间,将专注于有质量的增长,并明确设定了在农业、医疗保健和能源效率方面的目标。拜耳的定位是通过我们的产品组合和创新能力帮助中国解决其面临的核心挑战。故此,拜耳推出了拜耳中国的十点计划,承诺利用本公司的产品组合和创新技术配合中国可持续发展的迫切需求。中国的十二五计划对可持续发展和低碳发展投入了前所未有的关注,并计划在2015年实现单位GDP的能耗较2010年减少16%,二氧化碳排放量减少17%。为了帮助中国实现这些雄心勃勃的目标,拜耳材料公司不仅提供了轻量型机动车用材料,同时也为可持续型建筑和基础设施提供了解决方案。

从生产之初一原料便体现了我们对气候的保护。三分之二的碳足迹可以追

溯到原材料,因此,我们正在仔细评估利用可再生材料替代化石原料的可能性。我们有些重要原料已经或即将完成生物技术化生产,比如乙烯乙二醇、丙二醇、丁二醇和琥珀酸。而对于其他的原料,如苯、甲苯或丙酮,我们正在努力攻关,目前还有很长的路要走。

拜耳技术服务公司对于利用生物质生产燃料和原材料做了非常重要的工作,尤其是后者,对我们这样一个大的化学和制药公司,很重要。其中的一些工作接下来将做更详细的介绍。

为了选择自己的可再生燃料和化学品的生产方向,我们需要了解整个生物质使用领域的概况,并将研究资源集中在最相关和最有前途的路线上。选择在哪些路线上加以专注的原则包括(1)可持续发展:聚焦于不可食用生物质为原料的第二代技术(如废弃油脂、生物质废弃物);(2)效率:聚焦于具有高时空产量的过程(即热化学过程);(3)效力:聚焦于本行业相关目标产品(如芳烃)的合成。

以下我们将展示在生物质能的使用领域中我们的发展和评估工作:利用油料作物和废弃油脂生产生物柴油(BayFAME);利用废弃生物质生产燃料(生物质到液体,BTL);利用废弃生物质生产化工原料(快速催化裂解)。

生物柴油已被视为生物型经济的第一步,尤其是针对全球性可再生燃料的需求。在过去十年中,投资的热潮引发了很多中小产量($< 500 \text{ kta}$)生物柴油工厂的建立。在当时,欧盟针对生物燃料产品减税的政策促进甚至可能激发了这种发展,而相关的法律法规也不断地推动、提高了燃料中生物基成分的比例要求,到2020年将高达20%。然而,人们很快发现,原料来源和价格限制了生物燃料的进一步发展。例如在欧洲,2010年已经有54%的菜籽油用来作为生物柴油的原料。现在已没有更多的面积用于扩大油菜种子的生产,原料油短缺导致其价格的强劲增长。这一动向对生物柴油产业很关键,因为生物柴油的生产成本以原料成本为主,原料占据了80%的产品成本,而其他因素,如投资成本、公用事业和劳动力只占很少的部分。此外,原料价格和可获得性在当今的环境中是动态的。以可直接转化为生物柴油(FAME)的大豆油和菜籽油为例,在2008年的价格分别达到了1500元/吨和1400元/吨的历史最高值。便宜的原料也是可以获得的,但它们的游离脂肪酸(FFA)含量往往很高,不能在传统的生物柴油厂进行加工处理。以往,这些游离脂肪酸被视为废物或低附加值产品,但现在已经有一些游离脂肪酸酯化技术商业化,但是脱酸和废水处理方面仍存在很大问题。

为了克服这些限制,拜耳技术服务公司利用甲醇开发了将生物柴油原料中游离脂肪酸转化为脂肪酸甲酯(FAME)的技术,通常利用酸作为催化剂进行反应,如硫酸。然而,硫酸等强酸性的均相催化剂在建筑材料和安全方面的要求比传统

的生物柴油厂更高。拜耳的连续游离脂肪酸酯化工艺技术解决了这些限制,通过应用陶氏化学的 AMBERLYSTTMBD20 异相催化剂实现了工艺的优化。由于游离脂肪酸酯化的反应转化平衡受限于相对含量较低的游离脂肪酸,为了增加动力,我们加入了过量的甲醇以实现游离脂肪酸的全部清除要求。这个过程集成了多级反应器及级间去除副产品水的操作,它导致了热力学平衡的进一步改变,促使原料中的游离脂肪酸更多地向着酯化方向进行。同时多级的设计概念提供了一个灵活的工艺,确保任何游离脂肪酸含量(即使高达 100 wt%)的原料都可以达到最佳的产量和最低的制造成本。而对于游离脂肪酸浓度较低的原料,一级反应足以降低 FFA 浓度至 0.1 wt%;而一个三阶段的过程,将涵盖完整的 FFA 浓度范围(达 100 wt%)。

以优先使用粗放和简单的工艺设备为出发点,我们最大限度地减少生产过程的投资成本和运营复杂性。各级反应的核心部分是一个使用了 AMBERLYSTTMBD20 异相催化剂固定床连续流动反应器。每个反应阶段的水,连同过剩的甲醇,都通过蒸发去除。得到的甲醇水蒸气则经蒸馏干燥回收,用于下一次的 FFA 酯化使用。当使用多级反应时,最后一个阶段的甲醇将不用被去除,而直接进入下游的转酯化单元。这将降低转酯化对甲醇的要求,也减少了对甲醇干燥的热要求。在多级操作过程中,通过热蒸发器阶段和甲醇干燥柱之间的整合,能源需求将进一步优化。

酯化过程中的资本投资成本取决于用户需求如原料、生产能力、生物柴油过程和灵活性。一个典型的含有甲醇处理单元的二级装置安装成本,当产量是 3000 万加仑/年(13,600 万升/年)时,为 4~5 百万美元;当产量为 500 万加仑/年(2300 万升/年)时,是 1.8~2.2 百万美元。但是这也受当地条件的影响而有所不同,如现有的基础设施和建筑物、地方标准和规范、劳动力市场等因素等。典型的经营成本组成部分包括折旧、催化剂、操作设施(蒸汽,电力和冷却水)、维修和劳力,但额外的酯化单元应该可以很容易地通过已经在现场的工作人员来操作运行。总的来说,针对 FFA 丰富的原料通过拜耳技术服务公司的酯化技术 BayFAME 来进行生产,相比传统原料如油菜籽或大豆油,节省是非常显著的。通常情况下,两个方法的价格差异大概在 2 美分/磅(4.4 美分/kg),就可以抵消折旧和运行成本。

虽然游离脂肪酸丰富的油类、油脂和牛油的使用都有助于未来的燃料供应,但远远不能覆盖整个需求。预测到 2050 年,有机废物可以满足 3 EJ,而能源需求总量将超过 1200 EJ。这清楚地表明我们必须找到其他的原料来源。

在未来的第二代技术中,木质纤维素生物质将会得到应用。在科技文献中,

经常讨论到所谓的“生物质液化”过程(BTL)。BTL 技术经连续的步骤将生物质转化为合成气,再通过 Fischer - Tropsch 合成法 (FTS) 转化为液态烃。BTL 过程的优势是,对原料较低的敏感性和产生高品质的产品以满足市场需求。BTL 燃料不仅与目前使用的燃料,如柴油和汽油完全兼容,也减少了汽车尾气排放,因为它清洁,不含芳烃、硫和氮化合物。从技术角度来看,BTL 过程集成了成熟的技术模块。其生产合成燃料的中心环节是 FTS。FTS 已长期使用于煤(CTL)转化和天然气(GTL)转化。中国在 CTL 技术的发展中处于领先地位,具有优良的基础来部署 BTL 技术。拜耳技术服务公司未参与到我们自己的 FTS 或者 GTL 技术的发展中;然而,本公司将在技术评估和集成领域发挥作用。本分析就是从这一立场出发来完成的。

BTL 技术的主要缺点是它的复杂性。为了适用于现代高容量气化炉,如气流床气化炉,生物质需要是干燥的、颗粒状的和热裂解的。大型的高温分解技术发展较为逊色。在接下来的步骤中,对气化炉得到的合成气进行纯化,并调整其组成使之符合 FTS 的需求。BTL 工厂也将充分配备制氧机、能源供应和污水处理设施等设备。

乍看之下,合成气处理是一组操作简单的单元,但可以用来说明 BTL 过程的复杂性。FT 催化剂很容易中毒,即使是非常低浓度的硫(H_2S , COS , CS_2)也可造成不可逆的失活。此外,必须从合成气中去除焦油、灰尘、碱金属和其他气体杂质(NH_3 , HCN , HCl , HBr , HF)。各种气体净化技术,如洗涤器和吸附净化技术都可以应用。然而从操作的角度来看,要获得高品质的净化气体,尤其是考虑生物质属性的多变性时,是不容易的。因此 BTL 过程中,气体净化是一个非常关键且难以预测的一步。由于类似的问题也发生在 CTL 技术中,整合它们的运作经验将是有帮助的。合成气也是需要调整的,即其组成需要根据 FTS 的化学计量学要求进行调整。对生物质产生的合成气气化要求是 H_2/CO 之比为 1。但是根据化学计量学计算,FT 反应的合成气中需要 H_2/CO 之比为 2。一个简单的解决方案是提供集成的水煤气变换(WGS)反应堆。这种反应轻微放热,可以在简单的绝热固定床反应器中进行。然而,WGS 反应将部分的 CO 转换成 CO_2 ,由此,转而降低了碳的产量和 BTL 过程减少二氧化碳排放量的潜力。此外,二氧化碳需要从合成气中去除,以尽量减少 FTS 的投资成本。

BTL 的复杂性对投资成本造成巨大影响。一个 100 kt/年的工厂其资本开支总额估计为 3 亿欧元。且不论这个数字仅仅给出了投资成本的数量级,它还显示了投资的高壁垒所在。这些高支出相当均匀地分布在各个主要工艺单元上。FTS 过程投资成本高,主要是由于高压设备和昂贵的催化剂的需求。裂解装置还包括

干燥和研磨成本。从 BTL 过程制造的燃料其总成本还取决于折旧成本之高,同时也受高额的生物质成本和操作成本的影响。尽管一般认为废弃的生物质没有成本,但分析表明这种说法是不正确的。至少必须考虑到生物质的能量活性价格。对于大型生物质转化工厂物流成本也不能忽略。最后通过经济评估得出的总体结论是: BTL 路线的产品在当下,与由原油技术得到的燃料相比缺乏竞争力。

为了减少我们需要的生物基燃料或化学品的成本,我们需要不太复杂且低成本的技术。由于多年发展的快速热解生产生物油具有较高的选择性,所以一直被视为很有前途的替代品。该技术允许一步法在低压状态和较低温度下($<600^{\circ}\text{C}$)进行热化学生物转化。与 FT 路线相比,它的投资成本更低,加工效率更高(体现在产品的净能源值与生物质原料的能源值的百分比)。这项技术的主要缺点是生物油的热值低(由于氧含量高)和它的酸度。因此,生物油要进行脱氢后才可以作为燃料使用。

这项技术的进一步发展是催化型快速热解。反应由两个连续的步骤组成:生物质颗粒快速热解为挥发性产品和炭,之后产生低聚化反应和裂解产物芳香化。选择性生成芳香烃和烯烃的反应与非选择性生物质氧化为碳氧化合物和水的反应相关联。此外,催化剂表面形成焦炭。尽管这种技术仍然处于发展初期,它应该是可行的,因为它结合了现有的两种技术:热解和重整。

我们将用流程图说明快速催化裂解技术比 BTL 路线更为简单。生物质在一个充满了沸石催化剂流化床反应器发生转换,生成芳烃、烯烃、甲烷和 CO。碳价值产品收益率可能超过 50%。在 BTS 实验室进行的实验研究证实了这种技术的潜力。然而,所有热化学生物质能转换技术的两个典型的缺点也应该提及。首先,复杂的生物质预处理:原料既需要干燥至水含量 10% ~ 20% 的水平,也需要研磨获得毫米大小的微粒。而这种颗粒大小对于避免热量和质量传输限制是很重要的。第二个缺点与结果相关: BMX 进程(几乎)总是产生一系列的产物,类似炼油厂。这一点与化工产业只需要一个产品的情况是矛盾的。因此, BMX 过程应该应用于生物炼油厂或集成性化工产业。

碳产量是所有生物质转化过程中的关键问题之一。 BTL 路线可以用来说明这个问题。生物质能转换路线的碳产量低主要是因为氧含量达到了 50% (以重量计),产量低的另一个原因是石油衍生原料的有效氢碳比为 1 ~ 2,而木质纤维素生物质的有效氢碳比为 0 ~ 0.3。因此,生物质能转换的碳产量大约在 20% 左右,比原油低 5 倍。同时也明显低于 GTL 路线。此外,生物质转化技术的复杂性更高,因为 GTL 的过程中不需要处理能量密集的固体。反过来,投资成本也比

GTL 工艺要高。产量低不仅造成成本问题,还有可行性问题。当假设产量为 20%,则 100 kta 的工厂需求植物原料将是 500 kta。这一点将导致大量耕地和物流需求。

生物质的固有弊端是能量密度低、产量低,这些都已经讨论过。为了克服这些缺点,新颖的工厂设计方案是必要的。最简单的解决方案意味着建立小型的、非地域化的工厂,同时整合了大型的、含农业基础设施的农场。这种方法的例子是转化伴生天然气的技术。在这种方法中,我们有望通过建立一系列的生产厂来实现成本的降低。FZK(Forschungszentrum Karlsruhe)已经提出了一个更复杂的方法。它是一个多阶段方法,结合了小单元的优势与规模经济的特点。根据 FZK 的概念,裂解操作单位应分布和建设在原料来源的附近。在裂解步骤中,生物质转化成生物油料和炭的步骤导致能源密集化。炭和生物油料可以运到大型工厂,在那里它们通过连续气化和 FTS 步骤实现接下来的转化。液态烃和蜡则可以运输到世界范围的炼油厂进行进一步的产品升级。

展望中国,我们了解到的具体情况是:50% 的人口生活在农村地区,而改善农民的生活条件是一个重要的目标。石油产品满足了接近一半的国内需求。因此,石油替代物将有助于减少对石油的依赖。12% 的土地是可开垦的,而只有 1.5% 是永久性农田。这意味着有一个潜在的机会来增加生物质的生产,即培育新的要求较低的油料植物。

考虑到这些要求,我们制定了一套对中国的生物质废弃物利用技术领域的建议:

- 增加研发经费,发展生物质废弃物转化为燃料和化工原料的技术
- 发展在非耕地上生物质原料的种植
- 建设生物质废弃物物流基础设施
- 在生物质来源地附近建立生物质能源的配套示范设施,显示该技术的可行性
- 对涉及的相关行业给予激励,促进工业界/学术界的合作关系并充分利用国外技术
- 鼓励以生物质为原料的技术生产绿色产品



Hans-Joachim Leimkuehler 博士是上海拜耳技术工程服务公司的技术开发部主管,负责化学和制药工艺的研发和优化。Leimkuehler 博士的部分工作领域包括微反应技术、环保技术和技术咨询。该部门为拜耳和其他化学和制药公司提供高效的可持续发展工艺。

Leimkuehler 博士于 1989 年加入拜耳。从担任工程部项目经理开始,参与了欧洲的多个资本项目。1995 年以来担任聚合物生产项目的组长。1997 年,接手了工艺技术部,研究过程建模和工艺整合。从 2003 年到 2011 年,Leimkuehler 博士领导着工艺设计部。2011 年,他的工作转移至中国并担任目前所在的职位。Leimkuehler 拥有德国卡尔斯鲁厄大学的化学工程博士学位。

中国生物质能源和资源发展路线

易维明

山东理工大学

一、开展生物质能源研究与开发迫在眉睫

生物质是唯一的物质性可再生能源和碳源。生物质能源开发可以提高农民收入、改善农村面貌、促进农业生产、并带来综合效益。

生物质能源利用可以达到 E3 效应—清洁能源 (Clean Energy)、经济效益 (Economy)、生态效益 (Ecology)。

二、生物质能源开发要多种形式并举

我国生物能源的发展体现了日新月异、百花齐放的局面。各种技术各具特色,成熟度亦不同。传统生物质能源技术例如发电技术、沼气技术形成了中国特色,进步明显;新型生物质能源技术,例如燃料乙醇、生物柴油、二甲醚、裂解液化、水相重整及水热提质、微藻等与国际水平接近,处于上升阶段。

这些技术和工艺都应该具有各自的发展空间,通过互相竞争和促进,最终形成具有自主知识产权的核心技术,打造我国的生物质能源产业链。

三、应该发展一种粮食—能源共生产的“新型粮能模式农业体系”

生物质能源发展在中国最大的瓶颈之一就是资源总量和收集成本。按照传统农业发展规律,生物质资源能够提供作为能源的量占到我国总能耗的 10% 左右。随着社会经济的发展和化石能源的消耗,必将导致生物质资源量有所提高,在能源体系中发挥更大的作用。

传统农业生产的终极目的就是提供粮油产品,一切工作都是围绕如何提高产量,保持地力进行。在把粮食收获后,残余物(秸秆等)部分用于饲料、能源等,很大部分就地还田,使得土地的恢复能力较好,能够在很长时间内保持强大的生产力。

而对于越来越多的农业生产残余物用于生物质能源,或者说,对于生物质能源和资源的需求日益提高,对农业提出了两种发展模式:

一是依然保持传统种植、收获、土地保护模式不变,仅仅以粮食生产为核心,被动应付对于生物质资源的需求,能有多少就做多少。

二是通过改变农业模式,把农业生产目标转化为以粮食-能源生产有效协调,在保证粮食安全的同时,主动针对生物质资源需求,提供更多的生物质原料。

这两者中,后者显然优于前者。但是如果按照这样的生产模式,那么需要对传统的农业进行彻底的改造,形成一种新的农业生产系统模式——“粮能模式”。这需要在下面诸多方面进行必要的研究和改革:

(1) 土地的负担和土壤保护

传统农业以获得粮食为目的,从土地上取走的主要是粮食以及很少的皮壳附属物,大量的秸秆残余物都直接或者间接在短期内返回土壤中,保持了土壤结构和有机质含量。

如果把粮食收获后的残余物用作生物质能源(资源),那么就会有很大一部分不能很快返回土壤,特别是大规模应用生物质能源的项目,产生的灰分往往失去了肥力,不再适于返回土壤,这样势必导致土壤结构改变,地力下降,最终影响生产能力。

因此,如果要农业既提供足够的粮食,又提供大量生物质能源及材料,就需要系统地研究土壤的负担、土壤的恢复、及土壤的保护。只有保证生产活动在一个安全的限度内进行,才能使农业可持续发展。

(2) 新品种培育

要使农业实现提供粮食+能源的功能,就要研究培育新的作物品种,使该品种既可高产粮食,又可大量产出生物质能源和材料。特别对于玉米、小麦这样的大宗农产品,更加需要开展相关研究。目前,小麦和玉米的粮食秸秆比约是1:1.3;如果把这个比例提高到1:2,则将比目前多生产秸秆50%以上,相当于每年多产出3.5亿吨标准煤。

这样的话,农业生产每年可提供的秸秆总量相当于10亿~11亿吨标准煤,其中的60%可用于生物质能源,相当于6亿吨标准煤。比现在的每年3亿吨翻了一番。

(3) 新型种植模式

为了实现使农业提供粮食+能源,必须探索新品种培育的方法,也必须进行必要的农艺改革,探索新型种植模式,适应新的需要。

对于种植密度、套种模式、品种搭配、田间管理等,都需要重新深入研究。

(4) 新型收获与存贮模式

新品种,必然面临新的收获方式和存贮方式。开展适于粮能共收获的联合作业机械研究,新的生物质原料集中储运模式研究等。

粮能模式造成收获时喂入量大大增加,当前的收获机械不能适应需求,有必要重新制定生产标准,开发新一代农业机械。

(5) 加工技术

粮食和生物质材料加工技术也需要进行改革,适应新需求。

开展粮食到食品的高效转化生产技术研究,提高食品质量、营养,保障食品安全。

开展生物质能源和资源利用技术的基础和应用研究,通过深入研究和良性竞争,取得不同阶段适宜的生物质能源实用技术和资源高效利用技术,取得综合利用效益。

(6) 新型产业模式建设

形成新的农业产业模式,创造未来粮能共生的新农业。

选取特定地区和特定品种,开展粮能模式农业示范,以点带面,突破技术、经济、传统的瓶颈,真正形成良性的高效农业模式,达到 E3 效果。

(7) 中外农业模式和生物质能源开发的对比研究

发展需要借鉴,但是国情不同,措施不同,效果不同。只有取长补短,才能共同促进。比如美国土地辽阔,完全可以采用直接把农业转向以生产能源为主,而中国地少人多,必须粮能协调发展。但是不论中美,都需要互相学习,共同提高。那么只有进行必要的对比研究,发现共同点和差异点,才能有的放矢地互相引进和借鉴,实现我国需要的技术和发展模式。

四、中国的生物质能源和资源发展路线



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从纤维乙醇到生物炼制

杜风光

河南天冠集团

一、国内外纤维乙醇产业发展现状

生物质能源化利用是当前各国新资源战略的重点。世界各国,尤其是美国、德国、加拿大、瑞典、日本等发达国家,都在致力于开发清洁高效的生物质能利用技术,以达到保护矿产资源,保障国家能源安全,实现 CO₂ 减排和经济可持续发展的目的。生物乙醇已经成为全球利用最为广泛的一种生物能源,随着产品规模的扩大,用粮食生产乙醇已经受到限制,第二代生物燃料的开发越来越受到各国的重视,比较典型的是美国政府提出的发展“先进生物燃料”,美国将先进生物燃料定义为“寿命周期内温室气体排放比参考基准减少 50% 以上的、玉米乙醇以外的可再生燃料”。根据可再生燃料标准 RFS(Renewable Fuel Standard)的要求:可再生燃料生产从 2008 年的 90 亿加仑/年(2725.2 万吨/年)增加到 2022 年的 360 亿加仑/年(1.09 亿吨/年),其中,先进生物燃料的产量到 2012 年要达到 20 亿加仑(605.6 万吨),2017 年达到 90 亿加仑(2725.2 万吨),2022 年为 210 亿加仑(6358.8 万吨)。纤维乙醇被认为是最有望在近期获得研究突破的第二代生物燃料或先进生物燃料。

目前世界上在运行和在建的纤维乙醇示范装置主要分布在北美和中国,具体情况见表 1 和表 2。

二、从纤维乙醇到生物炼制

天冠集团是国内最早从事生物燃料生产和开发的企业之一,目前拥有 60 万吨/年的燃料乙醇生产能力。为了解决粮食原料对产业发展的限制,天冠集团在纤维乙醇研究和工业示范方面取得了显著的成效,并且结合多年的实践,提出围绕纤维乙醇生产发展生物炼制的构想。

表 1 世界上运行中的纤维乙醇示范项目

序号	公司名称	建设地点	规模	状态	原料	备注
1	能源公司 DONG Energy 的子公司 Imbicon	丹麦, 凯隆堡	4200 吨/年 (140 万加仑/年)	运行中, 已于 2010 年 7 月投入运营	小麦秸秆	该公司正致力于秸秆乙醇联合木质素发电模式的研究
2	Iogen 公司	加拿大, 安大略省 (Ontario), 渥太华 (Ottawa)	800 吨/年 (26 万加仑/年)	运行中	小麦秸秆	2004 年完成技术验证
3	阿文戈亚 (Abengoa) 公司	美国纽约	3.5 万吨/年 (1160 万加仑/年)	运行中, 已于 2007 年 9 月投入运营	玉米秸秆、小麦秸秆、高粱秆、柳枝稷和其他生物质	年实际产量情况不详
4	杜邦丹尼斯克纤维乙醇公司	田纳西州 佛诺尔 (Vonore)	760 吨/年 (25 万加仑/年)	运行中, 于 2010 年 2 月中旬投产试运行	柳枝稷、玉米秸秆	预计 2012 年投入商业化运营
5	Verenium 公司	路易斯安那州 Jennings	4000 吨/年 (140 万加仑/年)	运行中	甘蔗渣和高纤维含量的茎秆植物	目的在于开展商业规模纤维素乙醇设施成本模型的验证, 拥有五碳糖和六碳糖共发酵技术
6	河南天冠	中国南阳	1 万吨/年	运行中	玉米秸秆和小麦秸秆	稳定运行
7	山东龙力	山东禹城市	1 万吨/年	运行中	木糖渣	利用玉米芯生产木糖的剩余物, 主要是纤维素和木质素

