生物质水相催化合成生物汽油和航空燃油

Biogasoline and jet fuel production from biomass by aqueous phase catalytic processing

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2012-07-07　北京

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1. 研究背景 Background

生物质能是一种重要的石油补充能源

Biomass，a potential substitute for petroleum

现有资源
Current resources

农业秸秆6.5亿吨
6.5 billion tons of Straw
林业废弃物2.7亿吨
2.7 billion tons of Forestry residues

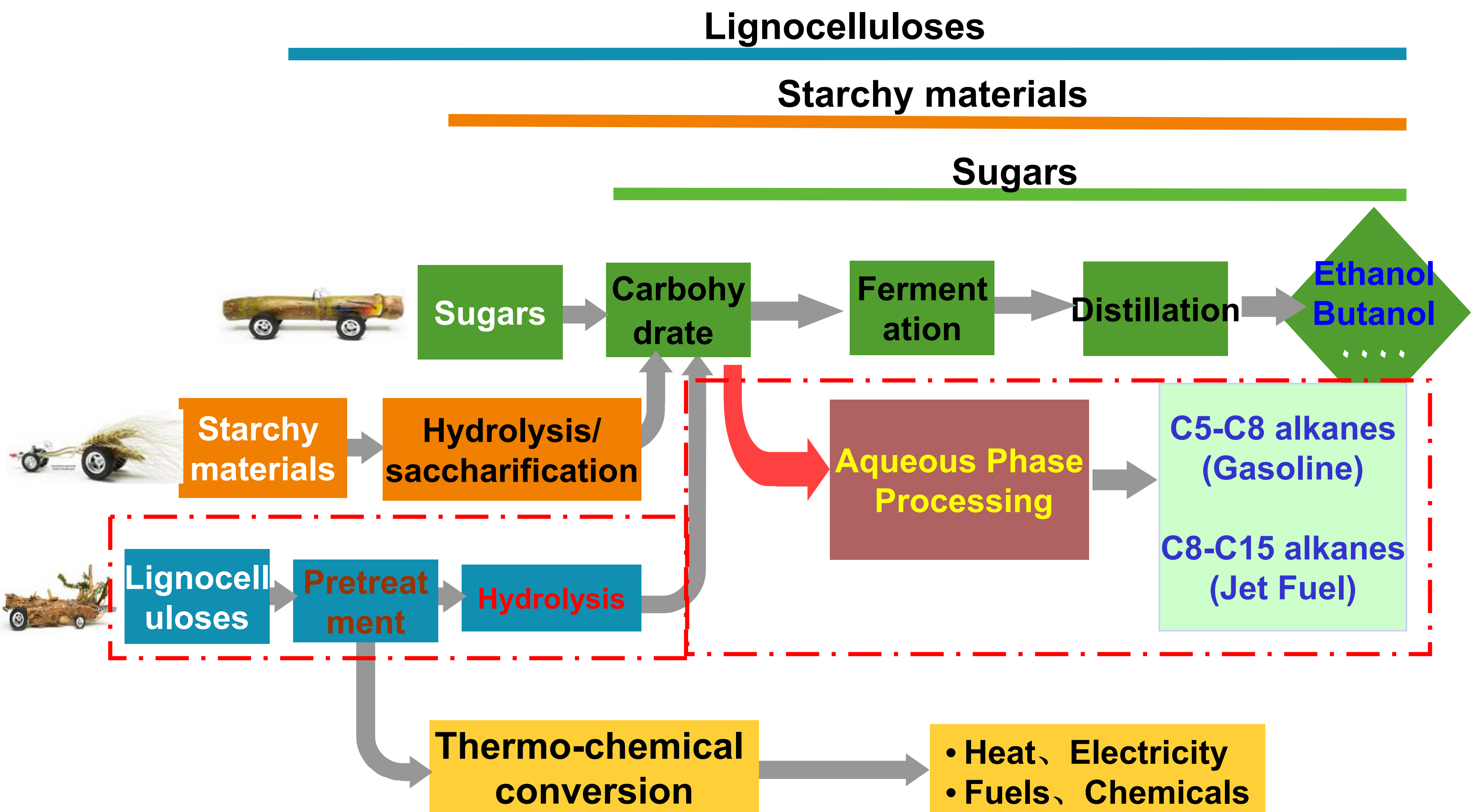
发展潜力
Potential resources

替代4000万吨石油
Replacing oil of 40 million tons
年减排CO2达1.5亿吨
Reducing CO2 emissions by 1.5 billion tons
实现5.5%的减排目标
Achieving the emission reduction target of 5.5%

40%能源利用
Utilization of 40%energy

生物质能是唯一可制备液体燃料的可再生能源
Biomass is the only renewable energy source for liquid fuel synthesis
碳循环、工艺清洁无污染
Carbon recycling and clean

Biomass liquid fuel production process



Biomass liquid fuel production process

木质纤维素 Lignocellulose → 水解 Hydrolysis → 糖 Sugar → 水相催化 aqueous-phase catalytic processing → 液体烷烃 (汽油、航空燃油) Liquid alkanes (Biogasoline and jet fuel)