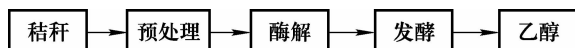
表 2 建设中的纤维乙醇示范项目

序号	公司名称	建设地点	规模	状态	原料	备注
1	丹麦诺维信与意大利 M&G 集团（摩西和基索菲）	意大利 Crescentino	4 万吨/年	建设中,2011 年 4 月开工,预计 2012 完工	利用当地农业废弃物、麦草秸秆、及能源植物为原料	M&G 集团技术来源于康泰斯,康泰斯于 2004 年加入该集团
2	BFE (BlueFire Ethanol Fuels, Inc.) 公司	美国密西西比州的富尔顿 Fulton	5.5 万吨/年 (1800 万加仑/年)	建设中,2010 年底开始建设,完工日期不详	利用农作物废弃资源	2010 年 7 月获得美国能源部 8800 万美元援助,该公司并提出 2.5 亿美元贷款的政府担保请求
3	BFE (BlueFire Ethanol Fuels, Inc.) 公司	加州 兰开斯特	940 吨/年 (310 万加仑/年)	建设中	废木料和其他城市生活纤维素废物	从废物收集分离的网点收集原料,预处理采用浓酸水解工艺
4	阿文戈亚 (Abengoa) 公司	美国堪萨斯州 Hugoton	4.8 万吨/年 (1600 万加仑/年)	2011 年开始建设,建设周期 18 个月	利用玉米芯和玉米秸秆为原料	运行模式是 1600 万加仑/年 + 125MW 的热电联产,总投资 6.85 亿美元,美国能源部资助 7 千万美元

续表

序号	公司名称	建设地点	规模	状态	原料	备注
5	California Ethanol + Power, LLC 加州乙醇+电力公司	加州 帝王谷	20 万吨/年 (6600 万加仑/年)	2011 年 2 季度开始建设,2013 年 2 季度建设完成并运行	利用当地甘蔗及甘蔗渣	联产 49.9WM 电力, 2.8 万吨肥料,由 Fagen 公司设计和建设
6	Frontier 再生资源有限公司	密歇根州 Kinross	12 万吨/年 (4000 万加仑/年)	建设中	混合硬木、纸浆材和混合硬木屑	
7	POET 公司	南达科他州 Scotland	9.5 万吨/年 (3125 万加仑/年)	建设中,有望于 2011 年投产	玉米芯和玉米秆	爱荷华州扩建的 12500 万加仑/年的产能中 25% 来自于纤维素乙醇
8	Verenium/BP 生物燃料公司	佛罗里达州 Highlands	11 万吨/年 (3600 万加仑/年)	建设中,该项目 2010 年开始建设,2012 年投入生产	甘蔗渣和高纤维含量的茎秆植物	英国石油公司 BP 出资 1.09 亿美元收购美国 Verenium 公司的纤维素生物燃料业务

纤维乙醇的生产一般包括如下几个基本流程：



在基本流程中，一般会面临以下几个问题，其一，预处理和酶解后的发酵底物中含有较多的戊糖，戊糖很难被酵母利用生成乙醇，秸秆的能源转化效率很低；其二，发酵底物中的抑制物浓度较高，不利于酵母的代谢和增殖，发酵后期的酒精度很低，一般都低于 5% (v/v)，乙醇的分离将耗费大量的蒸汽；其三，蒸馏后的糟液中含有大量的抑制物，沼气产率低，废水处理困难。

为此，天冠集团开发了新的生产工艺，避免了上述问题的出现。解决问题的基本思路是因繁就简，提高转化效率。例如：在预处理阶段，对半纤维素和纤维素、木质素进行分离，半纤维素水解后直接进入厌氧发酵罐生产沼气，纤维素酶解后生产乙醇，蒸馏后分离残渣浓缩烘干后作为生物质锅炉的燃料（主要是木质素）或作为高附加值化工产品的原料。天冠集团纤维乙醇工艺基本流程见图 1。

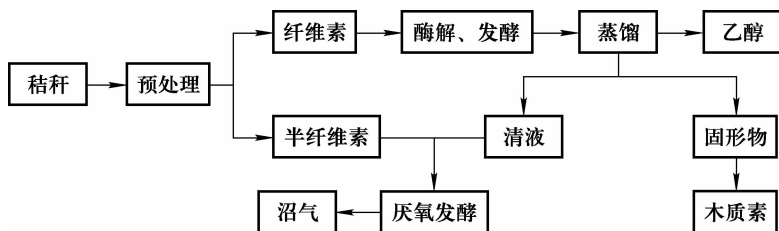


图 1 天冠集团纤维乙醇工艺基本流程图

基于以上流程，结合在生物能源生物化工领域的研究成果，我们得到从纤维乙醇到生物炼制新的构想示意图（见图 2）。

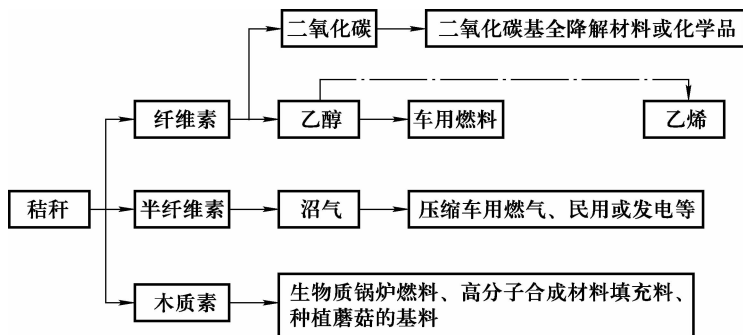


图 2 天冠集团生物炼制示意图

根据天冠集团 1 万吨/年纤维乙醇产业化示范线的运行情况，每 7 吨秸秆生产 1 吨的乙醇，同时 600 m³ 沼气和 2.5 吨木质素，三种目标产物系统能源转化效

率可达到 80%。从全生命周期分析,由于秸秆属于废弃物,所以不计算种植投入的化石能源,仅计算收集储运(3.25×10^5 千卡)、压块(1.08×10^5 千卡)和生产过程中投入的化石能源(9×10^6 千卡),则能源产出/投入比为 2.07。如果木质素在生产中自用,不需投入化石能源,从全生命周期分析,系统能量产出/投入比可达 22.2。同时还可对乙醇生产过程中伴生的二氧化碳进行回收,可利用二氧化碳合成二氧化碳基全降解材料(例如聚碳酸亚丙酯树脂)或化学品(例如碳酸二甲酯 DMC)。

(一) 乙醇

乙醇作为整个生物炼制过程中最主要的产物,其转化效率是整个炼制过程追求的最重要的目标。本工艺过程主要考虑利用纤维素水解产生的葡萄糖作为酵母利用的碳源,基本不考虑利用半纤维素水解产生的五碳糖。纤维素的含量和水解效率是影响乙醇产率的关键。通常情况下,7 吨秸秆可生产一吨的乙醇。乙醇除了作为汽油的替代燃料,还可用于生产基础化工原料乙烯,通过乙烯可构建碳二化工的平台。

(二) 二氧化碳(图 3)

理论上而言,每生产 1 吨乙醇可以副产 0.95 吨二氧化碳,天冠集团利用二氧化碳重点发展两个产业链,其一,PPC 及下游制品产业链,天冠集团与中山大学合作在二氧化碳基降解材料关键技术上获得突破,生产的二氧化碳基降解材料在阻隔、成膜等方面有特性,可完全生物降解,应用领域非常广泛。目前天冠集团已经建成 5000 吨/年的产业化示范线。其二,DMC 及下游化学品产业链。利用二氧化碳和甲醇直接反应生成 DMC(碳酸二甲酯),正在进行中试。

(三) 沼气

半纤维素水解后产生的五碳糖不容易被酵母利用,利用五碳糖及其它酒精糟分离后产生的有机质生产沼气,每吨乙醇可以副产 600 m^3 沼气,沼气可以通过提纯压缩后作为车用燃料,与压缩天然气成分很接近。

(四) 木质素

秸秆中的木质素不可用于生产乙醇和沼气,酒精糟经过固液分离后产生的固形物主要是木质素,木质素热值一般在 4000 千卡/公斤,该固形物通过浓缩烘干可作为生物质锅炉的燃料或作为高分子材料的填充物。

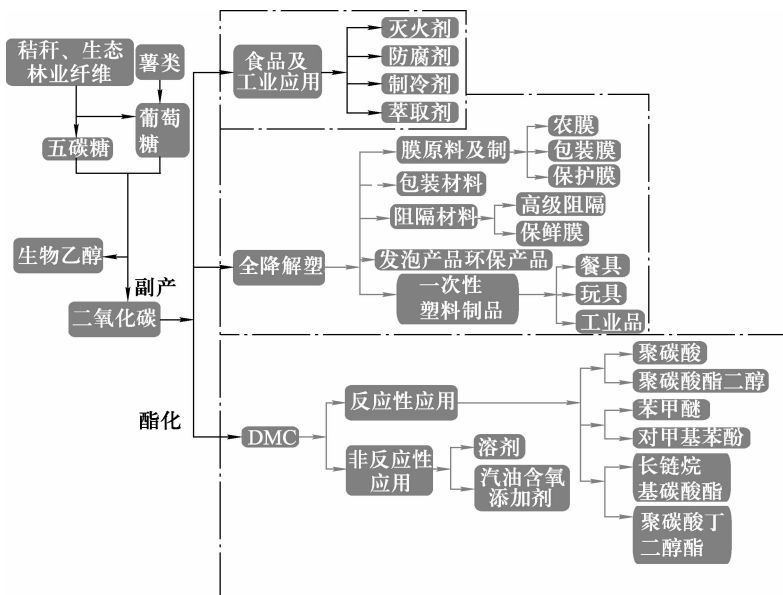


图3 二氧化碳基全降解材料和化学品产业链图

三、展望

天冠集团将依托现有产业基础,利用多项先进的生物能源与化工技术,实现关键链接技术的产业化突破,重点发展生物质废弃物→乙醇→乙烯及下游产品产业链、乙醇副产物二氧化碳→全降解材料(或化学品)及下游产品产业链、沼气生产及高值化利用产业链。从而实现能化并举,推进我国农业废弃物资源化的进程。



杜风光,1969年出生,博士,教授级高级工程师。现任河南天冠企业集团有限公司总工程师。长期从事生物化工产品生产工艺的研究、实施和技术改进,近年来主要从事生物燃料的研发工作。

擅长专业:化工机械与设备、节能技术、生化反应工程。

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Part I

Forum Review

Review

From July 7 to 9, 2012, the International Top-level Forum on Engineering Science and Technology Development Strategy—Approach for Achievement of Recycling Economy of Biomass Waste was held in Beijing. This forum was organized by the Chinese Academy of Engineering, with joint organization by the Metallurgical and Chemical Engineering Department and Beijing University of Chemical Technology.

Academician Xianghong Cao, who is the division chairman of Metallurgical and Chemical Engineering Department of Chinese Academy of Engineering, hosted this meeting and gave a welcome speech. Jingdun Jia, the director of Rural Technology Development Center of the Ministry of Science and Technology, and Qun Liu, the division chief of Energy Bureau, Development and Reform Commission of China, addressed greetings for this meeting respectively.

A number of prominent scholars and entrepreneurs were invited to attend this conference including, Jingdun Jia from the Ministry of Science and Technology; Qun Liu from the Development and Reform Commission; Prof. Moo-Young, Fellow of the Royal Society of Canada; Prof. Wagemann, the board chairman of the Dechema Chemical Engineering and Biotechnology; Academician Xianghong Cao, the council chairman of Chemical Industry and Engineering Society of China; Academician Xieqing Wang from the Research Institute of Petroleum Processing; Academician Weizu Wu from a certain Institute of the Headquarters of General Staff of Chinese PLA; Academician Hailing Tu from Beijing Nonferrous Metal Research Institute; Academician Qiye Yang from the Sinopec Beijing Design Institute; Academician Cheng'en Xu from the Sinopec Corp.; Academician Xingtian Shu from the Research Institute of Petroleum; Academician Bingzhen Chen from the Department of Chemical Engineering of Tsinghua University; Academician Tianwei Tan, president of the Beijing University of Chemical Technology, as well as six of the 973 Chief Scientists.

The theme of the International Top-level Forum on Engineering Science and Technology Development Strategy was Approach for Achievement of Recycling

Economy of Biomass Waste. Three main subjects were discussed on this forum. Firstly, the status and role of biomass recycling economy was described from the perspective of macroeconomic policy. Secondly, from the technical aspects of recycling economy, the feasibility and solutions of recycling economy was discussed at the level of chemical processing of biomass and bio-processing technology. Thirdly, the biomass recycling efficiency was discussed in terms of the formation of circular economy industrial chain from biomass. Experts from both China and overseas countries presented high-level reports. These reporters included Academician Moo-Young from the Royal Society of Canada, Prof. Tao Zheng from Nanjing University of Technology on behalf of Academician Pingkai OuYang who is the president of the university, Prof. Kurt Wagemann who is the council chairman of German Chemical Engineering and Biotechnology Association, Prof. Roland Clift who is from the Environmental Strategy Centre of England Surrey College and also the executive director of the Industrial Ecology for International Society, Academician Tianwei Tan who is the president of the Beijing University of Chemical Technology, and Dr. Armin Guenther who is R & D Officer of Renewable Energy from German Lurgi Group. The experts shared the latest research findings of biomass energy conversion with all delegates attending the conference and they made in-depth discussions on the issues about the technological approaches and innovation idea of biomass waste recycling economy.

A variety of different opinions and suggestions about the development of biorefinery and utilization of biomass to produce vehicle fuels, chemicals, polymers were collected from various levels of the government, enterprises, and research institutes. These are useful to decide the status, role and direction of technology development of biomass circular economy, providing important references and bases for making relevant national policy and strategy.

The experts gave the following conclusions and forward-looking suggestions:

1. Being the major resource of renewable energy in the future, bioenergy is a kind of stable energy supply in comparison with other ones. As an agricultural country and also a populous nation, China is rich in various biomass resources, including crop straw, forestry wastes, municipal organic refuses, organic industrial waste water, waste cooking oil, kitchen wastes, and so on. As the productions of biorefineries are also diverse, proper choice should be made according to the present situations of resources and market demand.

2. Biorefinery is an important prerequisite of the bioeconomy of the future to promote the development of world economy. Currently, biorefinery is still in the

beginning stages of technical development, with some productions just entering industrialization. On the whole, they are not commercially available, but the development potential is huge.

3. The following two problems of biorefinery need to be settled:

Firstly, the contradiction of distributed raw materials and centralization of production. Raw materials are distributed dispersly and low in energy density, while in conversion, large scale production is usually designed to lessen the investment and operation cost per product. Therefore, we should take into account both the transportation costs of materials collection and the production concentration, and decide the scale of production scientifically by overall balance.

Secondly, improve the conversion efficiency, and maximize the energy output and input ratio. Only when energy output is more than input, could the biomass energy utilization be promising.

4. As a big agricultural country, huge amount of scattered rural inferior biomass resources exist in China, such as human and animal waste. Development of bio-methane is an efficient way to utilize these resources. The bio-methane can be used for rural fuel as well as industrial fuel and vehicle fuel transported by pipeline after purification.

5. Bioconversion and thermo chemical conversion are two key technique platforms of biorefinery with their respective advantages. The products could be biofuels, also bio-based chemicals or materials. Thus appropriate technical route and product sollutions should be explored according to the local conditions.

6. For biorefinery, our government should organize at national level experts to study and formulate technology roadmap and related support policy for industrial development, achieving healthy development of biorefinery industry.

7. In development of biomass energy utilization, the life cycle energy & efficiency analysis and CO₂ emission analysis of different technical routes and product solutions is an important basic work, which is quite challenging, and requires hard efforts.

8. As the present situation unveils, using biomass to produce bio-based chemicals, bio-based materials is more economical compared with biotransport fuel. What's more, it is also a kind of substitute of petroleum. The economic benefit can be shown by industrial demonstration production of chemicals and bio-based materials through biorefinery. Thus by verifying its economic value, it is good for strengthening the society confidence for biorefinery, which should give much attention to.

Part II

List of Experts Attending the Forum

Murray Moo – Young	Emeritus Professor, University of Waterloo, Canada
Kurt Wagemann	Executive Director, DECHEMA, Germany
Roland Clift	Emeritus Professor, University of Surrey, Founding Director of Environmental Technology Centre for Environmental Strategy, UK
Armin Guenther	Director, Department for Project Management and Renewable Energies, Lurgi, Germany
Xianghong Cao	Sinopec Corp., Academician of Chinese Academy of Engineering (CAE), PR China
Xieqing Wang	Petroleum and Chemical Sciences Research Institute, Academician of CAE, PR China
Weizu Wu	Headquarters of the General Staff of Chinese PLA, Academician of CAE, PR China
Hailing Tu	Beijing Nonferrous Metal Research Institute, Academician of CAE, PR China
Qiyue Yang	Sinopec, Beijing Design Institute, Academician of CAE, PR China
Cheng'en Xu	Sinopec, Beijing Oil Design Institute, Academician of CAE, PR China
Xingtian Shu	Petroleum and Chemical Sciences Research Institute, Academician of CAE, PR China
Bingzhen Chen	Tsinghua University, Academician of CAE, PR China
Tianwei Tan	President of Beijing University of Chemical Technology, Academician of CAE, PR China
Jingdun Jia	Director, Rural Technology Development Center, Ministry of Science and Technology, PR China
Qun Liu	Division Chief, Energy Conservation & Technology Equipment Department, National Energy Bureau of Development and Reform Commission, PR China
Richard S. Parnas	Professor, Chemical Engineering of University of Connecticut, USA
Zisheng Zhang	Professor, Chemical and Biological Engineering, University of Ottawa, Canada

Hans – Joachim Leimkuehler	Supervisor, Technology Development Department of Bayer Technology and Engineering Services Company, Shanghai, PR China
Jun Fu	Professor of Engineering, Chief Engineer of Research Institute of Petroleum, SINOPEC, PR China
Xihong Li	Professor Level Senior Engineer, President of Economics & Development Research Institute, SINOPEC, PR China
Longlong Ma	Researcher, Vice Director of Guangzhou Institute of Energy Conversion(GIEC), Chinese Academy of Sciences(CAS), Guangzhou, PR China
Yinbo Qu	Professor, Dean of Life Science School, Shandong University, PR China
Runcang Sun	Professor, Dean of the Institute of Materials Science and Technology, Beijing Forestry University, PR China
Jianbing Ji	Professor, Dean of the School of Zhijiang of Zhejiang University of Technology, PR China
Bin Liang	Professor, Dean of the School of Chemical Engineering of Sichuan University, PR China
Guanyi Chen	Professor, Dean of Faculty of Environmental Science and Engineering, Tianjin University, PR China
Guoqiang Chen	Professor, Tsinghua University, PR China
Yuanguang Li	Professor, East China University of Science and Technology, PR China
Hai Zhao	Researcher, Chengdu Institute of Biology, Chinese Academy of Sciences, PR China
Weiming Yi	Professor, Division Chief of Department of Science & Technology, Shandong University of Technology, PR China
Lu Lin	Professor, Vice-Dean of the School of Energy Research, Xiamen University, PR China
Jianzhong Sun	Professor, Director of Biofuels Institute of Jiangsu University, PR China
Fengwu Bai	Professor, Dalian University of Technology, PR China
Xiujin Li	Professor, Associate Dean of Department of Environmental

	Science and Engineering, Beijing University of Chemical Technology, PR China
Tao Zheng	Professor, Nanjing University of Technology, PR China
Guojun Yue	Professor Level Senior Engineer, Board Director of COFCO Biochemical (Anhui) Co. , Ltd. , General Manager of Biochemical and Biofuel Division, PR China
Guangyin Meng	Board Chairman, Shandong Rising Holdings Limited, PR China
Fengguang Du	Professor Level Senior Engineer, General-engineer of Henan Tianguan Group Co. Ltd, PR China
Minsheng Liu	General Manager, Bioenergy Institute of ENN Science & Technology Development Co. , Ltd. , PR China
Jianping Wang	Business Director of Pacific Region, DuPont Industrial Biotechnology Division, PR China
Lin Xiao	R & D Center Director, Shandong LongLive Bio-Technology Co. , Ltd. , PR China

Part III

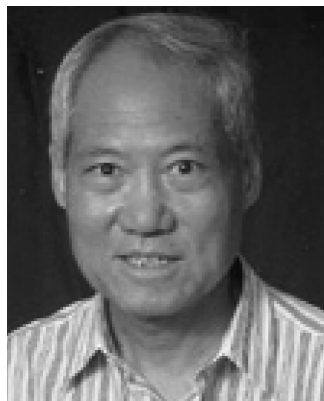
Approach for Achievement of
Recycling Economy of Bio-
mass Waste—Int' l Top-level
Forum

Eco-socioeconomics of Biomass–derivatives: An Appraisal Overview

Murray Moo-Young

University of Waterloo, Waterloo, Ontario N2L3G1, Canada

Increasingly eco-socioeconomic concerns about environmental pollution and shortages of affordable energy fuels have made headlines in the public media. Also increasingly, there is awareness of global abundance of renewable biomass materials normally regarded as waste that can be used to concurrently reduce potential environmental hazards and to produce biofuels and other commercial products by benign biotechnologies. In this overview we give snapshots with a general background of the biotechnology strategies for several related scenarios; the bioethanol biofuel dominance at present; biobutanol as a forthcoming attractive alternative; under-appreciated biomethane from anaerobic digestion of agricultural wastes; potential bioconversion of cellulosic wastes to protein-enriched food stuffs. Genetic and metabolic engineering approaches to improve these strategies are of paramount importance to future viable practical biomanufacturing applications.



Murray Moo-Young is a distinguished professor emeritus at the University of Waterloo, Canada, where he continues biotechnology research on bioprocessing strategies for environmental bioremediation and for biomanufacturing of biopharmaceuticals and biofuels. Before academia, he worked in England as a process engineer for the British Ministry of Industry. A Jamaican-born Chinese Canadian, Murray received his degrees from the University of London (BSc *Chemistry*, PhD *Biochemical Engineering*) and

University of Toronto (MSc *Chemical Engineering and Applied Chemistry*) followed by a postdoctoral fellowship at the University of Edinburgh (*Process Biotechnology*). Among his international academic experience, he has been a visiting professor at several well-known universities including MIT, UC Berkeley, Oxford University, Cambridge University, ETH Zurich, Federal University of Sao Paulo, Dalian University of Technology and Osaka University of Technology. He continues to be an invited keynote speaker at conferences worldwide.

To date, Murray has published 13 books, 10 patents and over 365 papers (seven during the past five years). He is a consultant worldwide to industry and government, including Dupont, Pfizer, UNDP, FAO, and OAS. He is the editor-in-chief of the journal *Biotechnology Advances*, IF 7.600 (www.elsevier.com/locate/biotechadv) and the 2011 second edition of the six-volume major reference work *Comprehensive Biotechnology* ([www.Elsevier.com ;books](http://www.Elsevier.com;books) link). Murray's honors include the premier awards of the Canadian Society for Chemical Engineering (CSChE), the Ontario Association of Professional Engineers (PEO) and the American Chemical Society (ACS), Biochemical Technology Division. He is an elected fellow of the American Institute for Medical and Biological Engineering (FAIMBE), “one of the highest honors for a bioengineer”, and the Royal Society of Canada (FRSC), “the highest accolade for a Canadian academic”.

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Development Strategy of Efficient Bio-methane System by Focused Utilization of Distributed Biomass

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1. Huge amounts of scattered rural inferior biomass resources exist in China, which could be effectively utilized through the establishment of high efficient agriculture and industry integrated bio-methane system

Using inferior biomass resources to produce biogas in China's rural country has achieved good results. However, the shortcomings of biogas project in traditional rural household are also evident, such as its low bio-conversion efficiency, no diversity in raw material (mainly human and animal manures). Currently, the development of centralized and large scale farming industry has promoted the more concentrated biomass resources. Meanwhile, the modern development of new rural areas, townships has called for a higher level of energy quality. Consequently, traditional decentralized and inefficient household biogas energy systems have become increasingly unsuitable to meet the requirements of a new era of agriculture and villages.

In order to efficiently utilize the huge dispersed biomass resources in rural country produced annually in China (Table 1) and to overcome the shortcomings of low efficiency in traditional household biogas project that could not satisfy the needs of high-end users, large quantities of small scale biogas plants can be built on the basis of modern biotechnology and engineering technology and distribution of biomass to realize the aim of efficient industrialization of biogas fermentation, which, in turn, produces large scale bio-methane from those biogas collected through biogas pipe by large-scale purification

devices. The bio-methane can then be used for rural piped gas, vehicle gas and chemical raw materials, so to construct a dispersed, centralized and integrated agricultural and industrial bio-methane system with high efficiency.

Table 1 Total inferior biomass resources in China

Resource types	Livestock and poultry manure	Crop straw	Forestry waste	Agroprocessing waste	Wastewater sludge	Urban and rural garbage	Organic wastewater	Total
Total amount								
(billion tons /year)	2.5	0.7	0.27	0.2	0.15	0.2	2	6.02

Bio-methane, as a promising renewable green energy, the component and thermal value of which is very close to that of natural gas, indicating an enormous resource potential (Table 2), could be employed as the alternative of fossil through the development of agro-industrial integration and efficient bio-methane system. Bio-methane can be applied as vehicle fuel, life energy consumption through pipe and chemical raw materials.

Table 2 Potential of the bio-methane resource produced by inferior biomass materials in China

Total resource			Currently available resources		
Total raw materials	Biogas production	Bio-methane production	Total raw materials	Biogas production	Bio-methane production
(billion tons/year)	(billion cubic meters)	(billion cubic meters)	(billion tons/year)	(billion cubic meters)	(billion cubic meters)
5.78	622	373.2	3.761	199	120

2. Establishment of high efficient agriculture and industry integrated bio-methane system is an important component of the renewable energy system and is also a significant way of emission reduction

China's demand for renewable energy is increasing with the aggravation of energy resources crisis. Natural gas consumption ratio in China is 3.9% currently and will increase to 8.3% by 2015, which means 260 billion cubic meter natural gas will be consumed one year, among which more than 90 billion is imported. Bio-ethane is

becoming the most promising renewable energy for its enormous potential in lowering the greenhouse gas emission, and it is able to contribute greatly to ensure the security of the country's energy supply.

Compared with fuel energy, there is no net CO₂ emission in consuming bio-methane owing to be generated from biomass resources. A bio-methane project that produces 150 million cubic meter natural gas per year is taken as an example. It can bring great social and ecological benefits by decreasing 750 thousand tons of COD, 2.75 million tons of green gas and 32.5 tons of nitrogen oxide emission, and saving approximately 900 thousand cubic meter water a year.

3. The high efficient agriculture and industry integrated bio-methane system is particularly suitable to be promoted in southern China

There is a scarcity of fossil energy in many parts of southern China, while biomass resource is rich in these regions. Therefore, bio-methane is particularly suitable to be promoted in the south of China. Take Jiangsu Province for example, natural gas consumption will reach 27 billion cubic meters in 2015, while the gas produced by the province's oilfield is only 55 million cubic meters, and the rest needs to be imported through the pipeline and sea transport. It is speculated that the natural gas supply gap will reach 3.6 billion cubic meters in 2015. On the other hand, there are about 40 million tons of agriculture straw and 30 million tons of livestock and poultry manure per year in Jiangsu Province, which will produce 7 billion cubic meter bio-methane, and it could fully satisfy the natural gas supply gap. Hence, bio-methane should be developed as an important component of the renewable resources from the rich biological resources of southern China.

The program design and investment cost of establishing the County Administrative Region of the bio-methane project was analyzed in accordance with the idea of integration of agricultural and industrial bio-methane system. It was calculated that the average amount of biomass resources in County-level Administrative Region of the southern China (mainly one million tons of straw, as well as other poultry manure) was fully adequate to support a 100 million cubic meter bio-methane project. Total investment input for a bio-methane project that produces 100 million cubic meters of bio-methane per year is 0.7 billion yuan. Sales income of bio-methane as vehicle fuels can

be 0.46 billion yuan (vehicles using natural gas price of 4.6 yuan/cubic meter); the fertilizer sales (300 yuan/t) is 0.15 billion yuan per year when the 500 000 tons of biogas residues are fully used. Both sales of bio-methane and fertilizer are 0.61 billion yuan, while the total production cost is 0.43 billion every year, which means the total profit is 0.18 billion yuan every year. Table 3 shows the difference between the natural gas pipeline transportation and the bio-methane produced by the inferior biomass resources industry.

Table 3 Bio-methane manufacture and natural gas pipeline transportation

	Total investment (hundred million yuan)	Bio-methane cost(yuan)	Nature of energy	Ancillary benifits	Promoted industries
Natural gas pipeline transportation	1500①	4 (The prices of import natural gas)	Non- renewable	/	Iron and steel, building materials, petrochemical, power
Bio-methane manufacture	840②	2.86	Renewable	Reduce carbon emissions and improve environment	Iron and steel, building materials, petrochemical, power environment protection ,agriculture

① Annual gas transmission capacity of 12 billion cubic meters(Data from East Gas Pipeline Project).

② The annual output of 100 million cubic meters of bio-methane project costs about 700 million yuan , and total investment for the 12 billion cubic meter bio-methane project is 84 billion yuan.

4. Problems that still need to be improved for the establishment of high efficient agriculture and industry integrated bio-methane system

The bio-methane industry in China has accumulated certain amount of experience to narrow the technology gap compared with abroad after years of scientific research and engineering practice under the support of the national policy. At present, there are more than 4700 large and medium scale biogas plants in China and part of them are combined in heat and power generator engines which convert the biogas into power and heat. Nevertheless, there are still some problems to be resolved and improved in some common key technologies, system integration, standardization, and energy end-application systems. The following are some examples.

- 1) Inferior biomass materials collection:Should be adapted to local conditions, and

biomass materials collection(e. g. straw) system needs to be further improved under the policy guidance.

2) Biotransformation process: Digestion raw materials are transformed from low solid concentration to high solid concentration, and co-digestion changes to multiple raw materials from single digestion raw material; digestion temperature changes from room temperature to middle and high temperature; process equipment standardization and completion is needed.

3) Bio-methane and related materials upgrading: Standardization of design and manufacture of complete sets of biogas purification engineering equipments are requested to meet the needs of the different scale industrialization of bio-methane projects.

4) Utilization of bio-methane: Making clear the position of bio-methane in the energy strategy and establishing energy end-use applications system which should be better integrated into the existing energy system under the guidance of national policy.

5) Policy support: Changing the biogas project construction subsidies into bio-methane sales subsidies with reference to the existing fuel ethanol system, and this will improve the actual difficulty in operating biogas plants after biogas project completes.



Pingkai Ouyang was born in Guangxi Province, China, in 1945. He graduated from the Chemical Engineering Department of Tsinghua University in 1968, and returned to Tsinghua ten years later and graduated with an M. Eng. in 1981. Pingkai Ouyang is a professor in biochemical engineering with Nanjing University of Technology, and has been president of the university since 2001. He was elected Academician of the Chinese Academy of Engineering in 2001. He went to University of Waterloo and Purdue University

as an advanced visiting scholar between 1985 and 1987. He received an honorary doctor's degree from University of Waterloo in 2010. Professor Pingkai Ouyang was president of Nanjing University of Chemical Technology before its merge with several independent colleges and renamed as Nanjing University of Technology. He has been active in professional communities both in academia and industry as a leading scientist and strategic director. Prominent ones among his

posts are; Chairman of Chinese Society of Biotechnology, Vice President of China Petroleum and Chemical Industrial Association, Chairman of the Association of Science and Technology of Jiangsu Province, etc.

Professor Pingkai Ouyang has devoted himself into biochemical engineering as an investigator and a mentor since the establishment of the discipline in early 1980s in China. As one of the founders in biochemical engineering and the Head of the National Research Center of Biochemical Engineering, he pioneered in the engineering and technology R & D in the field by using combinatorial methodology in the fabrication and optimization of biochemical processes. In the key steps of complex-enzymatic transformations, multiple coupling techniques were employed in reaction-reaction, reaction-separation, and separation-separation interfaces, which supported the innovation of biochemical industries and the leading position of couples of bioproducts in the world. For his outstanding academic achievements, Professor Ouyang was awarded the First Prize of National Science and Technology Advancement, the Second Prize of the National Technological Inventions, Prize for Innovation by DuPont, and Prize of He Liang-He Li Fund.

Contributions of Biorefineries to the Bioeconomy of the Future

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The importance of the use of biomass for food, feed, fuels, chemicals and materials has increased and will increase even more in the future. Different factors contribute to this trend: Fossil carbon resources are limited and CO₂-emission from their utilization should be limited for climate protection. In addition the world population is growing and its increasing standard of living further stresses the raw material demand.

Biomass as a source of energy as well as carbon source for chemicals production is renewable but nevertheless limited due to narrow agricultural areas. The competition between ground for food and energy production, the production of industrial goods and last but not least for preserving biodiversity defines the need for highly efficient utilization schemes of the limited biomass resource.

Biorefineries are the key for high resource efficiency taking economic and ecological aspects into consideration: They integrate different separation and conversion processes for realizing near zero discharge and sustainable utilization of different renewable raw materials. Different sectors will play an important role: Agriculture and forestry for biomass production, the chemical industry for the development of new conversion processes and new biobased products as well as the apparatus and plant construction sector. Their interaction will be crucial for establishing a biobased economy, in Europe already often called “the bioeconomy.”

The German Government has decided to have a roadmap being established by a group of independent experts from industry and academia (Fig. 1). This roadmap describes in a systematic way status and perspectives of the different biorefinery concepts (Fig. 2). It takes economic and ecological aspects into considerations and

analyses the R&D demand.

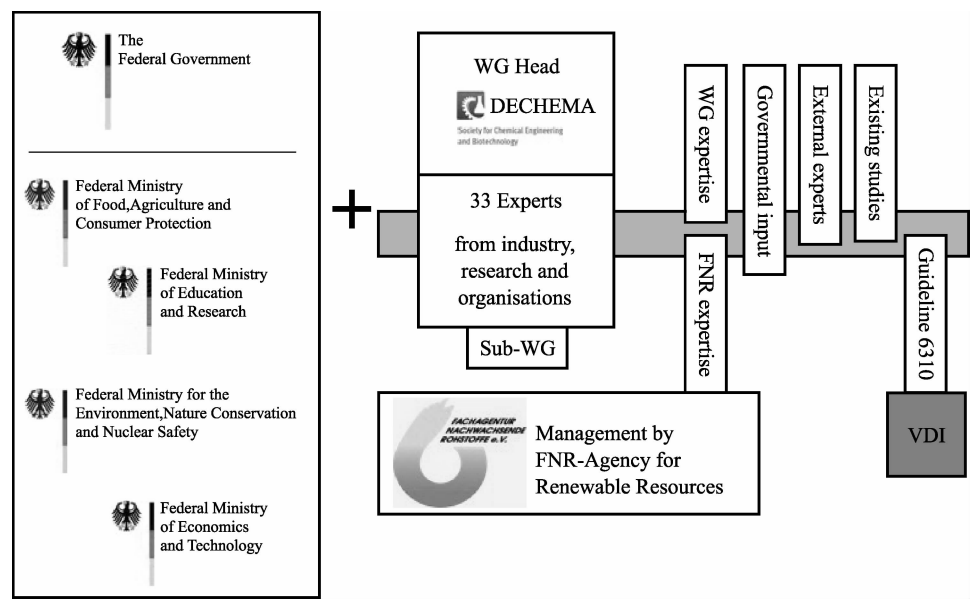


Fig. 1 The basic information of roadmap about Germany biorefinery project

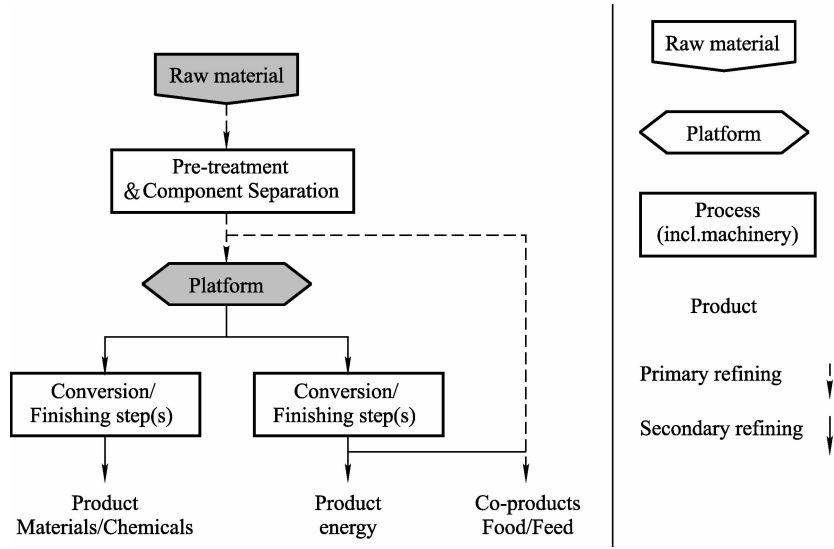


Fig. 2 The roadmap of Germany biorefinery project

The following definition is taken as a basis for the analysis:

“A biorefinery is characterised by having a dedicated, integrative overall approach, using biomass as versatile raw material source for the sustainable production of a spectrum of different intermediates and marketable products (chemicals, materials,

bioenergy and food/feed co-products) by using the biomass components as complete as possible. ”

The analysis considers the following promising concepts:

1. **Sugar** biorefinery and **starch** biorefinery(Fig. 3)

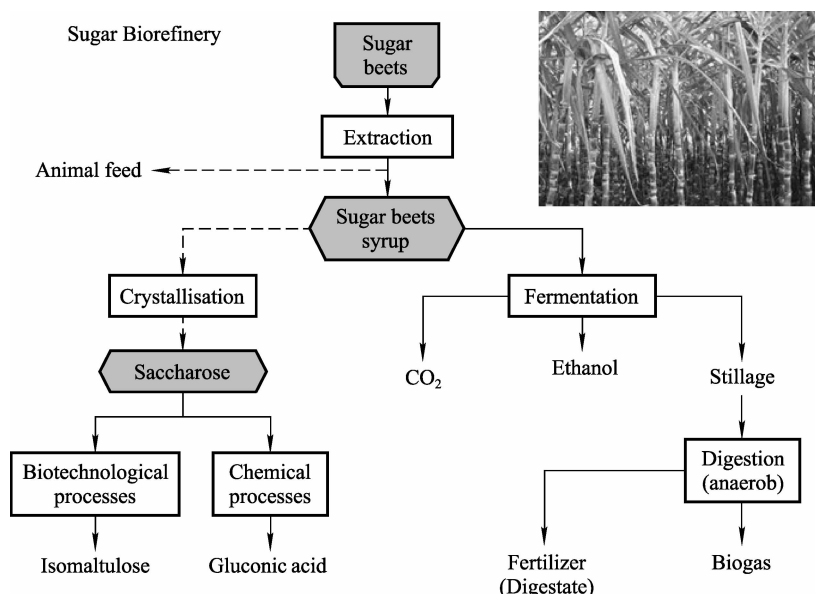


Fig. 3 The flow chart of sugar biorefinery and starch biorefinery process

2. **Plant oil** biorefinery including **algae lipid** biorefinery(Fig. 4 and 5)

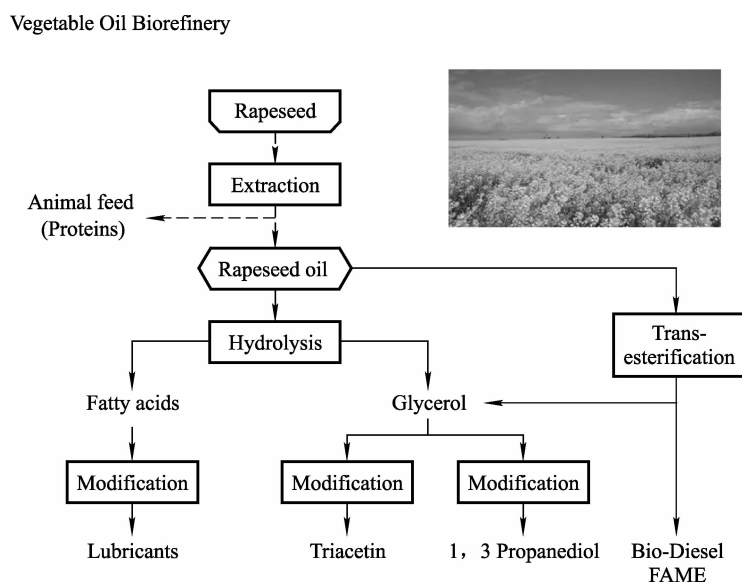


Fig. 4 The flow chart of plant oil biorefinery process

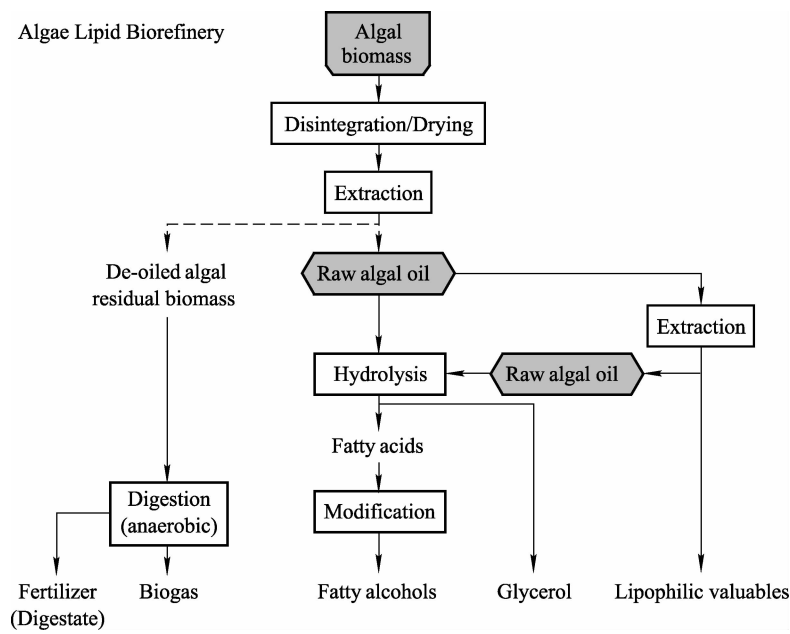


Fig. 5 The flow chart of algae lipid biorefinery process

3. 1 Lignocellulose(**Cellulose/Hemicellulose/Lignin**) biorefinery(Fig.6 and 7)

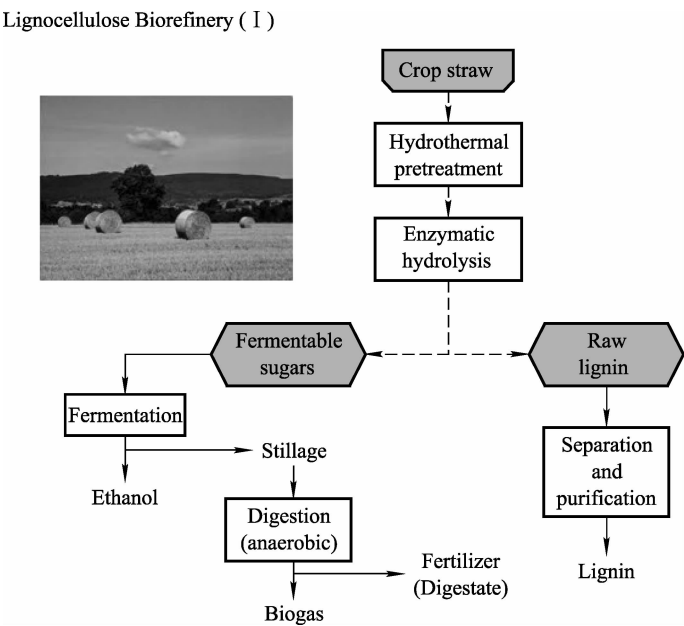


Fig. 6 The flow chart of lignocellulose biorefinery process I (Raw material :Crop straw)

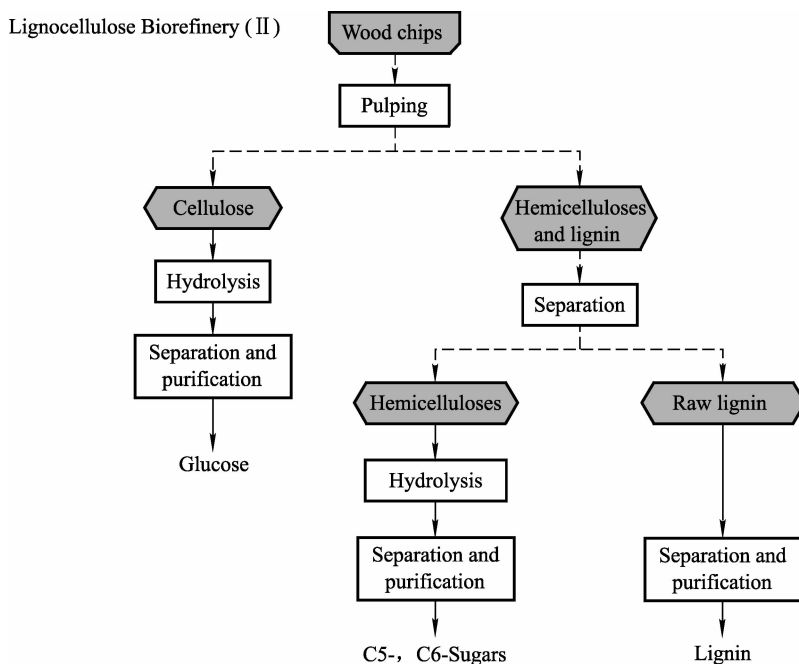


Fig. 7 The flow chart of lignocellulose biorefinery process II (Raw material: Wood chips)

3. 2 Green(green fibre/green juice) biorefinery

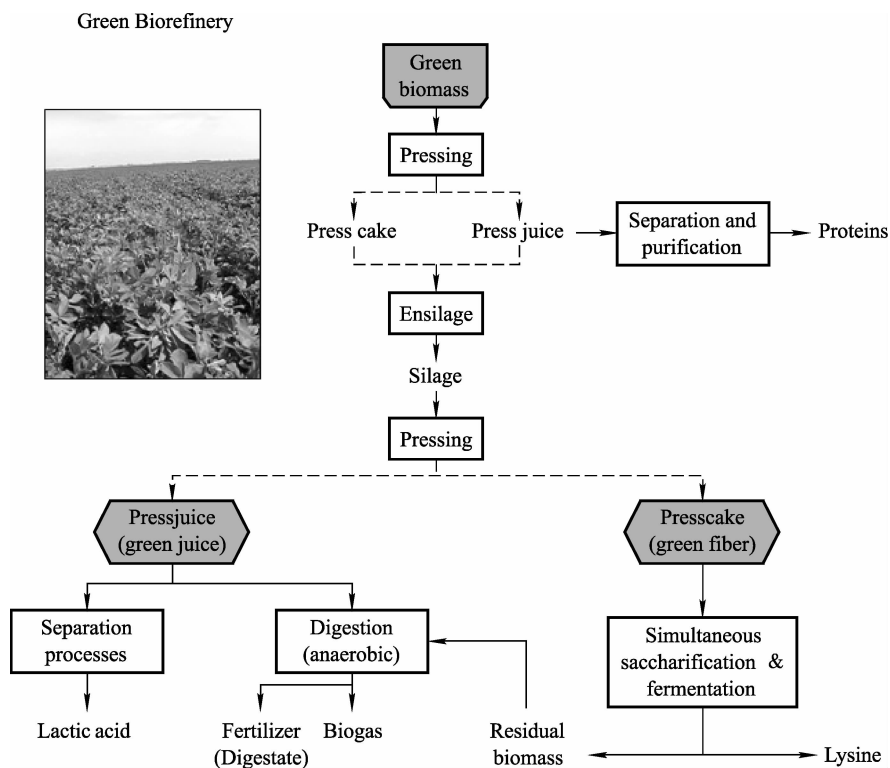


Fig. 8 The flow chart of green(green fibre/green juice) biorefinery process

4. **Synthesis gas** biorefinery(Fig.9)

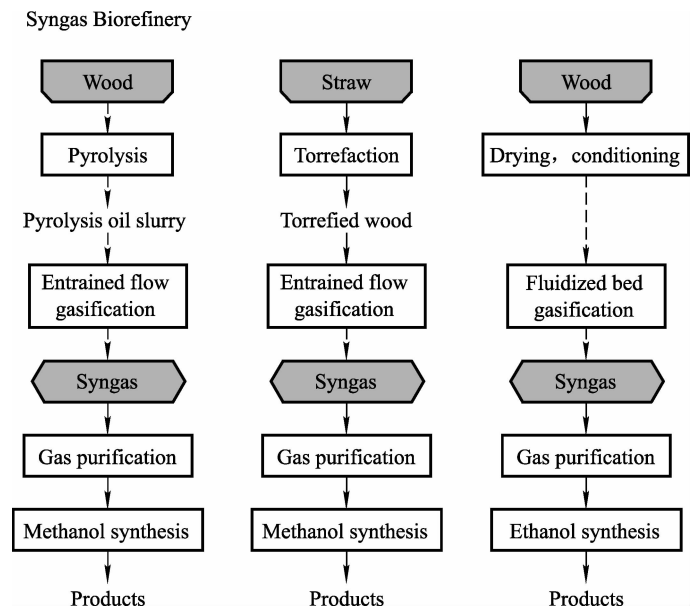


Fig. 9 The flow chart of synthesis gas biorefinery process

5. **Biogas** biorefinery(Fig. 10)

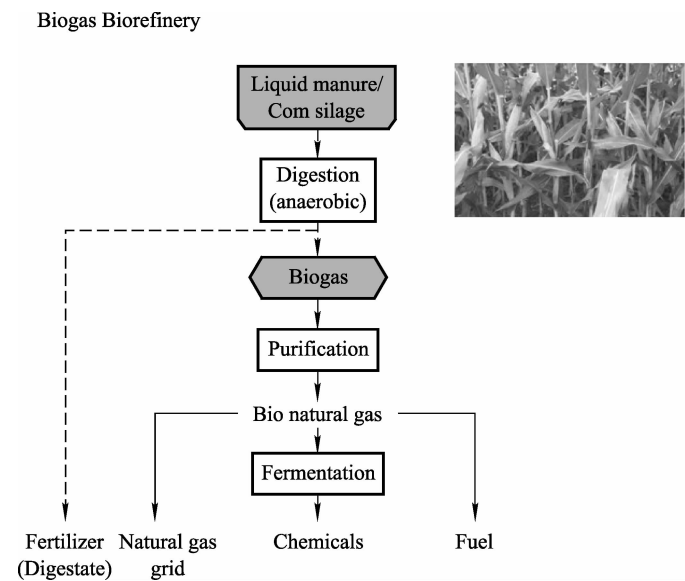


Fig. 10 The flow chart of biogas biorefinery process



Prof. Dr. Kurt Wagemann was born in 1959 in Munich. He received his PhD in 1989 at the Max-Planck-Institut für Quantenoptik. Since 1989 he headed some of the large departments at the DECHEMA, as those for Research Planning, Congresses and for Research Management and Administration.

Besides this, he held the offices of executive director of fmse. V. in Dresden and of ProcessNet in Frankfurt. In 2010 he took over the position of DECHEMA's executive director.

In February 2011, he was appointed to be an honorary professor at the University of Stuttgart, where he has fulfilled a teaching assignment since 2006.

An Industrial Ecology Approach to the Use of Biomass Waste

Roland Clift

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Management of any waste, including biomass, must be assessed by analysing the whole system within which the waste is generated and materials and energy recovered from the waste are used. This is an obvious area for application of Life Cycle Assessment (LCA) along with other, more site-specific tools for environmental assessment. The basic framework for this application of LCA is well established, and is already embodied in a number of generally available software packages which can be used to compare the environmental effects of alternative strategies for waste management.

The basic approach is shown in Fig. 1. The “Foreground” waste management activity delivers the primary service of managing waste. It will need to use materials and energy, including transport fuels, provided by the background economic system. Materials and/or energy may also be recovered from the waste, for use in the background economic system. The full system analysis must allow for these exchanges. It is normally assumed that the other functional outputs from the “Background” system are unchanged, so that materials and energy used in waste management represent additional economic activities and the recovered materials and energy displace background economic activities. The total inventory—i. e. resource inputs and environmental emissions—therefore comprises the direct burdens associated with waste management *plus* the indirect burdens associated with producing the materials and energy used in waste management *minus* the avoided burdens displaced from the background because they are substituted by materials and energy recovered from the

waste.

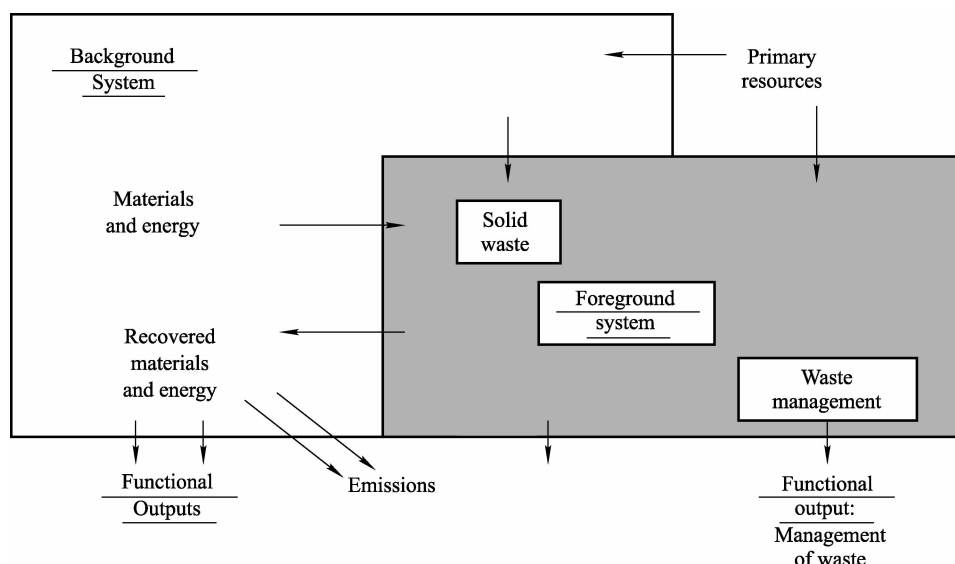


Fig.1 Life Cycle Assessment of waste management (from Clift, R. , Doig, A. , & Finnveden, G. (2000). The Application of Life Cycle Assessment to Integrated Solid Waste Management; Part 1—Methodology. *Trans IChemE (Process Safety and Environmental Protection)*, *Special Issue: Sustainable Development*, 78:279 –287.)

One of the principal concerns in applying a life cycle approach is to identify the economic activities which will be replaced by materials and energy recovered from the waste, and specifically whether the assessment should be based on marginal or average activities. This issue has been debated in LCA circles for at least 20 years. Introduction of standardised approaches to apply LCA for labelling, particularly calculating the “carbon footprint” of products, has forced the argument to a methodological conclusion. However, the discussion over when to use “attributorial” (i. e. accounting) and when to use “consequential” (i. e. prospective) analysis continues. It is essential for anyone evaluating recycling strategies to understand the methodological and practical differences between the two broad approaches and hence which should be applied in any specific case.

The context in which a waste management system operates, including the activities displaced by recycling and the quantity of waste to be treated, varies over time, especially in an economy which is going through a rapid transition. Careful and systematic development of possible future scenarios is therefore an essential complement to life cycle assessment.

The question to be asked in planning waste management and recycling is “What is the most beneficial use of this resource?”, rather than “How can this resource contribute to a particular sector?” In a carbon-constrained world, the objectives for biomass use must be to maximise life cycle energy yield or reduction in greenhouse gas emissions relative to fossil fuels. These two objectives are not identical but are sufficiently close for most purposes. Stating the objectives in this way also emphasises the importance of appropriate use of any biomass available as a source of energy or materials.

Simple thermodynamic considerations, summarised schematically in Fig. 2, show why these objectives argue for minimal processing of biomass. Biomass used as an energy source is ultimately converted to combustion products, whatever the utilisation pathway. If it is simply burnt, as in the upper pathway in the diagram, the energy yield is the calorific value of the biomass, net of any energy inputs into cultivation, harvesting and transport, leading to the familiar arguments for small-scale exploitation of biomass with minimum transport of the low-density material. The lower pathway shows the case where the biomass is processed, for example, into a liquid transport fuel. In this case the processing plant is usually large, to achieve economies of scale, so that the biomass must be drawn from a large area and the transport distances and associated energy inputs are correspondingly larger. More importantly, conversion of the biomass to refined products needs energy input and is also associated, as a thermodynamic inevitability, with energy (strictly, exergy) losses. Therefore when the refined products are burnt, for example in an internal combustion engine, the net energy release is inevitably smaller—usually much smaller—than when the unprocessed biomass is burnt.

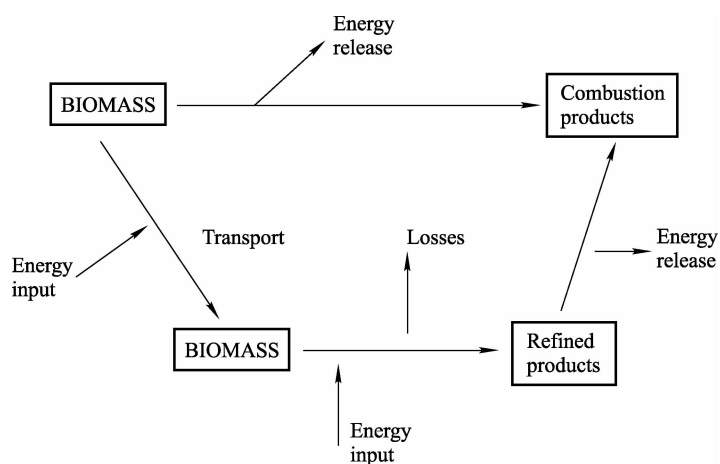


Fig. 2 Pathways for the use of biomass

It follows that processing biomass into liquid transport fuels is rarely an optimal strategy; if biomass is to be highly processed, it should be transformed into much higher value products. Furthermore, the increasing availability of shale gas is changing the energy sector; the possibility of making liquid fuels from natural gas puts the whole development of transport biofuels into question. Thus it is possible for a process to be technologically clever but strategically ill-considered. What the world needs, far more urgently than second- or third-generation biofuel technologies, is small-scale reliable biomass-fired CHP plant.



Roland Clift, Emeritus Professor of Environmental Technology and founding Director of the Centre for Environmental Strategy at the University of Surrey; previously Head of the Department of Chemical and Process Engineering at the University of Surrey; Visiting Professor in Environmental System Analysis at Chalmers University, Göteborg, Sweden; Adjunct Professor in Chemical and Biological Engineering at the University of British Columbia, Vancouver, Canada; Executive Director and immediate past

President of the International Society for Industrial Ecology; past member of the Royal Commission on Environmental Pollution, UK; Ecolabelling Board and Science Advisory Council of Defra; and a Vice President of Environmental Protection, UK. His research is concerned with system approaches to environmental management and industrial ecology, including life cycle assessment and energy systems.

Production of Bio-energy from Low-value Biomass by Bioconversion

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Recently, the World Energy Outlook 2012, which was released by the global petrochemical giant Exxon Mobil, reported that the global energy demanded will increase by 30 percent in 2040 compared with 2010 with the economic growth and influences of demographic factors. Since 1993, China has become a net importer of energy from a net exporter. The total energy consumption has been greater than the total supply, and the external dependence of the energy demand increases rapidly. China's crude oil import volume and imports amount reached 253.78 million tons and 196.664 billion U. S. dollars in 2011, a growth rate of 6.00% and 45.30%, respectively, year-on-year. The significant increase in demand for oil and the caused structural contradictions are increasingly becoming the biggest challenge of China's energy security.

The energy crisis has not only touched everyone's nerves, but also sparked a strong desire to find alternative energy. Which are and what can be used of the low-value biomass? What are the types of biofuels production and the advantages and disadvantages? How are the prospects of biomass fuels in China? These issues need to be answered one by one by the biofuels experts.

1. The low-value raw material

1.1 The kinds of low-value raw material

The low-value biomass, which includes crop straw and agro-processing residues, wood and forestry processing residues, livestock manure, industrial organic waste water and

waste residues, municipal solid waste and energy plants, can be converted to a variety of energy, such as electricity, gas, solid fuels and liquid fuels. The most attention is the biomass liquid fuels(bio-fuels). Many countries of the world have begun development of bio-fuel industry, including bio-fuel processing industry and its related industries, such as energy agriculture and forestry. The common purpose is to protect the oil security.

Lignocellulose is the most abundant renewable resource on the earth. It is estimated that the annual output of lignocellulose is up to 150 billion tons and there is a lot of bio-energy. China is a large agricultural country, and crop residues are very large, such as rice straw, wheat straw, etc. There are 0.7 billion tons of crop residues every year, which is equivalent to 0.5 million tons of standard coal. According to statistics, the straw utilization rate is 33%, but only 2.6% is used and converted to bio-fuel, while most of the rest are directly used to burn. So, the prospects of using lignocellulose for bio-energy are very bright.

In China, the generation of municipal solid waste is growing rapidly with the continuous improvement of social progress and living standards. According to statistics, nearly 170 million tons of the municipal solid waste were transported and treated every year in China. In Beijing, for example, organic ingredients in the garbage rapidly increased to about 60% from 20% in the 1970s. A lot of food waste mixed with urban living garbage collection system which was the reason for the rising of organic components in the garbage. There are 60 million tons of food waste in China annually, while the number is 2 thousand in Beijing everyday. The proportion of food waste in municipal solid is 37% in Beijing.

In fact, life waste treatment and disposal system has gradually formed in which sanitary landfill is the main method and supplemented by incineration and composting in China. So far, there are 479 landfills, 46 composting plants and 66 incineration plants in 661 cities of China. The treating abilities, by proportion of landfill, incineration and composting, are 85%, 10% and 5%, respectively. Due to the lack of disposal of food waste, the food waste and ordinary garbage were treated together in China. That will improve the content of organic matter and moisture, and gradually cause a series of problems for the three life waste treatment and disposal methods. Compared with other refuses, food waste has the characteristics of higher water content, organic content, fat content, salt content and richer nutritional elements. So, the food waste has the great value of recycling. Food waste will realize separate collection and disposal in the future

along with the improvement of environmental protection awareness and the collection methods. That will reduce the difficulty of the processing of municipal solid waste.

1.2 The situation of biofuel feedstock in China

(1) 800 000 tons of fuel ethanol and more than 2 million tons of biodiesel can be produced annually using molasses, waste oil from food processing industry and catering sector, cottonseed oil and other waste of sugar and oil resources.

(2) The crop straw and forestry residues, which can be used for the resource utilization, are about 0.25 million tons and the number continues to increase annually. That can satisfy for 30–50 million tons of second-generation biofuels production in the medium to long term.

(3) About 32–76 million hectares of marginal land can be developed for energy plants, such as sweet sorghum, cassava and jatropha, through the promotion of good seeds, varieties of replacement plants.

Overall, (i) fuel ethanol production potential is 15 million tons using non-food grain carbohydrate crops as raw materials; (ii) biodiesel production potential is 2 million tons using waste oil as raw materials; (iii) biodiesel production potential is several millions of tons using oil plants; and (iv) the biofuels production potential is tens of million tons every year using cellulose and algae biomass as raw material in the long time.

2. The bio-energy

2.1 The kinds of bio-energy

At present, the main bio-energies include fuel ethanol and butanol, biological hydrogen, bio-oil and bio-diesel. A lot of things can be substituted for gasoline. In China, the prospects of biomass fuels development are very bright, and the development of fuel enterprises is mainly in two directions: the cassava ethanol and cellulosic ethanol, both of which are non-food crops. The cassava ethanol is in the large scale production stage and the technology has been relatively well, while the cellulosic ethanol is still in the testing stage and the technology should be improved.

2.2 The progress of biofuel research in China

(1) The utilization of cassava, sweet sorghum, jatropha and other non-food crops

plants to produce fuel ethanol and biodiesel technology has entered the demonstration phase. Cassava and sweet potato ethanol technology can also achieve commercial applications, such as, the completion project of an annual output of 0.2 million tons of cassava ethanol in Guangxi in 2007.

(2) Lignocellulosic ethanol in the pretreatment of raw materials, conversion of cellulose and enzyme production costs has achieved substantial progress. For example, Heilongjiang, Henan and other places have built demonstration production plants with an annual output of hundreds of and thousands of tons of ethanol, respectively.

(3) The time of bio-diesel industrialization demonstration work has been mature basically. Limited by the waste oil collection and slow progress of the oil plants planting base construction, only a small number of biodiesel companies can achieve large scale, continuous production. There is no finished oil into the main circulation system.

(4) The other second-generation biofuels (such as synthetic fuel technology) are still in the laboratory studies and small-scale phase.

3. The studies of bio-energy by bioconversion

3.1 Sweet sorghum has been considered as a viable energy crop for alcohol fuel production

This review discloses a novel approach for the biorefining of sweet sorghum stem to produce multiple valuable products, such as ethanol, butanol and wood plastic composites. Sweet sorghum stem has a high concentration of soluble sugars in its juice, which can be fermented to produce ethanol by *Saccharomyces cerevisiae*. In order to obtain a high ethanol yield and fermentation rate, concentrated juice with an initial total sugar concentration of $300 \text{ g} \cdot \text{L}^{-1}$ was fermented. The maximum ethanol concentration after 54 h reached $140 \text{ g} \cdot \text{L}^{-1}$ with a yield of 0.49 g ethanol per g consumed sugar, which is 93% of the theoretical value. Sweet sorghum bagasse, obtained from juice squeezing, was pretreated by acetic acid to hydrolyze 80%–90% of the contained hemicelluloses. Using this hydrolysate as raw material (total sugar $55 \text{ g} \cdot \text{L}^{-1}$), $19.21 \text{ g} \cdot \text{L}^{-1}$ total solvent (butanol 9.34 g, ethanol 2.5 g, and acetone 7.36 g) was produced by *Clostridium acetobutylicum*. The residual bagasse after pretreatment was extruded with PLA in a twin-screw extruder to produce a final product having a PLA, a tensile strength of 49.5 M and a flexible strength of 65 MPa. This product has potential

use for applications where truly biodegradable materials are required. This strategy for sustainability is crucial for the industrialization of biofuels from sweet sorghum. The pilot processes of production of 1000 t/year fuel ethanol and production of 200 t/year butanol have been established by BUCT.

3.2 Starch wastewater here is used as raw material to produce microbial lipid and the 2000 t/day fermentation equipment has been built

Sterilization and pH adjustment is not involved during the fermentation process. After 35 h, 28–33g/L biomass, 28%–37% lipid content and more than 80% COD degradation is achieved. The process has obtained the national invention patent and passed the pilot technology appraisal by the Petrochemical Association. The result is that the overall level of this technology reached the international advanced level.

3.3 The food waste has the characteristics of high organic content, complex composition and high water content

Our groups use different technology combinations and select for treatment of the food waste. After pretreatment, oils and fats are extracted firstly and used in preparation of biodiesel. The residual material is used for methane by anaerobic fermentation, and methane is refined by Pressure Swing Adsorption. After pretreatment, anaerobic fermentation slurry can be condensed into concentrate liquid and water. The concentrate liquid can be used for agricultural fertilization, while water can back to the anaerobic system. After the above processes, the food waste of resources achieves maximized recycling and maximized economic benefits. The demonstration equipment of this process (80 t) has been established in the Changping Campus of Beijing University of Chemical Technology.

Using urban waste oil as raw materials, the lipase catalytic biodiesel production technology and new enzyme immobilization methods have been developed by BUCT. In Shanghai, BUCT has established an industrialized device, which is able to produce 10 000 tons of biodiesel annually. Currently, the biodiesel production has been applied by taxi in Shanghai.



Tianwei Tan received his Ph. D. in biochemical engineering in 1993 and BSc in chemical engineering in 1986 from Tsinghua University. He joined the Biochemical Engineering faculty of Beijing University of Chemical Technology(BUCT) in 1995.

In 2001, Prof. Tan was awarded the prestigious Yangzi River Outstanding Professorship by the Ministry of Education of China. Recognizing his contribution in biorefinery and utilization of biomass, he was awarded National Innovation Prize (2nd class) twice by the Chinese Government and first class Ministry-level Innovation Prize 8 times in China. In 2003, he received an Outstanding Young Scientist Award from National Science Foundation of China. He served as the dean of College of Life Science and Technology of BUCT from 2003 to 2007, and then to date as the Vice President of BUCT. In 2011, he was elected as an academician of the Chinese Academy of Engineering. Prof. Tan's research emphasizes on bio-based chemicals, fuel and materials. In 2012, he served as the President of BUCT. He also serves as members of the editorial boards of several key journals in his area including "*Enzyme and Microbial Technology*" and "*Applied Biochemistry and Biotechnology*".

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Conversion of Renewable Feedstocks for the Production of 2nd Generation Biofuels and Products: the Thermochemical Route

Armin Guenther

Innovation Renewable, Lurgi, Germany

Energy demand worldwide will strongly increase in the next 50 years with a large potential for renewable energies and alternative fuels.

Since only the crops are used in case of first generation biofuels and not the whole plant, there is a limitation of raw material or, as the case may be, a food vs. fuel competition.

A wide range of biomass and agricultural and forestry residues as well as the possibility to utilize the whole plants are opening up a mass potential that is far above that of first-generation biofuels, biodiesel and bioethanol.

There are different possible paths to convert biomass, coal, refinery residues and natural gas into FT-synfuels, MeOH, DME, SNG and chemical products.

Considering biomass as a feedstock for thermo chemical conversion such as straw, hay and residuals is characterized by extremely low energy density, so the transport of this material would only be economically feasible over short distances.

The bioliq process which is under development by the Karlsruhe Institute of Technology in cooperation with Air Liquide/Lurgi Technologies and funded by the German Ministry of Agriculture, Food and Consumer Protection combines the need for large industrial scale of synfuel production with economic biomass logistics.

Prior to the gasification, biomass will be treated in regionally distributed fast pyrolysis plants to increase the energy density. The products from the fast pyrolysis: char and liquid condensate, are mixed to form a stable and transportable liquid

suspension(biosyncrude) .

In central plants this liquid suspension will be gasified in an entrained flow gasifier , an oxygen blown slagging reactor with an internal cooling screen. The conversion to syngas takes place at high temperatures and at high pressure up to 80 bar according to the demand of the following synthesis steps.

A costly interim compression step of the gases involving high technical risks is made redundant.

Almost all important chemical base materials as renewable products (btc) and clean and environmental friendly synthetic motor fuels(btl) can be produced from such a bio based syngas.

An overview of the actual status of the joint development will be given.



Dr. Armin Guenther is Director Innovation and Development Renewables at Air Liquide/Lurgi GmbH in Frankfurt. Dr. Armin Guenther studied chemistry at the University of Frankfurt, worked also for the diploma at the CNR Consiglio Nazionale delle Ricerche in Bologna, graduated with a PhD in chemistry at the University of Frankfurt and worked at the Center of Environmental Research (Frankfurt) .

As Head of Department for Project Management and Renewable Energies at an engineering company, he was responsible for national and international projects in the traditional engineering sector as well as for renewable energies and biodiesel. At Lurgi Dr. Guenther was responsible in several functions for the Renewables, e. g. as Sales and Product Manager as well as Director for the Market Group renewables. Presently his position at Air Liquide/Lurgi GmbH in Frankfurt is “Director Development and Innovation Renewables”.

Part IV

The Development, Demonstration and Application of the Bio-fuel Industry Key Technology

The Importance of Separations in Biomass Conversion Processes

Richard S. Parnas

University of Connecticut, USA

1. Introduction

Biomass conversion is the critical step for producing biofuels and bioenergy at a large scale. Once the biomass is converted into well-defined feedstock, processes to produce biodiesel and alcohol fuels are well developed. For example, several review articles have documented the critical role of sugar and lipid extraction processes for the economic use of micro-algae biomass.

There are two important classes of biomass available for conversion: low grade waste products such as brown grease, and high yielding cultivars such as *Jatropha* and algae. Data for brown grease and algae is given below. In both of these cases, low energy, high yield processes can be developed if sufficient attention is given to the separation processes.

2. Brown grease

Brown grease is accumulated fats, oils and greases (FOGS) left over from cooking and cleaning, and is distinguished from yellow grease by its typically very high free fatty acid (FFA) content. Brown grease typically has FFA content ranging from 75% to 100%, although FOGS with FFA over 50% are also classified as brown grease. Economically processing these materials to fatty acid methyl esters, or biodiesel, has proven quite difficult. Several chemical routes are well known, including esterification and glycerolysis/transesterification. In the case of esterification the separations are difficult, and in the case of glycerolysis/transesterification the reaction is relatively slow.

Figure 1a illustrates the ease of esterifying FFA directly to biodiesel at mild conditions, and Figure 1b illustrates the difficulty of phase separating the excess methanol and water after the reaction has reached a high level of conversion. After 2 stages of esterification to convert 99.5% of the FFA to biodiesel, and 1 stage of transesterification to convert the 10% triglycerides in the brown grease to biodiesel, the poor separations led to an overall product yield of only 50%. Improvements in the separations by careful addition of low cost additives can improve the efficiency of each separation stage to above 95%, leading to product yields of over 85%.

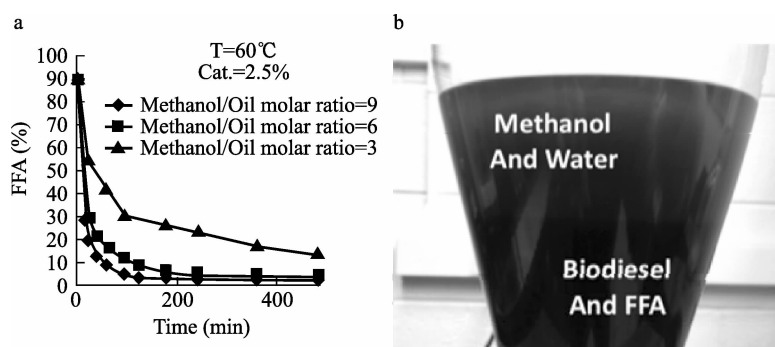


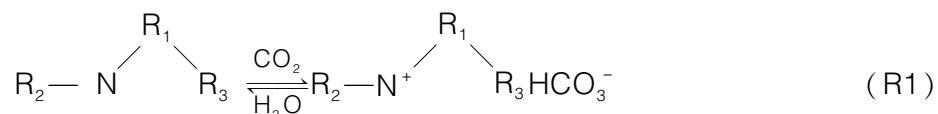
Fig. 1 a. Esterification kinetics to convert FFA to biodiesel.

b. Indistinct phase separation after reaction, providing only 80% product recovery.

3. Algae

Recently developed switchable polarity solvents (SPS) provide a unique opportunity for extracting sugars and other products from algal biomass.

The mechanism for a recently developed class of SPS relies on the reversible reaction of carbon dioxide with water and tertiary amines.



The non-polar form of the amine on the left side is immiscible with water while the ionic form on the right side is completely miscible with water for many choices of the substituent “R” groups. Most interestingly, these compounds display excellent ability to degrade the cell walls of algal biomass. A recently designed process allows the simultaneous extraction of mono- and di-saccharides, lipids, and the polysaccharide of galactose known as agar. The solvent is recycled at ambient conditions by simply

changing its polarity to effect phase separation, providing a highly efficient, safe, and cost effective means of converting algal biomass to high quality feedstock for biofuel production.



Richard S. Parnas is a Professor of Chemical Engineering at the University of Connecticut, a member of the polymer program and head of the UConn Biofuels Consortium. Dr. Parnas has patents for biofuel reactor designs, material formulations for bio-based plastics, and fiber optic sensors for fuel cells. Dr. Parnas's current research focuses on membrane separations for biochemicals and liquid phase extraction technologies for biomass conversion.

Sugar Platform of Lignocellulosic Resources

Guojun Yue

COFCO, Beijing, PR China

Global plants produce estimate 170 – 200 billion tons of biomass every year, and biomass supplies an estimation of 10% of global primary energy supply. The biomass feedstocks that can be utilized for biomass to sugar conversion cover a rather wide range of resources with a variety of forms. Besides the conventional energy crops such as grain crops, sugar plants and oil plants, the biomass resources could roughly be divided into three categories: lignocellulosic feedstocks from agricultural and wood residues, dedicated energy crops like perennial grass and trees; other feedstocks types such as waste from food industry and pulp/paper industry, and municipal solid waste. Based on the intrinsic compositions and geographic distributions of different biomass feedstocks, diversified conversion technologies were developed for transportation fuels, biobased chemicals and other useful products. To this end, the lignocellulosic saccharification technology is the most important step in biomass conversion.

China is currently still a big agricultural country. According to the *National Agricultural Crop Straw Resources Investigation and Assessment Report 2010*, the collective agricultural crop straw is approximately 687 million tons, among which, 265 million tons are corn stover, 205 million tons from rice straw and 150 million tons from wheat straw. Up till now, the utilization rate of China's agricultural crop straw is about 69%. Animal feed, solid fuel and manure are three major uses for this lignocellulosic waste. How to achieve the high efficient logistics is a big challenge in utilization of the huge waste resources. We have now used the agent mode in China for the transportation and logistics of dispersed material like wheat straw, cotton straw and corn stover, which contains collection of waste from the local farmers, the packing and storage of the waste in centers and delivery of the compact waste to processing plants.

There are three major products derived from lignocellulosic feedstocks, differing in types of end use: for heat and power; for transportation in the form of biofuels; for the purpose of synthesis of fine chemicals and polymer materials. The latter two have become more and more important and urgent to our society today since both of them can now only rely on petroleum supply, the price of which sneezes, the world economy would shiver. Biorefinery is used to define the processes of converting biomass waste to useful fuel or chemical products. The common feature of these two conversion routes is the saccharification step of the lignocellulosic material before downstream processing when we are talking about this refinery concept, because if we take a look at the composition of the lignocelluloses, we can always find that in most of the material, around 30%–40% is cellulose and 15%–20% is hemicellulose. In another word, the major two constituents of lignocelluloses are just polymers of monosaccharides (glucose, xylose, arabinose, mannose, galactose, etc.) with the rest of around 20%–30% is lignin complex. In this regard, the establishment of the sugar platform is the prerequisite of biorefinery for important fuel and chemical products.

Currently the environmentally friendly saccharification platform mainly involves two vital steps: pretreatment and enzymatic hydrolysis. The major idea for pretreatment is to alter the recalcitrant nature by breaking the structure of lignocelluloses, which is achieved by opening the bonds between hemicelluloses/lignin and cellulose to expose the cellulose part and to increase the surface area and the accessibility to cellulases. The pretreatment is really important to successive enzymatic hydrolysis not only in the efficiency of the hydrolysis but also the cost of such enzymes. Physical, chemical, physicochemical pretreatment methods are regularly chosen and proved to be effective, and among those, neutral cooking and diluted acid steam explosion techniques are validated in most of the demonstrative plants for cellulosic ethanol globally.

The hemicellulose derived xylose and cellulose derived glucose are major saccharides which could be used to produce biochemical and bioenergy products. In fact, those products like amino acids, organic acids, polyols and biofuels are already manufactured in quite mature ways using starch based grain crops, and also constitute the major businesses of COFCO's biochemical & bioenergy division. But the increasing capability of grain manufacturing and over consumption of food material, has inevitably triggered worldwide concerns about the change of land use and food safety. Meanwhile, building the platform of lignocellulosic derived saccharides to replace the

starch resources, and also to supply the biochemical production industries (such as starchy sugar, organic acids, amino acids manufacturing) with abundant cheap material, will extend the downstream industrial chain and create more profit-growth opportunities, showing significant impact. This would also be strategic direction for COFCO's biochemical & bioenergy division, and remain the technical hurdles.

Fuel ethanol is the major business of COFCO's biochemical & bioenergy division with a stable annual production and 46% market share, which tops of all Chinese producers. The R&D of cellulosic ethanol becomes the most important business of COFCO's biochemical & bioenergy division, the National Energy of Biological Liquid Fuel R&D Center, and also the COFCO Nutrient and Health Institute. As a convenient and facile renewable energy source, cellulosic derived biofuel relies heavily on the feedstocks from food production and processing, with the biomass processing ideas and techniques representing COFCO's philosophy of "Life, Health, Sustainable Development."

The construction of COFCO's 500 t/a cellulosic ethanol pilot plant was accomplished by September, 2006. The testing and running of the facilities has been on for almost 6 years ever since, with non-stop optimization and modification and the ability for long term runs. The pilot plant has been equipped with auto feeding system and domestic pretreatment devices. After the continuous steam explosion, the technology achieved a total solid recovery rate of 90%, hemicelluloses conversion yield of 90%, cellulose enzymatic hydrolysis rate of 80%, sugar-ethanol conversion yield of 80% during the C5/C6 co-fermentation, and beer ethanol concentration of 6% (v/v). The corn stover consumption for per ton of ethanol product is 6 t. Large amount of useful experimental and running data has been collected during the last 6 years, and the distribution of stover resources has been investigated with the establishment of feedstock collection and logistics systems. The preliminary version of process design package for 50 000 t/a cellulosic ethanol plant has been released. Right now, the cost of cellulase has been greatly reduced by 20%, leaving the feedstock cost and energy consumption the major parts. Our next goal in our R&D could be to increase the utilization yield of feedstocks, the energy coupling rate and reduce the infrastructure cost, accelerating the construction of the demonstration plant.



Mr. Guojun Yue, aged 49, professor level senior engineer, was appointed as an executive director and the vice-president of the China-Agri Holding Limited in January 2007, acting as the general manager of biochemical and biofuel division. Mr. Yue joined COFCO Group in November 2005 and has been the assistant president of COFCO Corporation since February 2007. Since November 2007, he has been a board director of COFCO Biochemical(Anhui) Co., Ltd., a company listed on the Shenzhen

Stock Exchange, and as the chairman during the period from November 2007 to July 2011.

Mr. Yue is an expert in chemical engineering accredited by the State Council via a scholarship program in 2007. He was elected as one of the deputies of 11th National People's Congress of the People's Republic of China in February 2008.

Mr. Yue holds a Bachelor's degree from Chemical Engineering Department of Jilin Institute of Chemical Technology, a master's degree from Environmental Engineering from Harbin Institute of Technology and an Engineering PhD's degree from Chemical Engineering and Technology from Beijing University of Chemical Technology. He has over 20 years of experience in the production and sales of bio-chemical products. He was elected as the chairman of China Starch Industry Association in November 2011.

The Role of Duckweed in Bio-liquid Fuel Production and Environmental Protection

Hai Zhao

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With the world economic development, population growth and improvement of people's living standards, the energy shortage has become the core issue of restricting the development of the world economy. China is in the phase of strong economic growth and high energy demand. In 2007, China became a net importer of coal; five years later, became the world's largest coal importer. In 2009, China's dependence on foreign oil was more than 50%. In 2010, China surpasses U. S. as world's biggest energy consumer. Short of supply and with soaring oil prices, gasoline prices have soared from 2.3 yuan/L to 8 yuan/L between 2004 – 2012. Chinese energy supply is already "stretched to the limit"; we should limit electricity in summer. The energy shortage has seriously affected the social and economic development, and would be more intense in future. There is no time for delay on solutions to the energy crisis.

At the same time, environmental pollution is becoming increasingly severe. Currently, China has more than 100 million vehicles, about one tenth of the world; large amounts of greenhouse gas emissions cause serious air pollution. In 2010 total CO₂ emissions of China was 6.8 million tons, 2.3 times of that in 2000. The air pollution index was 2–5 times that of developed countries in Shanghai and Beijing. Water is the source of life; water pollution will directly impact on human life. In China the demand for water is increasing, while water resources are scarce and suffer pollution. 70% of rivers and lakes are polluted and eutrophic, 47% is phosphide rich, and 44% nitride rich. The environmental cost of water pollution was 286.28 billion yuan, accounting for 55.9% of all environmental costs. Control of water pollution is emergency requirement.

With the energy crisis, environmental protection and global climate change, the development of clean renewable biofuels is essential, has attracted the attention of many countries, and achieved remarkable results. The development of biofuels in China is vital at present and will be so in the future, as well as in the past. According to China's energy strategy, the proportion of non-fossil energy consumption has been set to be increased to 11.4% in 2015 and 15% in 2020. However, only 10% of fuel ethanol increase target was finished in 2010. Why couldn't we fulfill the planning target? —food supply security. Food supply security is a priority consideration issue than any other issue. China has a large population but limited arable land. Thus, we need to facilitate new biomass and bio-energy programs according to the strategic principles of Chinese national conditions and national development of bioenergy.

Duckweed, or water lentils, are aquatic plants which float on or just beneath the surface of still or slow-moving fresh water bodies and wetlands. Being the world's smallest flowering plants, they have five genera, 38 species, and are distributed all over the world. Duckweed can feed off wastewater and it can suck up CO₂. Similar to some strains of algae, duckweed contain large amounts of starch that can be processed to create ethanol. This would not only lessen the burden on current corn to ethanol production and the debates on fuel vs food, but it would also lower CO₂ emissions and hence contribute to mitigating climate change. In July 2008 the U. S. Department of Energy (DOE) Joint Genome Institute announced that the Community Sequencing Program would fund sequencing of the genome of the giant duckweed, *Spirodela polyrhiza*. The research is intended to facilitate new biomass and bio-energy programs.

Advantages of duckweed for energy production: Duckweed has a distinct advantage on energy yield. It almost does not contain lignin, but the total starch, which can be converted to fermentable sugars; content of duckweed can vary from 3%–75% of the dry weight depending on strains and species. Its biomass and starch has a great potential to be fermented into butanol and ethanol. Duckweed growing on nutrient-rich wastewater can produce more than five times in biomass than that of corn and is about a third of the theoretical maximum output of algae. The critical advantage of duckweeds is their ready deployment on and easy harvesting from wastewater. If 1% of fresh water surface in China was used to cultivate duckweed, the annual ethanol yield from duckweed biomass would be 1.72 million tons and direct output value would be 10.3 billion yuan. At the same time, 10 million tons of CO₂ emission would be reduced, 12 thousand tons of P

and more than 100 thousand tons of N in waste water would be reduced.

In addition, duckweed grows rapidly, its biomass doubling accumulation time: 2–7 d, which is beneficial for large scale production and a good model for the study of plant growth and development; it has a longer production period (Duckweed can grow when water temperature is above 5 °C): it is possible to supply the feedstock whole year to overcome the bottleneck of seasonal availability of feedstock supply; is almost free of lignin; maximize the utilization of biomass; it is able to treat wastewater, convert CO₂ to biomass and inhibit algae growth; ecological and environmental value; it is high valuable natural product; comprehensive development.

Advantage of Chengdu Institute of Biology on duckweed research

The CIB research areas cover ecosystem, botany, microbiology, breeding, natural product, environment pollution treatment, etc. A more than 30 persons integrate research group was organized to focus on the duckweed as a platform to carry out the following research work: Resource investigation, collection, conservation and evaluation; Novel strain breeding; Scalp cultivate technologies; Pretreatment technologies for bio-fuel production; Fuel ethanol and butanol fermentation technologies; Nature product discovery and comprehensive utilization.

Our work was supported by: The National Key Technology R&D Program “Key Techniques and Demonstration of Fuel Ethanol Fermentation by Non-grain Feedstocks” (2011BAD22B03), and The Knowledge Innovation Program of the Chinese Academy of Sciences.

Duckweed resource: About 600 duckweed populations were investigated and sampled from various locations in China and some of the neighboring countries in Southeast Asia. As a rapid method to estimate multiple parameters of these isolates, near infrared (NIR) absorption spectrum is being applied as a possible method to rapidly index water content, protein content, starch content and total phosphorous. In addition, cultivation of duckweed on domestic wastewater is being performed at a demonstration site next to Dianchi Lake in Yunnan, China. Effective municipal wastewater treatment by duckweed was found to be effective within 7–10 days with a minimum biomass production rate of 36.6 t dry weight/ha · a⁻¹.

Duckweed cultivation and waste water treatment: Duckweed cultivation project on domestic waste water was established—further studies will carry out in the project. The base covers an area of 5 acres; four areas: Y, and A, B, and C; 15 wastewater treatment ponds with multiple processes of the pretreatment. A determination method in

the field of mass culture conditions has been established. Comparison between influent (rural domestic wastewater) and effluent is as follows: Domestic wastewater: COD 125 mg/L, $\text{NH}_4 - \text{N}$ 21.7 mg/L, $\text{PO}_4 - \text{P}$ 3.6 mg/L, turbidity 132.8 NTU; effluent: COD 41 mg/L, $\text{NH}_4 - \text{N}$ <4.5 mg/L, $\text{PO}_4 - \text{P}$ 0.77 mg/L, turbidity 3.1 NTU. Preliminary result of demonstration project indicated that duckweed system is a promising system for waste water treatment and biomass valuable product production: Duckweed biomass accumulation 36.5 t/(ha · a) (dry weight), CO_2 fixation 48.9 t/(ha · a), total N 2.1 t/(ha · a), total P 0.55 t/(ha · a). After treatment, wastewater reached the water effluence standard.

Bio-liquid fuel fermentation: Duckweed is a good resource for bio-alcohol fermentation. Compared with potato starch granule, the duckweed starch granule is smaller, irregular in shape and presented as flake starch granules. According to X-ray, duckweed starch was A-type which was more stable than other types. Pretreatment technologies were developed to increase the fermentation efficiency and reduce 96.37% viscosity of fermentation mash. The ethanol concentration of 7.52% (v/v) was obtained from high-starch *L. punctata*. The achievement means that the ethanol fermentation directly from whole biomass of duckweed is feasible. Butanol from duckweed biomass will have more bright future—The 11.65 g/L butanol, 18.65 g/L total solvent and high butanol ratio of 62.46% were obtained from the high starch *L. punctata* mash, which could be comparable with the fermentation of corn and *canna edulis* ker.

Nature products of duckweed: As energy feedstock, the quantity of duckweed biomass is enough to produce high valuable products after fuel fermentation. But there has been no systematic investigation on nature products from duckweed. We focus on flavonoids compounds and flavonoids component diversity. Cycloartane triterpenoids were discovered in *S. oligoarrhiza* for the first time—a potential value compound. Chemical constituents varied greatly in *S. polyrhiza*, which may correlate with the characteristics of multiploid. Fingerprint data of flavonoids of duckweed will be used to identify duckweed population and develop valuable nature products and evaluate the risk of feedstuff.

Establish a platform and mechanism for international cooperation of duckweed research: The 1st International Conference of Duckweed Research & Applications (ICDRA) was organized and took place in Chengdu, China, from October 7th to 10th of 2011. Hosting of this meeting by Chengdu Institute of Biology (CIB, part of the Chinese Academy of Sciences) is especially appropriate since this Institute has now committed

over 30 researchers to studies relating to duckweed research and applications, and is thus currently the site that has the largest concentration of duckweed researchers in the world. Co-organized with Rutgers University of New Jersey (USA), this Conference attracted participants from Germany, Denmark, Japan, Australia, in addition to those from the US and China.

Future studies on duckweed: Collection, identification and preservation of duckweed resource and new strain breed; Interaction between environment and duckweed (physiology and environment); Genomics, transcriptomics and proteomics study of duckweed; Development of duckweed as a new model organism for botany research; Bioreactor for production of important protein and peptides; Cultivation and harvest technologies development in large scale; Optimum of waste water treatment and biomass production; Duckweed dewater, storage and logistics; Conversion of whole biomass including cellulose and hemicelluloses to ethanol and butanol.

Call for cooperation on duckweed: share of resource, data, information; People exchange; Collaboration on specific project of duckweed.



Hai Zhao received his master degree in microbiology at Chengdu Institute of Biology (CIB) CAS in 1990, and worked first as an assistant researcher and now as a researcher in CIB.

Hai's Zhao research interest is non-grain bioenergy, and his research area includes fresh sweet potato storage technology, rapid ethanol fermentation technology, VHG ethanol fermentation technology, higher ratio butanol fermentation technology and comprehensive utilization technology for sweet potato and duckweed. His work obtained financial support from 17 projects and had some achievement on ethanol fermentation from sweet potato. This technologic achievement will increase net energy outcome and lower the manufacture cost by improving the fuel ethanol productivity. He has authored more than 60 papers, and applied 5 patents.

Breaking the Biomass Recalcitrance for Fuels and Chemicals: Current Challenges and Our Opportunities and Strategies

Jianzhong Sun

Biofuels Institute of Jiangsu University, School of the Environment,
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Current global energy system is largely relied on hydrocarbons such as oil, gas and coal, which provide the basis of most of our energy and chemical feedstocks—in fact, over 90% of all organic chemicals are derived from petroleum. However, crude oil reserves are finite and world demand is growing in an unprecedented scale. It has been reported that the world primary energy demand will grow by 1.6% each year on average during next two decades; and China, if together with India, accounts for just over half of that increase. In the meantime, there is an increasing concern over the impact of these traditional energy consumptions on the environment. In line with the requirements for sustainable economy and clean environments, biofuels from cellulosic biomass have recently received tremendous attention both in industry and academic communities worldwide. It has also been recognized by a number of governments that we need to sustainably reduce our dependence on petroleum feedstock by establishing a biomass-based economy. Indeed, the use of biomass could lead to the creation of a new biomass industry and a new type of agriculture/forestry, i. e. “energy agriculture”, which would help revitalize and expand current formats of the agriculture and forestry.

Biomass has a unique characteristic compared with other forms of renewable energy, which can take various forms such as liquids, gases, and solid, and so can be used for electricity, or mechanical power generation and heat. Today, bioethanol and biodiesel are predominantly produced from corn kernels, sugarcane or soybean oil. But

researchers and investors are increasingly upbeat about another biofuel feedstock, lignocellulose—the most abundant biological material on the earth. Bioenergy developed from energy plants, as well as agricultural residues/forest residues, will play a more and more important role in future energy supply, which can account for at least half of the demands as a energy potential to replace the fossil fuels by 2050 in China. No doubt, alternative and renewable biofuels derived from lignocellulosic biomass, the so-called second generation of biofuels, will offer the biggest potential to reduce our dependence on fossil fuels and mitigate global climate change. However, despite the surging popularity of bioethanol and biodiesel as transportation alternatives, both in current have barely put a dent in our use of oil. It is clear that breakthrough technologies are still needed to overcome barriers, particularly for biomass recalcitrance, to develop cost-effective processes for converting biomass to fuels and chemicals.

To make the designs for cellulosic biofuel industries more efficient and cost-effective, bioengineers are shaving costs from pretreatment that is a crucial challenge for efficient biomass conversion, and biologists are focusing on another two primary bottlenecks that have plagued the technology for decades—the high cost of cellulase complex, and the limited ability of the microbes to ferment the breakdown products. However, over the past two decades, industrial bioethanol technology has mainly been based on biocatalysis and fermentation technologies from bacterial and fungal cellulolytic systems, in combination with breakthroughs in molecular genetics, enzyme engineering and metabolic engineering. In practice, the current state of technology with respect to biomass conversion is still far away from being mature for a large scale application due to its efficiency and processing economics. To improve our current technology, it seems that we need to review our ongoing strategy and explore/learn from other sound cellulolytic systems in nature, such as cellulose-eating animals, wood-feeding termites/insects, or other biomass utilization systems. Animals surviving on lignocellulosic biomass, after a long period of evolution, possess many adaptations, including highly specialized deconstruction systems for a variety of lignocellulosic materials. Such natural biomass utilization systems can process lignocellulosic biomass much more efficiently with their highly specialized biocatalyst systems than those technologies we currently developed, which can truly be considered as the most efficient bioreactors. Thus, recent studies on the utilization of termites or other bioconversion systems may offer a possible option to realize biomass conversion in an

efficient and economical way. At present, it has become a world leading-edge research field to evaluate and mimic a variety of natural lignocellulosic systems, such as wood-feeding termites, to achieve efficient conversion and utilization of lignocellulosic biomass for fuels and chemicals.

This review addresses various lignocellulolytic systems, their potential values, challenges, and opportunities that exist for scientists and industries to advance the biofuel technology, where the following topics will be further addressed: 1) Scientific and industrial potentials of the natural biomass utilization systems; 2) Novel biocatalysts explored from natural biomass utilization systems and their engineering potential for industrial uses; 3) Novel microbial symbionts discovered from natural biomass utilization systems by “omics” technologies; 4) Bioreactor innovations mimicked and advanced from the efficient biomass utilization systems. With this overview, I hope that you can sense the excitement of the scientific endeavors both from China and the rest of the world to crack the hard nut in developing lignocellulosic biofuels.



Jianzhong Sun is a distinguished professor, who also has many other professional titles: Graduate faculty for Ph. D/MS students, Director of Biofuels Institute of Jiangsu University, Associate Dean of School of the Environments, Jiangsu University, PR China, Adjunct professor in Dept. of Biological Systems Engineering, Washington State University, USA, and so on.

Present research interest and areas: 1) develop the advanced technologies for the efficient biomass conversion and utilization; 2) mimic highly efficient natural lignocellulolytic systems (e. g. wood-feeding termites or other cellulose-feeding animals) to advance current bioreactors for biomass conversion; 3) develop dedicated energy crops using bioengineering technology on the structure of plant cell walls for easy bioconversion and processing; 4) develop the advanced technologies for biomass-based plastics and other bio-products; 5) develop the advanced technologies for microbial fuel cells.

As a director and coordinator in Biofuels Institute of Jiangsu University, his ongoing programs, including his research team, mainly focus on the utilization of wood-feeding termites or

other cellulolytic insects to develop the novel bionics technologies for efficient biomass conversion. Currently, ten professional laboratories with different functions have also been established and equipped with the advanced instruments/devices in his team, which mainly include utilization of natural cellulolytic systems, gene engineering, enzyme engineering, bioprocess engineering, symbiotic microorganisms, bionics and novel bioreactor engineering, bio-based products, cellulosic energy crops, microbial fuel cell, and so on. Uniquely, with the exploratory investigations in various natural biomass degrading systems, his research team aims to provide up-to-date and revolutionary technologies via “bioprocessing mimicking” for cost effective and competitive biofuels production using biological pathways.

Separation of Components of Corn Stalk with Active Oxygen and Solid Alkali and Their Enzymatic Hydrolysis

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A novel environmental friendly process of cooking of corn stalk was studied. Firstly, the process condition was researched and optimized, and then the better conditions were obtained. Secondly, it studied the surface characteristics of pulp and discovered the difference between the two pulps from cooking with active oxygen and a solid alkali and alkali cooking. The cooking mechanism of solid alkali and its protection mechanism for cellulose were researched. Thirdly, the change of lignin during cooking was studied. At last, the enzymolysis effect of different pulps or samples was studied.



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Professor Lin is interested in research work of biomass bio-energy and high-value chemicals from conversion of lignocellulosics. He has published more than one hundred peer-reviewed papers in various academic journals at home and abroad, with his

monograph *Chemistry and Technology of Levulinate Acid* published in 2009. He is the laureate of five prizes awarded by the Ministry of Education of China for his active achievements.

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Current States and Perspective of Collection , Treatments and Utilizations of Kitchen Wastes in China

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1. Where it's from and its hazards

Kitchen wastes are mainly produced from the residues from the daily food consumptions. They mainly source from households, the restaurants, and the canteens. The sources of kitchen wastes have some differences with that in developed countries. For example, most universities in China are generally organized well. The university canteens are the necessary department. They take the responsibility for food supply for all the students and faculties in the university. The population in a university is generally 15 thousand. Thus, we can image the produced kitchen wastes are surprisingly huge.

In addition, with the development of economy in China, the scale of cities and the population in cities are increasing dramatically. Thus, the kitchen wastes from the cities grow very fast. Taking Beijing city as an example, it was 1700 ton kitchen waste produced only in one day last year. However, the capacity for the kitchen wastes treatment in Beijing city is only 600–800 tons per day. Thus at least 1000 tons of kitchen waste could not be effectively treated. Actually this is the amount for only one day in Beijing city. How about the situation in whole China? It was 60 million tons for a year, and lower than 30% could be effectively treated. Thus we can image how huge amount of kitchen wastes is in China.

In order to utilize the kitchen wastes, the features should be known firstly. The main

features could be summarized as follows:

1) High content of organic materials. The organic materials approximately occupy more than 93% of the dry matters, in which it mainly include starches, dietary fibers, proteins, and plant or animal greases;

2) High water content. The water content is higher than 85%. High water in the kitchen wastes bring some difficulties in their collection, transport and the subsequent treatment. For example, because the high water content, the kitchen wastes are easily decayed resulting in bad smells and the potentially scattering pathogen;

3) High value utilization can be potentially achieved, for the high organic material contents, and richness in N, P and K, which can be easily used for microorganisms;

4) High grease and salt content, which potentially is not beneficial for treatment, especially with the biological methods.

Currently, most of such kitchen wastes are used for swine forage or for the wastes oils. As we known, these methods are prohibited in China for the reasons of food safety and potential hazards. For examples:

1) Bad smells for people's living conditions;

2) The potential pathogen scattering to threaten human beings' health;

3) The waste oil from kitchen was potentially used illegally as the edible oil, which also threatens people's health.

As a summary, the kitchen wastes should be reasonably utilized based on such features themselves. The suitable utilization method could reduce environmental pollution and obtain high values as well.

2. Current states of collections, treatments and utilizations

From the 1990s of last century, the developed countries, such as Germany, Japan, and South Korea, put much work on the utilizations of the kitchen wastes. The related technologies have been developed very well. For example, the standards for kitchen waste discharge, for the forage and fertilizer were made in the year of 2000. More than 300 kitchen waste treatment processes have been established from 2007 in South Korea. The composting technology was widely developed in USA for supplying the fertilizer to farms. In Germany, the mixing anaerobic digestion and compost were employed for kitchen waste with other organic materials.

In China, the utilization ways for the kitchen wastes mainly included the followings:

1) Directly feed animal as forage and this is the most common way in China.

2) The protein forage by fermentation. The microorganisms were employed to analyze the kitchen waste for the protein from microorganisms. This technology features with high efficiency, short processing time, and low energy consumption. The protein forage could be sold with high price in current market. However, there are still no related national standards for the process. And some potential safety issues should be paid attention to. For example, the harmful microorganisms, the harmful metabolites.

3) Composting technology. The aerobic digestion technology is employed to stabilize the kitchen wastes. Meanwhile, the organic fertilizer also could be obtained. The scale of 200 t/d composting process has been founded in Nangong Composting Plant, Beijing. The obtained fertilizers are mainly used for gardening.

4) Anaerobic digestion for kitchen wastes. The kitchen wastes are digested in the stick anaerobic conditions, and the organic materials are analyzed into CH_4 and CO_2 . As the main products from the anaerobic digestion, the CH_4 could be used for power generation, alternative fuel for vehicles. The residues of the anaerobic digestion could be used as the excellent fertilizer. This way could be maximally utilized for the kitchen waste. Technically, it should be good to completely use the waste. However, there are still some issues that should be resolved before it can be used in application. For example, the pretreatment technology for the kitchen waste, selection technology for raw materials, and the easy acidification in digestion.

Over recent years, this technology has been developed rapidly. For example, the anaerobic digestion plants have been established in Beijing (200 t/d), Shanghai, Shenzhen and other 10 cities

3. The perspective in China

Based on the statements about the kitchen wastes utilization in China, we think it is totally possible to form a high efficient system to utilize the waste in China in recent future. However, some aspects should be given special attention.

1) The information system for the logistics for kitchen wastes including collections, selections and the like. The legislation should be improved to avoid the illegal collection and utilization.

2) The suitable pretreatment ways should be developed and improved according to the features of kitchen wastes in China. Especially for such complex, high salt and oil

kitchen wastes with a few of indigestible materials. Meanwhile the technology for maintaining a stable pretreatment system also should be developed.

3) The thermophilic digestion and high moisture digestion also should be developed to solve the high efficient energy conversion and the health and safety issues

4) The synergic digestion of kitchen waste with other materials with dry fermentation technology to solve the issues of the inhibitions from high salt and oil content, and the difficult utilization of digestion residues with single kitchen waste.

5) The high efficient microorganism reagent should be specially developed for the kitchen waste to overcome the issues of long-time digestion, low digestion rate and high cost.

6) The high efficient digester and related auxiliary equipments for mixing, feeding, heat-exchanging, thermal insulating, data collecting and safety monitoring.



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Xiujin Li studied in Chinese Agricultural University (CAU) and University of California at Davis (UCD) from 1994 to 1998 as Ph. D student and obtained his Ph. D degree from CAU in 1998. After that, he continued his research at UCD as a post-doctoral associate until the end of 2000. Then, he returned to China and joined BUCT. He worked as an assistant professor in Anhui

Agricultural University (1985 – 1987), engineer in Chinese Academy of Agricultural Engineering (1990 – 1994).

His main research interest is solid waste treatment and reutilization with emphasis on biological conversion of biomass wastes into bioenergy and bioproducts. He has participated as principle investigator over dozens of research projects, including national hi-tech R&D project (863 project), national 12th Five-year Plan Key Project of Science and Technology, and other projects from the Environmental Protection Ministry. He currently serves as vice president of China Biogas Association.

Biogasoline and Jet Fuel Production from Biomass by Aqueous Phase Catalytic Reaction

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Now, let's begin with the background of the research shortly. As we all know, China is a big energy consumption country. In 2009, she consumed about 3.066 billion tons of standard coal in the whole year, accounting for 17.5% of the total energy consumption in the world. Moreover, China's crude oil support mainly depends on imports, and in 2012, the amount of importation was 239 million tons, and the import dependence was beyond half of the total oil demand. In the long term, this trend will lead to a serious impact on our national energy security. At the same time, large-scale combustion of fossil fuels can also cause grave environmental pollution. Thus, it is urgent to seek and develop new energy sources, especially environment-friendly renewable energy from biomass due to its abundance of raw materials and cleanness

Biomass is the only organic carbon source of renewable energy, which is very abundant in China. The annual reserves can reach about 920 million tons and release tremendous amounts of energy comparable to that of 40 million tons of oil if making full use of 40% of the total biomass reserves. Therefore, biomass is considered as a potential substitute for fossil fuels. Biomass is traditionally used to produce liquid fuels such as ethanol or butanol through fermentation of sugars which are derived from the hydrolysis of biomass, but this process shows some defects of high energy consumption and low sugar utilization. Herein, our strategy is that biogasoline ranging from C5–C8 alkanes can be obtained from biomass-derived carbohydrates by aqueous phase catalytic processing, wherein biomass is firstly transformed into sugar monomers (e.g., xylose and glucose) via acid or enzymatic hydrolysis. Jet fuel ranging from C8–C15

alkanes can also be generated from the hydrolyzate of biomass containing xylose and glucose, in which process sugars are firstly converted into furfurals therefore carrying out aldol condensation with acetone to form some intermediates, followed by successive hydrogenation and isomerization. This technique has the advantages of simple process, lower system energy consumption and complete conversion of biomass because of fast reaction rate in the liquid phase and the spontaneous separation of alkanes from water. Therefore, it is prospective and promising of biogasoline and jet fuel synthesis from non-grain lignocellulosic biomass by catalytic processing.

Secondly, I describe briefly to you about the technical route of bio-gasoline and jet fuel of biomass. In the process of biogasoline production, hemicellulose in the lignocellulosic plants was pretreated by acid or enzymatic hydrolysis to form xylose, and then cellulose was converted into the corresponding glucose. A hydrogenation catalyst was then adopted to hydrogenate xylose and glucose into xylitol and sorbitol, respectively, which can be successively hydrogenated and reformed and isomerized into C5–C8 alkanes, main components of biogasoline. However, in the process of jet fuel production, sugar monomers (e.g., xylose and glucose) in the hydrolyzate were dehydrated into furfurals or HMF in the presence of strong acid, which then perform the aldol condensation with acetone added into the jet fuel intermediates, followed by successive hydrogenation and isomerization into jet fuel components ranging from C8 to C15 alkanes.

Next, I'd like to mention about the key technologies in the production of biogasoline and jet fuel, such as hydrolysis, aqueous phase reforming, carbon chain growth and synthesis of long chain alkanes. In these experiments, some techniques including high temperature liquid water, ultra-low acid and enzyme hydrolysis and bi-acid coupling hydrolysis were used to investigate the hydrolysis of biomass. The depolymerization of hemicellulose and cellulose can be easily carried out with low energy consumption, high yield of functional monomer and high selectivity of products. Meanwhile, the hydrolysis process and the process aided by metal salts were also explored in detail. Notably, there are two methods that can convert these sugar monomers into high energy fuels. One of them is to adopt the aqueous phase catalytic processing technique to hydrogenate and reform sugars into the corresponding components of biogasoline ranging between C5–C8 alkanes. The technical difficulties in the process are focused on those about the design of the catalyst, the combination of hydrogenation and isomerization and the stability of the catalyst. Herein, we have developed a high

performance nickel-based catalyst supported on zeolite for polyols hydrogenation to replace those noble metal catalysts based on the well designed research of catalyst structure. The catalyst showed excellent activity for the reaction with more than 80% of polyol conversion and 90% of liquid alkane yield. A good isomerization of alkanes was obtained to be about 45.6% in our lab. It is noticeable that the first national 150-ton bio-gasoline pilot plant was built by our institute in 2010, and the system worked stably.

Another technique is to use catalytic processing to control the number of carbon chain by aldol condensation into jet fuels with the combination of two step successive hydrogenation with isomerization. The technical difficulties in the process are mainly those about the design of the catalyst for aldol condensation, the combination of hydrogenation and the design of the reactor. The MgO/NaY catalysts were prepared by a simple and green procedure and exhibited excellent catalytic performance for furfural/acetone aldol condensation in water-ethanol solvent. The furfural conversion and the total selectivity of adol products were both up to 98%. Moreover, the maximum yield of C13 alkanes, one of jet fuel components, arrived at about 90% in the fixed-bed reactor, and the catalyst showed good stability of continuous reaction for 120 h, indicating a promising industrial application. In addition, the 100-ton bio-jet fuel pilot plant is currently under construction.

Finally, some possible problems in the future biorefinery are proposed briefly, and the corresponding solutions are also put forward. The problems may occur in the following four aspects. The first one concerns the lack of a specific evaluation system for bio-gasoline or jet fuel. The second is related to the difficult annual production for the territory and seasonal biomass. The third is focused on the improvement of the key technologies for liquid fuel production. The last one is how to promote comprehensive utilization of biomass. In order to achieve the industrialization of biofuels, some efficient measures should be taken to solve the abovementioned problems. The evaluation standards and norms should be firstly built as soon as possible. Cultivation of herbaceous energy plants should be taken into account to meet the diversification of biomass so as to solve the uncertainty of biomass feedstocks. It is also urgent to develop more efficient pretreatment technology of biomass hydrolysis and utilize fully carbohydrate derivatives and lignin residues for high-value aromatic products or some fine chemicals.



Prof. Longlong Ma is a chief scientist for the 973 Project, vice director of Guangzhou Institute of Energy Conversion (GIEC), Chinese Academy of Sciences(CAS), professor in biomass energy of GIEC, Secretary-General of Biomass Energy Innovation Alliances (BEIO), expert of Agriculture and Forestry Biomass Conversion Technology theme in 12th Five-Year Plan, 863 Program, Director of China Renewable Energy Society, the deputy director of Committee on Biomass Energy Professional Committee.

Prof. Longlong Ma has been working in the field of biomass energy efficient conversion and utilization, energy strategy and etc. , including: 1) the biological fuel efficient preparation and use, 2) biomass pyrolysis, gasification and power generation, 3) biomass total component efficient transfer and utilization, 4) energy technology evaluation and economic analysis.

In recent years, Prof. Longlong Ma has presided over and completed over 30 projects including the national “973”, “863” and some key projects, major projects of international cooperation, the Chinese Academy of Sciences KNOWLEDGE Innovation and Guangdong Province projects and achieved high levels of scientific research achievements and great economic benefit. Prof. Longlong Ma has published more than 70 papers, applied for 30 national patents, 7 monographs and was awarded second price of the National Science Progress in 2008.

Biorefinery of Lignocellulosics

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China's oil import has surpassed 50% of total oil consumption, and greenhouse gas emission ranks at front row worldwide. Resources and environmental issues have become the main bottleneck for China's sustainable economic and social development. By use of huge annual production of renewable non-food lignocellulosic resources to produce liquid fuels and chemicals, which are in urgent need, we can partially substitute scarce oil resources, break through these bottlenecks, and achieve sustainable economic and social development. Its core technology is the key technology to achieve the economic system reform and develop new industries after the financial crisis. Among them, the cellulosic ethanol production technology has been chosen as first breakthrough point for long term. However, because lignocellulosic materials are a result of long-term plant evolution to form their supportive and protective structures, direct degradation and conversion by microorganisms and their enzymes are very difficult. So the process is complex. This, together with the fact that ethanol as a fuel has too low product prices, has led to the situation that cellulosic ethanol production is unable to compete economically with petrochemicals and food processing products.

At present, most of the research institutes and enterprises are trying to produce ethanol as a unique product from straws and other raw materials, which results in the cost of raw materials and pretreatment becomes the highest proportion in the total cost of production. The components in raw materials cannot be fully utilized, and the final value is not maximized. This is one of the main reasons why cellulosic ethanol process has not been able to be industrialized. Especially, fundamental breakthrough in enzyme production technology and construction of pentose fermentation strains has not been made yet in China. If the low-price fuel ethanol was the only product, it is estimated that

production costs would be significantly higher than the cost of the current grain ethanol. In present pilot studies, the raw material consumption per ton of cellulosic ethanol is usually more than six tons. The estimated production cost is more than 8000 yuan/t ethanol, and the actual operation may be even higher; thus it cannot achieve large-scale industrial production. Therefore, to introduce new ideas and technologies is urgently needed. The introduction of the biorefinery concept and practice is one of the fundamental ways to resolve these contradictions.

An important experience in modern petrochemical industry is that each component in the complex substrate such as crude oil should become different products by fractionation and catalytic conversion technologies, respectively. Even the residue in the industrial processing, such as asphalt, should be converted into an appropriate product, in order to maximize the total value. This is the so-called “refining (refinery).” This concept has been introduced into the biomass resource exploitation. A new concept of “biorefinery” is proposed; the biomass-based chemical industry is also necessary to break the traditional concept in which only a single product was produced from original complex raw material. We should fully utilize every one of the main components in the raw materials, transform them into different products, in order to maximize the value of products and efficiency of land utilization.

Lignocellulosic biomass can be refined into food, feed, chemicals, materials and fuel and so on, to meet social needs of human being. To achieve a refining, first of all, the complicated raw material should be separated into its components, and then convert them to different products. Lignocellulosics in plant cell wall contains three main components—cellulose, hemicellulose, and lignin. The components can be converted into different chemicals: cellulose can be disconnected to glucose, then glucose fermented to ethanol, organic acids or solvents; hemicellulose can be hydrolyzed into xylose and other monosaccharides or oligosaccharides, xylose derivatives can produce a variety of functional foods, furfural and furan resin precursor; lignin is polymer of phenyl propanoid derivatives, which has high calorific value, can be used as high-quality solid fuel, or used as additives for concrete, asphalt, other construction materials or plastics such as polyurethane, or for the production of high value aromatic compounds (such as vanillin). By the production of a variety of products at the same time, we can take full advantage of a variety of lignocellulosic components and intermediates with different performance, to get the maximum value from lignocellulosic

materials.

Shandong University has long been engaged in the basic and applied research of cellulases, and made a lot of achievements. Shandong Longlive Company in Yucheng has established a corncob-process technology for production of xylose series, and has achieved large-scale industrialization. Based on these, we proposed a technical route to use corncob-xylose to process residue, producing cellulases and fuel ethanol. By successful production of value-added products such as xylitol, xylooligosaccharides (XOS), etc from corncob hemicellulose, the solid structure of cellulose, lignin, is loosened during the processing, providing a raw material which is easy to be enzymatically hydrolysed for the next step. The cost of raw materials and pretreatment can be merged into the production cost of high value-added products, so the economics of cellulosic ethanol production is improved remarkably. Since the hemicellulose part of the corncob has been converted into high-value products, the difficulties in hemicellulose to ethanol conversion have been solved. The remaining lignin can also be used to produce high-value chemical products, to form diversification of products and reasonable industrial structure, thereby increasing the overall economic benefits of the production process(Fig. 1).

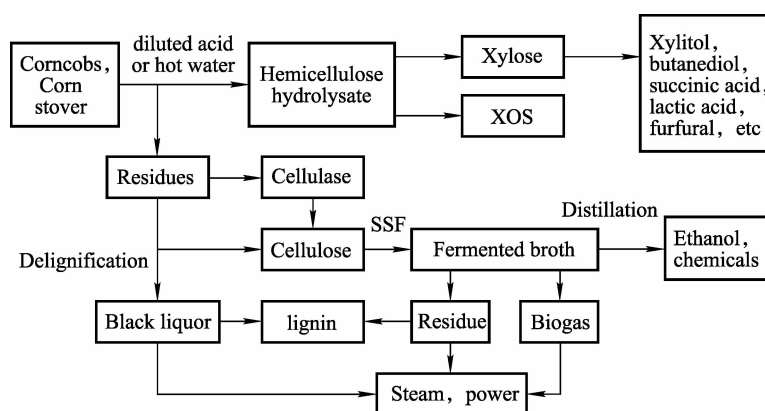


Fig.1 Corncobs or corn stalks biorefinery process schematic diagram

In the new technology, by using proprietary industrial cellulase over-producing strains of *Penicillium decumbens*, using xylose residue and other industrial waste as the main component of fermentation medium, and on-site production of crude cellulase fermentation broth in order to avoid the increased cost of processing enzyme preparation and large scale transportation, the enzyme cost for cellulosic ethanol production has been significantly reduced. In the same time, by the functional genome study, protein

secretomics analysis, and using simultaneous saccharification and fermentation, fed-batch fermentation, pH segmented control and other new technologies, series of technical problems, such as lack of nutrients in the xylose residue medium, increased broth viscosity, unstable pH, easiness to spray material or material pegged to the wall of fermentors during cellulase production, low product ethanol concentration, have been overcome. A complete set of production technology has been invented.

On the basis of these technological inventions, we have built a first pilot plant and a set of demonstration units, which can produce 3000 and more than 10,000 tons of cellulosic ethanol per year from corncob residues, and implemented new technology on a large scale pre-production. The production cost is close to the level of grain ethanol production. Related technology has obtained a Chinese patent, and won the Technical Invention Award of Shandong Province in 2009, and the National Technology Invention Award in 2011. The new technology has successfully passed the environmental assessment by the State Ministry of Environmental Protection. Recently, the 50,000 t/a cellulosic fuel ethanol project of Shandong Longlive Biotechnology Co., Ltd. has been approved by the National Development and Reform Commission, bringing it to be the first state formally approved cellulosic ethanol production plant.

After the lignocellulose biorefinery concept was raised, new technology rapidly expanded. Jinan Shengquan Group has developed an integration of new energy – new materials (furfural—ethanol—lignin Power co-generation) technology, has completed the construction of industrial-scale installations, and will enter production phase soon. Through cooperation between the Institute of Process Engineering of Chinese Academy of Sciences and other scientific institutes with Songyuan Biochemical Butanol Co., Ltd., Jilin, etc, the “butanol fermentation of straw hemicellulose with comprehensive utilization technology” project has been completed. By the new technology, corn straw biorefinery cogenerating butanol – cellulose derivatives—polyol—has entered the stage of industrial development.

Through arduous efforts, we hope to eventually be able to use all of biomass feedstock (starch, sugar, cellulose, lignin, etc.), to diversify the products (fuels, bulk chemicals and fine chemicals, pharmaceuticals, feed, plastics, etc.), forming a giant biomass refining industry, partially substituting fossil resources, achieving a sustainable economic and social development based on carbohydrates.



Yinbo Qu is professor of microbiology, director of State Key Laboratory of Microbial Technology, Dean of Life Science School, Shandong University, Vice President of Chinese Society for Microbiology, Advisory Board Member of Asia Federation of Biotechnology, deputy editor of *Acta Microbiologica Sinica*, Editorial Advisory Panel Member of *Biofuels*.

Research interest: Biodegradation of lignocellulosics by microorganisms; lignocellulosic enzyme system of *Penicillium decumbens*; enzyme engineering; microbial technology for bioconversion of renewable biomass resource, especially cellulases production and biorefinery of corncobs for cellulosic ethanol production. With cooperation with his colleagues, more than 270 papers and 10 books were published in his research fields.

State-of-the-art Research Progress of Aviation Biofuel Using Biomass Wastes in Tianjin University

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1. Background

According to the International Energy Agency (IEA), aviation contributes approximately 2–3 percent of the world's anthropogenic carbon dioxide (CO_2) emissions, but has received considerable attention regarding these emissions. In 2007, the European Parliament voted to bring aviation into the European GHG-emission trading system (EU-ETS). This legislation would require all airlines flying within or into Europe region decrease their greenhouse gas (GHG) emissions by 10 percent or buy CO_2 allowances on the open market after it takes effect in 2012. The aviation industry is facing billions of dollars in added costs from their prospective, required carbon credit purchases via their entry into the EU's emissions trading scheme. In order to deal with this crisis, aviation industries explored several improvements on engine & airframe technology, operation & fleet management and other measures. Moreover, alternative fuel is an imminent part of the aviation industry's future. Renewable jet fuels could significantly lower GHG emissions and can provide a long-term sustainable alternative to petroleum jet fuel. Following the first successful biofuel flight of a Virgin Atlantic Airways 747–400, three more commercial airlines conducted successful in-flight tests using sustainable alternative jet fuel. The fuel was produced from second generation sources, including camelina, jatropha and algae, reducing the fuel's carbon footprint by 80% relative to jet

fuel without competing for resources with food production.

2. Technologies

2.1 FT

Fischer-Tropsch (FT) chemistry understandably is often regarded as the key technological component of schemes for converting synthesis gas (or “ syngas ”) to transportation fuels and other liquid products. German researchers Franz Fischer and Hans Tropsch developed this method bearing their names in 1922 as a method for making liquid fuels from coal over alkalized iron chips at 673 K and under high pressure (> 100 bar). FT fuels have several characteristics that make them attractive as a jet fuel. Their higher specific energy leads to a small reduction in the amount of energy required to fly a given distance with a given payload and could allow for increased payload capacity. FT fuels are clean burning without sulfur dioxide (SO_2) or sulfuric acid (H_2SO_4) aerosol emissions, thus leading to increased combustor and turbine life, and their improved thermal stability should reduce deposits on engine components and fuel lines.

The FT process produces a mixture of hydrocarbons (HC) with carbon chains corresponding to gases (range from C1 to C4), liquids (from C5 to C20) and even waxes (> C20). The FT approach provides a series of production of liquid fuels, including jet fuel, from various carbonaceous feedstocks, of which the most relevant are coal, natural gas, and biomass. The first plant used coal as the starting material; this conversion is called coal-to-liquids or CTL. The current generation of plants will use natural gas as the starting material; this is called gas-to-liquids or GTL. Biomass can also be used as the starting material by going through a gasification step to produce carbon monoxide; this process is called biomass-to-liquids or BTL.

2.2 Hydrotreating renewable process

Alternative fuel is an imminent part of the aviation industry's future. The aviation industry is hopeful about alternative fuels for the potential environmental benefit of reduced life cycle greenhouse gas emissions and the economic benefits associated with increased fuel availability and lower fuel costs. Vegetable oils and animal fats can also be hydrotreated to produce high cetane numbers and straight chain alkanes ranging from

C9 to C18 that can be used in the aviation industry. The hydrotreating process conditions are with temperatures of 350°C–450°C, pressures of 40–150 atm, liquid hourly space velocities 0.5–5.0 h⁻¹, and sulfided NiMo/Al₂O₃ catalysts. Then the alkanes can also be isomerized using molecular sieve or zeolite catalysts. Syntroleum has licensed its Bio-Synfining process to Dynamic fuels. UOP has successfully commercialized the deoxygenating process to convert vegetable oils and wastes to green jet fuels. UOP has produced several thousand gallons of renewable jet fuel from a variety of feedstocks, including first generation oils such as palm and soy, as well as transition and second generation oils like camelina, jatropha and algal oils.

2.3 Synthetic hydrocarbon process

Alkanes can also be produced from sugars by chemical processes including a step called aqueous phase reforming (APR). This involves catalytic dehydration, hydrogenation and aldol-condensation reactions. The Virent ‘BioForming’ process is an integrated catalytic method, which combines the APR technology and other conventional catalytic processes, to convert sugars into high-energy conventional liquid fuels (hydrocarbon molecules). The feedstock is a solution of water and water soluble oxygenated hydrocarbons, like sugars, sugar alcohols, and other polyhydric alcohols. First, the water soluble carbohydrates may undergo an initial hydrotreating step to convert the sugars and organic acids into polyhydric alcohols. Then, the aqueous product stream from the hydrotreating step above is fed into the APR reactor to proceed the aqueous phase reforming, which is the key step in the bioforming process. Usually, the aqueous phase reforming process utilizes heterogeneous catalysts at moderate temperatures and pressures to reduce the oxygen content of the carbohydrate feedstock. At last, the jet fuel products can be produced using a base catalyzed condensation route.

3. Materials

3.1 Jatropha

Jatropha is native to Central America with a height of about 3 m and good adaptability in tropical and subtropical climates. The non-edible oils and fats contained in the trees can be used to produce fuel and each seed can produce 30%–40% of oil. Jatropha is

resistant to drought, pests and diseases without competing with food resources. After 2 or 3 years, jatropha could grow to maturity and can live for 40 years with a height of over 4 meters. The carbon dioxide absorbed from the atmosphere by jatropha is far beyond that they released to the atmosphere. Moreover, the *Scientific American* magazine evaluated jatropha as “green gold in the bush” in 2007, just because this miraculous tree species can also stabilize and restore degraded soil.

The world's first commercial aircraft flight test was carried out by Air New Zealand on December 3, 2008. A 747-400 aircraft was used in the flight test, while one of the Rolls-Royce RB211 engines was driven by mixed fuel, which was mixed by second-generation sustainable biofuel and Jet A-1 conventional jet fuel with the ratio of 1:1. The biofuel test flight results showed that 12% of the fuel would be saved in B747 with the 50:50 mixtures of jatropha oil fuel and standard jet fuel. Also, the carbon dioxide emissions will reduce by about 60 to 75 percent.

3.2 Microalgae

Microalgae are currently under consideration as a next generation feedstock for the production of biofuels. Compared to first generation biofuel feedstocks, microalgae are characterized by higher solar energy yield, year-round cultivation, the ability to grow in lower quality or brackish water, and the use of less and lower-quality land.

Biofuels from algae are promoted as the environmentally sustainable alternative to current agrofuels. There are inherent problems with this technology, at least as far as nongenetically engineered algae are concerned: Algae either maximise growth or they maximise oil production, not both. Growing just one ‘optimum’ type of algae would be difficult because those would be vulnerable to predators and to being out-competed by other algae. Closed ‘bioreactors’ provide higher yields than open ponds, but they require significantly greater capital and energy input. One company—Solazyme (supported by Chevron)—is using algae to produce a different type of biofuel, one which the company state has passed “the biggest hurdles” to being approved as a jet fuel. Solazyme has used synthetic biology to ‘engineer’ algae which get their energy not through photosynthesis, but through immersion in sugar. This means that they would rely on agrofuel feedstocks such as sugar cane, which have large land requirements.

3.3 Camelina

Camelina is also known as “happy gold” or false flax with high oil content (usually

containing 35%–38% oil) and alternately planted with wheat and other cereals. First from Northern Europe and Central Asia, it is mainly grown in the milder areas, such as the northern plains of the United States and Canada.

Japan Airlines first carried out a test flight with the Pratt & Whitney engine fueled by three second-generation biofuel mixtures, whose compositions contained camelina oil (84%), jatropha oil (less than 16%) and algae (less than 1%). Michigan Technological University researchers determined greenhouse gases emissions throughout the life cycle of aviation fuel with camelina as raw materials. The results show that some of the unique properties were detected for the camelina, such as low demand for fertilizer and high oil production. Besides, its byproducts can also be used as the high value-added materials. According to this study, a 60%–85% reduction in GHG emissions can be achieved from current technologies that produce bio-SPK relative to petroleum-derived jet fuel.

4. Technology progress

Among these jet fuel technologies, the FT synthesis and the renewable jet fuel process will supply alternative fuels for the potential environmental benefit of reduced life cycle GHG emissions and the economic benefits associated with increased fuel availability and lower fuel costs.

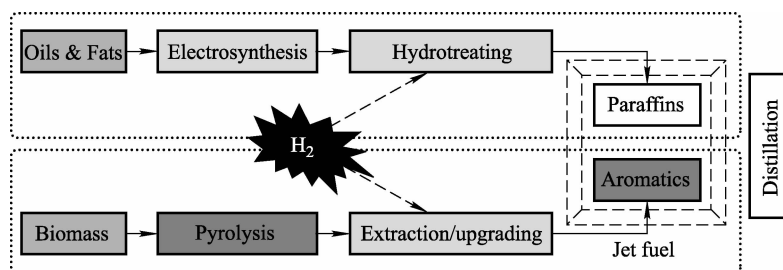
The FT approach provides a means of producing a slate of liquid fuels (including jet fuel) from various carbonaceous feedstocks, of which the most relevant are natural gas, coal, and biomass. All jet fuels produced using FT synthesis have similar characteristics, regardless of which feedstock is used. Fischer-Tropsch (FT) chemistry understandably is often regarded as the key technological component of schemes for converting synthesis gas (or “syngas”) to transportation fuels and other liquid products. However, syngas production itself accounts for more than half of the capital investment. The availability of FT jet fuels within the next decade depends on feedstock, the world price of oil, resolving uncertainties in production costs, and regulatory and technical issues associated with capturing and sequestering large quantities of CO₂.

The renewable jet fuel processes such as Bio-Synfining (Syntroleum) and Ecofining (UOP) both are low capital cost processes for producing high quality synthetic paraffinic kerosene (SPK) from bio-renewable feeds like vegetable oils, animal fats, greases, jatropha, algal and wastes. The SPK has superior product properties to other

options available today, with higher cetane number, lower cloud point and lower emissions. The renewable jet fuel SPK can be used in today's tanks, pipelines, pumps and automobiles without changes, which will save significant expense as demand for renewable grows.

5. Technology from TJU

Fatty acid methyl esters (also called biodiesel) are renewable fuels manufactured by the transesterification of vegetable oils or animal fats. It was also considered as an alternative to jet fuel components with the reason that it can be used as a substitute for or as an additive to mineral diesel. However, its poor low-temperature properties and high oxygen content limit its wide commercial application as jet fuel component. Tianjin University developed a new method (C – LTM process) to produce wide-cut aviation biofuel (carbon number ranged from 5 to 15) from fatty acid methyl esters. There are three main steps in this technology. First, the feedstock fatty acids or fatty acid methyl esters were hydrotreated to eliminate the side effect of double bonds. The products from the hydrotreating process undergo the Kolbe reactions to convert into long chain hydrocarbons. The optimum conditions for Kolbe reaction were that the potential was higher than 7.5 V and 20 wt. % of KOH was used as the support electrolyte with a temperature of $45^{\circ}\text{C} \pm 5^{\circ}\text{C}$, while the methanol as solvent. At last, the hydrocracking process was used to change long chain hydrocarbons into desired jet fuels, which have similar properties with bio-SPK obtained from UOP's Ecofining SPK process. However, this process could undergo effectively at lower hydrogen pressure and the hydrogen consumed during the whole process would be supplied by this closed system itself (hydrogen was byproduct during Kolbe electrosynthesis).



6. Concluding remarks

All renewable jet fuel processes such as Bio-Synfining (Syntroleum) and Ecofining as

well as C – LTM process(Tianjin University) are low capital cost processes for producing high quality SPK from bio-renewable feedstocks like vegetable oils, animal fats, greases, jatropha, algal and wastes. The SPK has superior product properties to other options available today, with higher cetane number, lower cloud point and lower emissions. The renewable jet fuel SPK can be used in today's tanks, pipelines, pumps and automobiles without any changes, which will save significant expense as demand for renewable grows.



Guanyi Chen is Dean of Faculty of Environmental Science and Engineering, Tianjin University. He has been responsible for a number of large research and development projects at local, national and international level in the field of Energy Production from Biomass and Wastes in last 5 years. The donors for those projects are National Science Foundation of China, Ministry of Science and Technology, Ministry of Education, Tianjin Municipality, and European Commission as well as domestic and international industrials.

He participated in a number of professional international/domestic conferences as jointing organiser, oral speaker, plenary session speaker, and scientific committee member. He has published more than 70 scientific papers, obtained 6 patents, and served in several professional societies including international scientific journals and Chinese scientific journals. Currently he is a member of International Solar Energy Society, member of American Chemical Society, executive member of Chinese Renewable Energy Association, executive member of Chinese Society of Agro-Ecological Environment Protection, and executive member of Chinese Association of Urban Environment and Sanitation. He is the associate editor of *Chinese Engineering Thermophysics*, *Journal of Chinese Solar Energy*, and *Journal of Chinese Biomass Conversion Process*. He plays an active role in reviewing different-level R&D projects and scientific journals.

Research interest includes: Biomass to bioelectricity, syngas, hydrogen by innovative thermo-chemical process; Biomass-based liquid fuels production coupling innovative thermal-chemical-biological process; Algae-based energy plant and biomass energy system assessment; Waste incineration process improvement and pollution control. External experiences: academic visiting

and exchange at Washington State University, University of California at Davis and Los Angeles, National Renewable Energy Lab (USA); Lund University (Sweden); Delft University of Technology, Leiden University, Netherlands Energy Research Centre(the Netherlands); Perugia University(Italy); Technical University of Denmark(Denmark); Technical University of Vienna (Austria), Technical University of Berlin(Germany), University of Nantes(France), etc.

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Fuel Ethanol Production from Agricultural Residues by Self-immobilized Yeast

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High cell density and productivity cannot be achieved for freely suspended cell culture and fermentation systems under chemostat conditions, due to the auto-balance between cell growth within bioreactors and the washing-out of cells with the effluent. Immobilized cells with supporting materials were thus proposed in the 1970s, and have been intensively studied within the past decades, but unfortunately most of them were not successful in industrial applications, particularly in the production of bulk commodities like fuel ethanol. The reasons for this phenomenon mainly rest with: 1) cell growth is significantly compromised by the physical constraint of supporting materials, making immobilized cells unsuitable for the production of primary metabolites like ethanol, whose production is tightly coupled with cell growth; 2) extra cost in the preparation of immobilized cells at large scale and high risk of microbial contamination make the immobilized cells economically not competitive; 3) contamination of the supporting materials to the quality of co-products like yeast biomass in ethanol production further makes immobilized cells unacceptable in industry.

Some cells can flocculate during culture and fermentation to form flocs with desirable size distributions, which are suitable for immobilization within bioreactors without consumption of supporting materials. Apparently, the self-immobilized cells can overcome technical and economical disadvantages of immobilized cells with supporting materials. Taking ethanol fermentation as an example, a self-flocculating yeast with excellent ethanol fermentation performance was developed by the protoplast fusion technique from the self-flocculating yeast *Schizosaccharomyces pombe* and the non-flocculating yeast *Saccharomyces cerevisiae* for ethanol production in industry, and

the suspended-bed bioreactor (SBB) suitable for continuous ethanol fermentation with the self-immobilized yeast cells was figured out, correspondingly. Furthermore, the ethanol fermentation system was optimized based on the kinetics of yeast growth and ethanol production, and a pilot plant composed of 4 – SBB in series, each with a working volume of 100 m³, was established with an ethanol production capacity of ~40 t/d to verify the technical and economical performance. Finally, this innovative ethanol fermentation technology was commercialized in the BBICA's fuel ethanol production.

Update research progress indicates that stress tolerance can be improved significantly when cells self-flocculate due to enhanced synergistic effect associated with the morphological change through the quorum sensing mechanism, indicating that robust strains could be developed from the self-flocculating yeast by engineering it with the pentose metabolic pathway for fuel ethanol production from lignocellulosic biomass like agricultural residues.



Fengwu Bai received his BSc and MSc at Dalian University of Technology (DUT), China, and PhD at University of Waterloo, Canada, majoring in Chemical Engineering. He has been working as a fulltime professor at DUT since 1999, and currently his research focuses on the robust production of biofuels, bioenergy and bio-based chemicals, with more than 120 papers, 4 book chapters and 3 books published, and 3 patents licensed.

He is a member of the IUPAC Subcommittee on Biotechnology, an executive board member of Asian Federation of Biotechnology (AFOB) and Editor of *Biotechnology Advances* (Elsevier). He also serves on the editorial board for other flagship biotechnology journals including *Biotechnology for Biofuels*, *Biotechnology and Bioengineering*, and *Journal of Biotechnology*. His research achievements have been acknowledged internationally with awards like the UNESCO – ASM MIRCEN Award and lectures invited at prime international biotechnology conferences as well as visiting professor at world-famous universities including Massachusetts Institute of Technology (MIT), USA. As the main organizer, he successfully organized the IUPAC-sponsored 13th International Biotechnology Symposium (IBS2008) in Dalian, China.

Integrated Production of Both High Value Bioproducts and Biofuel from Microalgae as well as CO₂ Biofixation Based on A Series of Novel Cultivation Techniques

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With the dwindling of fossil fuels supply and the urgent need for the development of low-carbon economy, microalgae bioenergy and CO₂ biofixation have become two of the worldwide focuses. The commercialization of both microalgae bioenergy and CO₂ biofixation are the representative bio-product engineering process combined with agriculture and industry, which involves multiple disciplines. High cost and various kinds of resources matching problems (e.g., CO₂, water, land, etc) are bottlenecks limiting the commercialization of both microalgae bioenergy and CO₂ biofixation, which must be overcome. Due to the current low price of energy products, the technology, which can achieve the industrialization of both microalgae energy and CO₂ biofixation in the near future, must be able to produce some microalgal products with high values in the meanwhile. Namely, in the development of the strategic emerging industries of both microalgae energy and microalgae CO₂ biofixation, the technical upgrading and application expansion of current microalgae industry will be necessary.

There are various categories of microalgae, but only a few species have been phototrophically cultured outdoor in large scales. However, *Chlorella* sp. is the only one species that can not only be cultured massively with sunlight but also accumulate lipid with high content.

Our group has pioneered a novel cultivation technique namely Sequential

Heterotrophy-Dilution-Photoinduction (SHDP) in the field of microalgae cultivation. By using the novel technique, *Chlorella* sp. cultivation with high density and high quality has been realised. With many advantages, such as low cost and enclosed cultivation, this technology is expected to completely replace the photoautotrophic cultivation technology commonly used for producing the *Chlorella* powder which is widely applied in the fields of food and feed. Moreover, *Chlorella* sp. can also accumulate both lutein and lipid with high content by optimizing the culture media and cultivation process, which can be combined to reduce the production cost of biofuel. In addition, the application of the technology can achieve the cultivation of *Haematococcus pluvialis* with high density and high quality to produce the high-value product.

To overcome the long period of seed cultured photoautotrophically and inadequate cell supply for the inoculation of microalgae photoautotrophic cultivation, a novel technology for the photoautotrophic culture of *Chlorella* sp. with heterotrophic cells as seed (PC – HS) was developed for large-scale biomass and lipid production. In addition, the optimization method of photobioreactors based on computational fluid dynamics (CFD) has been established initially, and the sensitivity parameters for photobioreactor optimization and its scale-up have been obtained.

In order to implement the CO₂ biofixation, the fermentation and boiler exhaust gas generated from the *Chlorella* heterotrophic process can be used as CO₂ source for photoautotrophically cultivating *Chlorella* sp. with high lipid productivity. Furthermore, the proposed process combining the production of *Chlorella* powder and the biofuel can not only exhaust no CO₂, but also resolve the matching issue of CO₂ source for commercialising microalgae bioenergy.

Based on the series of novel cultivation techniques including SHDP and PC – HS, the above development strategy, which integrates the production of both *Chlorella* powder and microalgae bioenergy as well as CO₂ biofixation, is expected to accelerate the industrialization process of both microalgae energy and CO₂ biofixation.

The pilot process of the development strategy was investigated in Jiaxing Zeyuan Biological Products Co., Ltd, in order to firstly achieve the following three industrializations at home and abroad; the first one is the industrializations of the SHDP culture technology to produce the high quality products of *Chlorella* and *Haematococcus pluvialis*, the second one is the industrializations of microalgae energy, and the final one is the industrializations of microalgae CO₂ biofixation, while achieving low or zero net

emissions of CO₂ in the processes.

In this paper, the pilot results will be introduced systematically, and the industrialization process will be out-looked.



Yuanguang Li is the founder and head of Marine Bioprocess Engineering Group, State Key Lab of Bioreactor Engineering, East China University of Science and Technology (ECUST). Li has over 17 years of R&D experience in microalgae, and serves as the Chief Scientist of National Basic Research Program of China in the field of microalgae biofuel. Li's academic training was at ECUST and Tsinghua University in China, where he received his M. S. and Ph. D degrees, both in Chemical Engineering.

His research fields include microalgal biotechnology; Microalgal bioenergy and CO₂ biofixation; Design, optimization and scale-up of photobioreactor; Photoautotrophic, heterotrophic, mixotrophic and Sequential Heterotrophy-Dilution-Photoinduction (SHDP) cultivation technologies of microalgae; Microalgal molecular biology; Biopesticides; R & D of novel microbial pesticide and commercialization, especially biopesticide to prevent earth born diseases with strains of *Paenibacillus polymyxa* and *Bacillus marinus*; R & D of novel agricultural antibiotics from marine microbiology; Fermentation engineering; Process development, optimization and scale-up as well as commercialization of fermentation processes for bioproducts.

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Fuels and Feedstock from Biomass: the View of Bayer Technology Services

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Bayer is a global enterprise with core competencies in the fields of health care, nutrition and high-tech materials. As an inventor company, it sets trends in research-intensive areas. Bayer's products and services are designed to benefit people and improve the quality of life. At the same time, the Group aims to create value through innovation, growth and high earning power. Bayer is committed to the principles of sustainable development and acts as a socially and ethically responsible corporate citizen. In fiscal 2011, the Group employed about 112,000 people and had sales of 36.5 billion. Capital expenditures amounted to 1.7 billion, R&D expenses to 2.9 billion.

Bayer is represented in Greater China by its Bayer HealthCare, Bayer CropScience and Bayer MaterialScience subgroups and the service company Bayer Technology Services, and operates several production facilities there. Local production now accounts for an increasing proportion of sales in Greater China. With a number of major investments under way, Bayer is positioned to remain a key partner in China's development.

We are convinced that Bayer can only be commercially successful over the long term if we balance economic growth with ecological and social responsibility. Bayer regards itself as a member of society and believes it needs society's long-term acceptance to be able to act entrepreneurially. We allow ourselves to be guided by long-term values in the implementation of our sustainability strategy. Our commitment to sustainability is underlined by clear references to the topic in our mission statement "Bayer: Science For A Better Life," our pledge to the ten principles of the United Nations Global Compact, and our participation in the Global Compact's new

“Corporate Sustainability Leadership—lead” initiative launched in 2011 and the chemical industry’s Responsible Care? initiative.

Bayer also wants to meet its responsibilities in matters of climate change. We take climate change as an environmental and economic challenge seriously. It affects the foundations of our commercial activity. On the one hand, endeavors in the field of environmental protection have to be strengthened. On the other, greater attention needs to be paid to innovative solutions to deal with the consequences of climate change. Bayer intends to make specific contributions to both.

We intend to intensify our efforts even further. We have set ourselves the following climate objectives:

Intensifying efforts in energy efficiency and emission reduction: We are continuously working on minimizing our own carbon footprint by improving operational efficiency as well as our customers’ carbon footprint by providing market solutions. Our efforts to reduce emissions cover all operations. When it comes to our production sites, we have already made great progress: Between 1990 and 2005, we cut our greenhouse gas emissions by more than a third, primarily as a result of improved energy efficiency through improved technologies, new chemical processes and the application of approaches like our Bayer Climate Check and our innovative energy management system STRUCTese. Our activities in production are supplemented by supporting initiatives in sales (e. g. improved car fleet) and administration (e. g. substitution of business travel by videoconferencing and initiatives like Bayer Green Office and Green Data Center). For the years 2005 – 2020 we set a new ambitious target: We want to further reduce our greenhouse gas emissions per ton of product sold by ~35 percent.

Developing market solution: In many different ways, our products play their part in saving energy and conserving resources. Examples are our polyurethane materials for insulation and our polycarbonate products for lightweight solutions in mobility. With its EcoCommercial Building Program, Bayer integrates all players in building construction and promotes the use of construction material to further reduce emissions. As an innovator company, we have initiated various research and development projects to develop new solutions. Our project portfolio covers solutions for climate mitigation—e. g. a technology that improves energy efficiency in chlorine production by 30 to 50 percent—as well as solutions for climate adaptation—e. g. the development of stress tolerant plants that can better adapt to changing climate conditions.

Expanding partnerships: Climate change is an enormous challenge that no player can tackle alone. We believe that high-profile partnerships are required to improve impact. Therefore we have joined forces with institutions like the UN Environment Program(UNEP) to promote environmental awareness, the International Rice Research Institute(IRRI), Philippines, to research environmentally sustainable rice production and the Innovative Vector Control Consortium to improve vector control. We have also entered into research and development partnerships with leading academic institutions and private sector companies to further develop solutions for climate mitigation and adaptation.

The Chinese government has clearly communicated that it will focus on quality growth during the 12th Five-Year-Plan period and has set clear targets in agriculture, health care and energy efficiency. At Bayer, we are in the position to help China address its core challenges through our portfolio and innovations. Therefore Bayer launched the Bayer China Ten Point Plan, a commitment of the company to align its portfolio and innovations with China's pressing demands for sustainability. China's 12th Five-Year-Plan also puts unprecedented focus on sustainable and "low-carbon" development. Goals include reducing energy consumption per unit of GDP by 16 percent and carbon dioxide emissions per unit of GDP by 17 percent from 2010 levels by 2015. To help China achieve these ambitious targets, Bayer MaterialScience not only provides solutions on light-weight mobility, but also on sustainable building and infrastructure.

Climate protection starts for us at the beginning of our production; with our feedstock. Two thirds of our carbon footprint can be traced back to our raw materials. Therefore we are carefully evaluating the possibilities of replacing fossil-based feedstock by renewable materials. Some of our important raw materials are already or in the near future partly bio-based, like ethylene glycol, propane diol, butane diol and succinic acid. On other we are working, but a longer road is still ahead of us. Examples are benzene, toluene or acetone.

Our service company Bayer Technology Services(BTS) has done important work on the topic of using biomass for the production of fuels and, important for us as a chemical and pharmaceutical company, raw materials. Some of these activities are described more in detail in this presentation.

In order to select the own direction of renewable fuels and chemicals production, it

is necessary to gain an overview over the entire field of biomass usage and to focus its research resources on the most relevant and promising paths. Some of the principles for focusing on certain paths are

Sustainability: Focusing on non-edible biomass as feedstock of the 2nd generation (e. g. used oils, biomass waste);

Efficiency: Focusing on processes with a high space-time-yield (i. e. thermo-chemical processes);

Effectiveness: Focusing on the synthesis of the relevant target products for our industry (e. g. aromatics).

Therefore we present in the following some aspects of our development and evaluation work in the field of biomass usage:

Biodiesel from oil crops and used oils (BayFAME);

Fuels from waste biomass (Biomass to Liquid, BTL);

Chemical raw materials from waste biomass (Catalytic Fast Pyrolysis).

Biodiesel has been seen as the first step to the bio-based economy, especially to the world's need for renewable fuels. In the last decade a real investment boom was observed yielding in a number of new plants with small and medium capacities (<500 kta). Politics in EU supported or maybe even originated this development by means of tax reductions for bio-based fuels and law regulations enforcing continuous increase of bio-based components in fuels, up to 20% in 2020. However, it shortly occurred that feedstock availability and its price are limiting factors for further development. For example in Europe, in 2010 already 54% of the produced rape seed oil was used as feedstock for biodiesel. There is no free area to extend production of rape seed. Shortage of raw oils caused strong increase of their price. This development was critical for the biodiesel industry since manufacturing costs of biodiesel are dominated by the feedstock costs. While the feedstock presents 80% of the cost of goods, other factors like investment cost, utilities and labor only play a minor role. Furthermore, feedstock prices and availability are a moving target in today's environment, since typical feedstock like soybean oil and rapeseed oil, which are easily turned into biodiesel (FAME), have reached price records of 1500/t and 1400/t in 2008. Less expensive potential feedstocks are available but they contain a significant amount of free fatty acids (FFA) which cannot be processed in conventional biodiesel plants. In the past, these free fatty acids had to be treated as waste or as a by-product

of low value. Some acid esterification techniques for these FFA were available in the market but presented significant issues in terms of acid removal and waste water treatment.

In order to overcome these limitations, BTS developed a technology that converts free fatty acids in biodiesel feedstock into fatty acid methyl ester (FAME) by esterification with methanol. This reaction is typically catalyzed by an acid catalyst, such as sulfuric acid. However, the application of strong acidic homogeneous catalysts like H_2SO_4 requires a significant extra effort in terms of materials of construction and safety compared to a conventional biodiesel plant. These restrictions are resolved by the Bayer Technology Services' continuous free fatty acid esterification process, which includes an optimized process design for the application of the heterogeneous esterification with AMBERLYST™ BD20 catalyst from Dow. As the esterification of free fatty acids is equilibrium limited at relatively low FFA conversions, the driving force to achieve complete FFA removal needs to be increased by using methanol in excess of the stoichiometric requirement. This is combined with a multi-stage reactor configuration with an inter-stage removal of the by-product water, which offers a further shift of the thermodynamic equilibrium towards complete conversion of even high FFA concentrations in the feedstock. The multi-stage concept offers a flexible process design, which ensures that feedstock with any FFA content up to 100 wt% can be processed with an optimum yield and minimum manufacturing costs. While for low FFA concentrations a single reaction stage is sufficient to reduce the FFA concentration to a level as low as 0.1 wt% , a 3–stage process will cover the complete spectrum up to 100 wt% FFA.

The process has been designed with the target to preferentially employ robust and simple process equipment, which minimizes investment costs and operating complexity. The core part of each reaction stage will be a continuous flow reactor containing a fixed bed of the heterogeneous esterification with AMBERLYST™ BD20 catalyst. After each reaction stage water is removed by evaporation together with most of the methanol excess. The resulting wet methanol stream is dried by distillation before being recycled and reused for further esterification of fresh FFA. In case multiple reaction stages are employed, the methanol will not be removed after the last stage. The final esterification product including excess methanol can be directly sent into a downstream transesterification unit. This will reduce the methanol requirement in the

transesterification and also reduce the heat requirement for methanol drying. In multi-stage process configurations the energy demand will be further optimized by heat integration between the evaporator stages and the methanol drying column.

The capital investment costs for the esterification process vary depending on user requirements with regard to feedstock, overall capacity, biodiesel process and flexibility. Costs for a typical installation of a 2-step configuration with methanol processing will range from 4–5 million US dollars for 30 million gal/year (136 million liters/year) or 1.8–2.2 million US dollars for 5 million gal/year (23 million liters/year), but will be depending on local conditions as available infrastructure and buildings, local standards and codes, labor market, etc. Typical components of the operating costs are depreciation, catalyst, utilities (steam, electricity and cooling water), maintenance and labor, though most likely the additional esterification unit can be easily run by the personnel already working on site. Overall the savings using an FFA rich feedstock with the Bayer Technology Services esterification technology BayFAME are significant compared to conventional feedstock like rapeseed or soybean oil. Typically, a price difference of about 2 c/lbs (4.4 c/kg) pays off for the costs of depreciation and operation.

While the use of FFA rich oils, grease and tallow can contribute to a future fuel supply, it can by far not cover the whole demand. Forecasts predict that in 2050 organic waste can cover 3 EJ compared with the total energy demand of more than 1200 EJ. This clearly shows that additional sources must be found.

In the future second generation technologies that utilize lignocellulosic biomass have to be applied. In the literature so called “Biomass to Liquid” processes (BTL) are frequently discussed. BTL technology converts biomass to syngas which in the consecutive step is converted to liquid hydrocarbons by means of Fischer-Tropsch synthesis (FTS). The general advantage of the BTL process is its relative insensitivity to the feedstock and high quality products accepted and demanded by the market. BTL fuels are not only fully compatible with the currently used fuels, i. e. diesel and gasoline, but also allow to reduce car emissions because fuels are clean and without aromatics, S and N compounds. From the technological point of view, BTL process integrates proven technology modules. The central step in the production of synthetic fuels is the FTS. FTS has been used for many years for the conversion of coal (CTL) and natural gas (GTL). Since China is in a leading position in the development of the CTL technology it has an

excellent base to deploy the BTL technology. BTS has not been involved in the development of our own FTS or GTL technology. However, BTS offers services in the field of technology evaluation and integration. The presented analyses have been done from this position.

The main disadvantage of the BTL technology is its complexity. In order to apply modern high capacity gasifiers, e. g. entrained flow gasifiers, biomass has to be dried, grained and pyrolyzed. Large scale pyrolysis is the less developed technology. In the next steps synthesis gas from the gasifier has to be purified and its composition adjusted to the demand of the FTS. BTL plant has to be also equipped with all kinds of utilities like oxygen plant, energy supply and waste water treatment facilities.

Syngas processing is at the first glance a simple set of unit operation that can illustrate the complexity of the BTL process. FT catalysts are very sensitive to poisoning. In particular, sulfur (H_2S , COS , CS_2) even at very low concentrations (practically on the detection level) can cause irreversible deactivation. Furthermore, tars, dust, alkali metals, and other gaseous impurities (NH_3 , HCN , HCl , HBr , HF) have to be removed from the synthesis gas. Various gas purification technologies like scrubbers and adsorbers are available. However, from the operational point of view the demanded high quality of gas cleaning is not trivial to obtain especially when considering the variability in the properties of biomass. Therefore for the BTL process gas cleaning is a very critical and uncertain step. Since similar problems occur in the CTL technology operational experience with them will be advantageous. Synthesis gas has to be also conditioned, i. e. its composition has to be adjusted to the stoichiometry demanded by the FTS. Gasification of biomass yields synthesis gas with the H_2/CO ratio of 1. But according to the stoichiometry of the FT reaction synthesis gas with an H_2/CO ratio of 2 is required. A simple solution provides integration of a water-gas shift (WGS) reactor. This reaction is slightly exothermic and can be carried out in simple adiabatic fixed bed reactors. However, WGS reaction converts part of CO into CO_2 . This, in turn, reduces carbon yield and the CO_2 reduction potential for the BTL process. Furthermore, CO_2 has to be removed from the synthesis gas in order to minimize the investment costs for the FTS step.

The complexity of the BTL has a strong impact on the investment cost. The estimated CAPEX for a 100 kt/a plant amounted to ca. 300 million. Though this number gives only an order of magnitude of the CAPEX, it illustrates well the high investment

barrier. These high expenditures are quite equally distributed between the main process units. The high investment cost for the FTS are mainly due to the high pressure equipment and the expensive catalyst. Expenditures for the gasifier suffer from the high pressure and high temperature demands for the equipment. In the pyrolysis unit also costs for drying and grinding are included. The overall cost of the fuel from the BTL process depends not only on the high CAPEX expressed by the high depreciation costs. They are also strongly influenced by high manufacturing costs resulting from the complexity of the process and by costs for the biomass. In spite of the general opinion the rest or waste biomass costs nothing, careful analysis indicates that this statement is not true. At least the price corresponding to the energetic value of the biomass has to be considered. For the large biomass conversion plants also not negligible logistic costs have to be taken into account. The overall conclusion from the performed economic evaluation was that products from the BTL route are nowadays not competitive with the fuels from crude based technologies.

In order to reduce the costs for the bio-based fuels or chemicals we need cheaper, that means less complex, technologies. For many years fast pyrolysis yielding bio-oil with high selectivity has been considered as promising alternative. This technology allows a one-stage thermochemical biomass conversion at low pressure and relatively low temperatures($<600^{\circ}\text{C}$). When compared with the FT route it offers lower investment costs and higher processing efficiency defined as the net energy of the product as percentage of the biomass feedstock's energy content. The main drawback of this technology is the low heating value of the bio-oil(due to the high oxygen content) and its acidity. Therefore, bio-oil has to be dehydrogenated before it can be used as fuel.

Further development of this technology is catalytic fast pyrolysis. The reaction consists of two consecutive steps: fast pyrolysis of biomass particles to volatile products and char, followed by oligomerization and aromatization of pyrolysis products. Selective reactions to aromatic hydrocarbons and olefins are associated by nonselective conversion of oxygen incorporated in biomass to carbon oxides and water. Furthermore, coke is formed on the catalyst. Despite that this technology is still at the early development stage, it should be technically feasible since it combines existing technologies: pyrolysis and reforming.

The simplicity of the Catalytic Fast Pyrolysis compared to the BTL route is illustrated in the flowsheet. Biomass is converted in a single fluidized-bed reactor filled with zeolitic

catalysts to aromatics and olefinic hydrocarbons, methane and CO. Carbon yield to valuable products might exceed 50%. Experimental studies performed in the BTS laboratories confirmed the potential of this technology. However, two general drawbacks typical for all thermochemical biomass conversion technologies should be mentioned. First, the complex preprocessing of biomass: mainly drying to obtain feedstock on the moisture level of 10% –20% , but also grinding to obtain millimeter size particles. This size is necessary to avoid heat and mass transport limitations. The second drawback is connected with the outcome: BMX processes (almost) always yield a broad product spectrum, like a refinery. This is not a desired situation for the direct interaction with chemical industry which mostly needs only one product. Therefore BMX plants should be operated either as bio-refineries or in integrated chemical sites.

Carbon yield is one of the critical issues for all biomass conversion processes. The BTL route can be used to illustrate the problem. The low carbon yield for the biomass conversion routes has its origin in the high content of oxygen which by mass amounts to almost 50% . Low yield is also a consequence of the low effective hydrogen to carbon ratio which for petroleum derived feedstock is between 1 and 2 whereas for the lignocellulosic biomass is between 0 and 0.3. Therefore carbon yield for biomass conversion amounts to ca. 20% . It is 5 times lower than that for crude oil. It is also significantly lower than yield in the GTL route. Additionally the technological complexity is higher, because in the GTL process there is no energy intensive solids handling. In turn, investment costs are much higher compared to the GTL process. The low yield is not only the question of costs but also of availability. When assuming 20% yield and a 100 kta plant the feedstock demand would be 500 kta. This, in turn, results in the large demand for the arable land and for the logistics.

The intrinsic drawbacks of the biomass, i. e. the low energy density and the low yields have been already discussed. In order to overcome these disadvantages novel approaches in the plant design are necessary. The simplest solution would mean to build small, delocalized plants at the best integrated with large farms or with the agricultural infrastructure. Examples for this approach are known from the technologies that were developed for the conversion of associated gas. In this approach it is expected that the cost reduction can be achieved by manufacturing plants in series. A more sophisticated approach has been proposed by the FZK (Forschungszentrum Karlsruhe). It is a multistage approach that combines advantages of small units with the

economy of scale idea. According to the FZK concept pyrolysis units should be distributed and localized near the sources of raw materials. In the pyrolysis step energy densification takes place by converting biomass into bio-oil and char. Slurry of char and bio-oil can be transported to large plants where it is converted in the consecutive steps by gasification and FTS. Liquid hydrocarbons and wax can be then transported to the world-scale refineries for further product upgrading.

Looking on China we see specific requirements: 50% of the population lives in rural areas. The improvement of the living conditions of the farmer is an important goal. Petroleum production covers less than half of the domestic demand. Substitution of petroleum therefore helps to reduce the dependency. 12% of the land is arable and only 1.5% is permanent cropland. That means there is a potential to increase biomass production by cultivation of new undemanding oil plants.

Considering these requirements we come to a set of recommendations on the field of biomass waste utilization technologies for China:

- Develop the transformation of biomass waste to fuels and chemical raw materials by R&D funding;

- Develop the cultivation of biomass in non-arable areas;

- Build up infrastructure for biomass waste logistics;

- Build up demonstration facilities close to the biomass sources to show feasibility of technologies;

- Involve industry by giving incentives, fostering industry/academia partnerships and making use of foreign technologies;

- Encourage production of green products via biomass based raw materials.



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Strategies in Utilizing Renewable Energy of Biomass

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In the past two decades or so, concerns of climate change from GHG emissions by anthropological fossil fuel usage has urged many countries in the world to take actions in developing technologies for CO₂ capture and storage, as well as effective utilization of renewable energies. By definition, there will be no (or much less) CO₂ emissions from renewable energy sources, such as geothermal, solar, wind, hydro, tidal, wave and biomass. It should be encouraged to increase renewable energy usage in the total energy supply portfolio. Amongst the above renewable energy sources, biomass is the most experienced fuel which human beings have been using since hundreds of thousands of years ago. It accounts for 65% of the total renewable energy production, only second to hydro. At the moment, wood and dung burning account for about 14% of the world's energy supply.

For hundreds of thousands of years during human evolvement, biomass was once the only energy source for space heating and cooking. Today, in some rural areas of the developing countries, biomass is still the main energy source for heating and cooking. In the early civilization, biomass even played an important role as energy source for various industries such as iron-making and lime kiln until Industrial Revolution (Started from 1750). Biomass mainly comes from earth vegetation: straws, trees, algae, agriculture wastes, etc. In natural growing cycle, plants absorb CO₂ from the atmosphere to build up biomass. The mechanism of biomass growth is through photosynthesis, where solar energy or light is captured by the pigments in vegetation and is used to reduce carbon dioxide from the atmosphere into carbohydrates such as cellulose, hemi-cellulose and lignin. Cellulose and hemi-cellulose are polysaccharides of

glucose. Lignin is an amorphous polymer, playing an important role in developing structure during plant growth. Fossil fuels require thousands of years to be converted into usable energy forms, while properly managed biomass energy can be used in an ongoing, renewable fashion. When biomass is burnt for energy extraction, the carbon in biomass is converted or reacted with oxygen into CO_2 , which is then released back to the atmosphere. There is no net release of CO_2 to the atmosphere. Therefore, as a renewable energy source, biomass is regarded as CO_2 neutral. Moreover, methane is released when biomass (bio-wastes) decay in natural state or landfill. The Global Warming Potential of methane is 21 times of CO_2 . So, using biomass and bio waste to generate heat, steam or electricity could bring extra benefit in reducing GHG emission.

The types of biomass for energy use could be woody biomass as well as herbaceous biomass: straw, miscanthus, switch grass. It could be residues (wastes, bi-products of various industrial and agricultural processes, ranging from woody and grassy materials) and dedicated energy crops:

- Crop residues: wheat straw, corn stalks, nut shells, orchid prunings, vineyard stakes, sugar cane bagasse;
- Forest residues: slash, forest thinning;
- Urban wood waste: construction residues, grass clippings, backyard prunings;
- Energy crops (plants grown specifically as biomass fuel) include short rotation coppice and perennial crops: miscanthus, switch grass, reed canary grass, willow.

There are several ways to utilize biomass, eg, direct firing, gasification, pyrolysis, biomass fuel conversion, biomass-coal co-firing, etc.

In Canada, biomass energy accounts for 540 PJ (petajoules) of energy use. It already provides more of Canada's energy supply than coal for nonelectrical generation applications and nuclear power, accounting for 5% of secondary energy use by the residential sector and 17% of energy use in the industrial sector, mainly in the forest industries. Including lumber and pulp and paper, forestry accounts for 35% of Canada's total energy consumption; the forest industries meet more than one-half of this demand themselves with self-generated biomass wastes. The forest industries have been increasing their use of wood wastes that otherwise would be burned, buried or landfilled. Principal uses include firing boilers in pulp and paper mills for process heat and providing energy for lumber drying. In some areas (eg, BC, Ontario, Québec, PEI, NB), forest industries supply wood waste (known as hog fuel), wood chips and

pellets to nearby industrial and residential customers and nonutility electrical generators. In addition, wood is the principal heating fuel for more than 100,000 Canadian homes and a supplemental(though largely decorative) heating source in several million others.

The other major sources of biomass are agriculture, food-processing residues, industrial wastes, municipal sewage and household garbage. Energy-from-waste projects include steam production for industrial or commercial use or electricity generation in several major metropolitan centres in Canada.

Biomass energy may be in solid, liquid or gaseous form, permitting a wide range of applications. At present, the majority of Canada's biomass energy is supplied in solid form(eg, hog chips, sawdust, pellets, charcoal, garbage), and in liquid form(eg, pulping liquors and ethanol). Other liquid forms of biomass energy include methanol (wood alcohol) and vegetable oils. Landfill gas(methane) from the anaerobic digestion of municipal solid waste in refuse sites is becoming more widespread in use and currently accounts for 100 MW.

When methanol or ethanol is mixed with gasoline, the product is sometimes called "gasohol." Methanol, produced from wood and forest waste by a distillation process, may provide an alternative fuel for transportation and industry at prices competitive with fuels from bitumen and coal liquefaction. Ethanol, although it is also a viable transportation fuel, is more expensive to produce when potential food supplies such as corn and wheat are used. However, ethanol made from biomass sources such as food and agricultural wastes has the potential to be cost-competitive with methanol and gasoline.

The emphasis of much current research is in the conversion of biomass to alcohol for use as a transport fuel(to extend or replace gasoline and diesel oil). For example, at present the production of alcohol from cellulose is a 2-stage process: converting cellulose into sugars and then the sugars into alcohol through fermentation. New, genetically engineered strains of bacteria have recently been made which show promise for combining these functions to make possible a one-step production process for alcohol from cellulose.

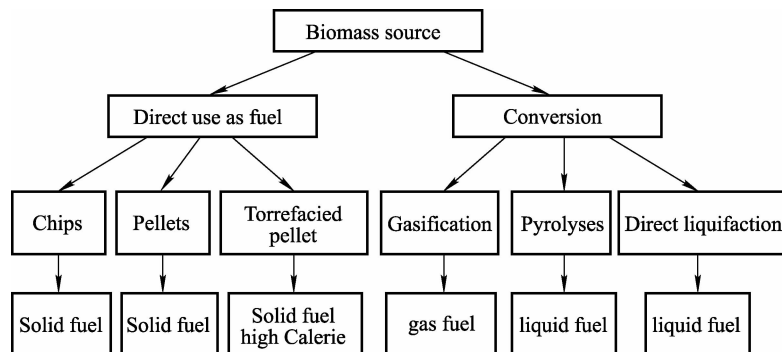
The gaseous form of biomass energy is called biogas, a methane-based gas with a low heating value. It is typically derived from the anaerobic(ie, without the presence of oxygen) digestion of organic material, such as municipal sewage or animal manure.

Canada is a signatory to the International Energy Agency Bioenergy Agreement, which promotes cooperation and collaboration among the 16 member countries.

Information is exchanged, new and promising technologies are tested and reported on, and advice is tendered to policymakers on the potential of increasing the proportion of energy generated using biomass.

The main problems facing expansion of biomass energy are the relatively high costs of new facilities and the need to make the industry truly renewable. The cost barrier may be overcome by government policy and rising prices of conventional energy sources. However, careful attention is also needed for problems of reforestation, land use, water use, soil quality, erosion and pollution. Producing energy, in addition to lumber and paper, could put new stress on the sustainability of a forest resource base that is already endangered by past practices of the forest industries. Biomass energy must be farmed, not mined; otherwise it will merely join coal, oil and natural gas as yet another nonrenewable energy source.

The following chart shows the routes of effective biomass utilization. There are still challenges and hurdles to overcome. Interdisciplinary and international collaborations are necessary to further develop and perfect biomass utilization technologies.





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The Development Path of Biomass Energy and Resources in China

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1. The necessity for carrying out the research and development of biomass energy

Biomass is the only material resource of renewable energy and organically bound carbon. The development of biomass can increase farmers' income, improve the appearance of rural area, promote the agricultural production and achieve integrated benefits.

E3 effects—Clean Energy, Economy and Ecology—can be achieved through the utilization of biomass energy.

2. To take multiple approaches for the development of biomass energy

The development of biomass energy in China progresses rapidly with various approaches. These approaches vary in technical characteristics and grade of maturity. Traditional biomass conversion processes, such as electricity generating technology and biogas production technology, have progressed significantly with Chinese technical characteristics. Newly developed biomass conversion processes, such as ethanol fuel, biodiesel, dimethyl ether, pyrolysis, aqueous-phase reforming and microalgae bio-fuel, etc., have been in the rising phase and closed to the world level of state-of-the-art.

All of these technologies and processes have their own developing spaces and their core technologies with our own independent intellectual property rights will be achieved eventually through competitive studies. As a consequence, our biomass energy industrial chain would be developed.

3. To establish “a new type of food-energy co-production agriculture system”

The major bottlenecks for the development of biomass energy are the total amount of biomass resources available and its collecting cost.

According to the agricultural development rules, the total amount of biomass resource would provide about 10% of the total energy consumption in China. With the social and economic development and fossil energy consumption, biomass production must be increased and biomass energy will play a more important role in the energy resources system.

The ultimate aim of traditional agricultural production, undoubtedly, is to provide food and vegetable oil and all of the efforts are focused on how to increase the yield and, at the same time, maintain the soil fertility. After harvest, most of the straws and residues are returned to soil for long term fertility excepting a small amount of them being used as feed and energy feedstock. However, since more and more agricultural residues are used as biomass energy feedstock, in other words, the demanding for biomass energy resource is ever growing, two different agricultural development molds are proposed as: 1) to maintain the traditional agricultural production pattern, only merely using as much biomass resource as possible for energy production in a passive way; 2) to change the aim of agricultural production from food production to food-energy co-production harmoniously in a more active way—producing more biomass resources in accordance with the need for energy while assuring the safe food production. Since the latter is superior obviously, the following aspects should be studied to establish such a food-energy co-production agriculture system:

(1) Soil capacity and protection

Since the aim of traditional agriculture is to produce food as well as small amount of straw and/or residues, most of straw and residues are returned to the soil for improving the soil structure and organic matter content. If most of them are used as biomass energy resource, the soil structure and fertility will be getting worse, resulting in a decreased yield eventually. Therefore, studies on soil capacity, soil restoration and soil protection must be carried out. Sustainable agricultural development would be achieved only if the production activities be conducted in a certain limits of safety.

(2) Breeding of new varieties of crops

In order to realize the aim of food-energy co-production, new varieties of crops, especially corn and wheat, must be bred for producing more food and more biomass resources. Presently, the grain to straw ratio for wheat and corn is about 1:1.3. If the ratio could be increased to 1:2, about 50% more of biomass would be produced which is equivalent to 0.35 billion tons of standard coal per year.

In this way, agricultural production could provide 1.0 – 1.1 billion tons of standard coal per year and about 60% of them, equivalent to 0.6 billion tons of standard coal, could be used for biomass energy. At present the biomass production is only equal to 0.3 billion tons of standard coal per year.

(3) New cultivation pattern

For food-energy co-production agricultural production system, new cultivation pattern should be explored and planting density, intercropping pattern, field management, etc. should be studied.

(4) New crop harvesting and storage pattern

Combined harvester for grain and biomass co-harvesting should be developed. Biomass transporting and centralized storing pattern should also be studied. It is also necessary to establish new standards for new generation of farm machines to meet the requirement of food-energy co-production agriculture.

(5) Processing technology

Food and biomaterial process technology also should be innovated to meet the new requirement. Efficient conversion production technology for grain and food should also be studied for improving the food quality, nutrition and safety.

Applied and fundamental studies on biomass energy and utilization should be carried out for developing practical and efficient biomass utilization technology suitable for different stages of the development to achieve overall efficiency.

(6) Establishing a new type of industrial mode

In order to establish a new type of agricultural production mode and create food-energy co-production new agriculture, an agricultural demonstration project should be established first to see if the E3 effects could be achieved. Considerations should include the site of experiment, variety of crops, crop cultivation pattern, technology employed, etc.

(7) Comparative study of agriculture pattern and biomass energy development between

China and foreign countries

Since national conditions, natural environments, varieties of crops, crop cultivation patterns, technologies employed vary a lot for countries, the final results would be different. It is necessary to draw lessons from each other. Therefore, a comparative study of agriculture pattern and biomass energy development between China and foreign countries should be conducted to determine the similarities and differences between different countries for choosing the most suitable technology and development mode.

4. The development path of biomass energy and resources in China



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