能量转化效率更高
Higher Efficient Energy Conversion

产物液体烷烃保存了水解糖80%以上的能量，反应均在液相中进行，避免了原料的汽化；反应产物烷烃可以与水相自动分离，避免了蒸馏等耗能过程，该过程的热效率大约是燃料乙醇的2倍。

Saving more than 80% of the hydrolysis-sugar energy in liquid phase

Avoiding the energy-consuming process (such as distillation) because of products automatic separation

反应效率更高
Higher Reaction Efficiency

水相催化采用多相催化材料，反应速度快，生产强度高。

Heterogeneous catalysis for APR

Faster reaction rate

Higher production

实现全糖利用
Full Utilization of Sugar

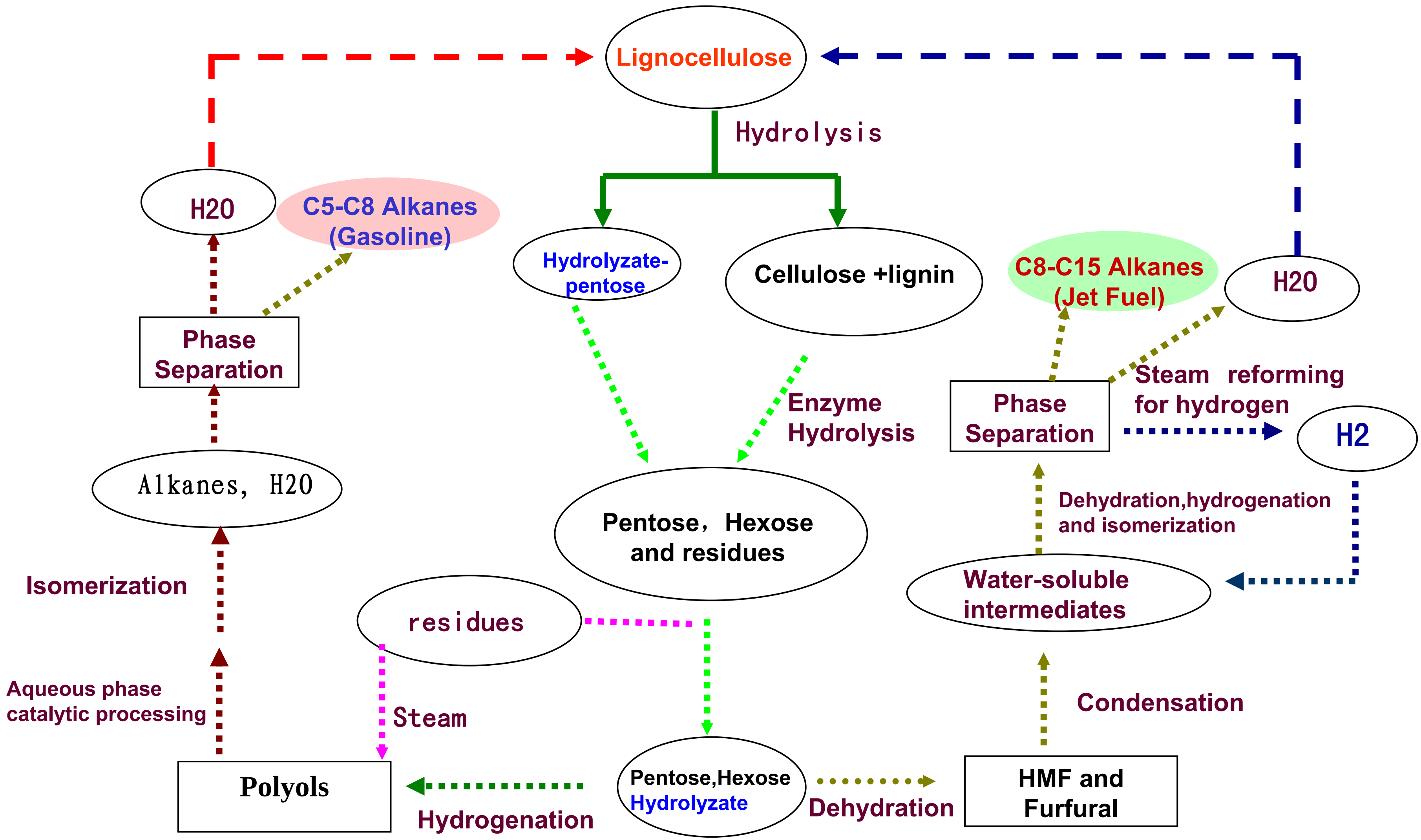
可实现水解液中单糖及低聚糖的全利用，克服了传统纤维素乙醇生产过程中五碳糖难以被有效发酵利用的问题

Complete utilizing monosaccharide and oligosaccharides in the hydrolyzate (even pentose)

以木质纤维素类生物质为原料经高效水解、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

Technology advantages of biogasoline and jet fuel by catalytic processing from lignocellulosic biomass

2. 技术路线 Technical Routes

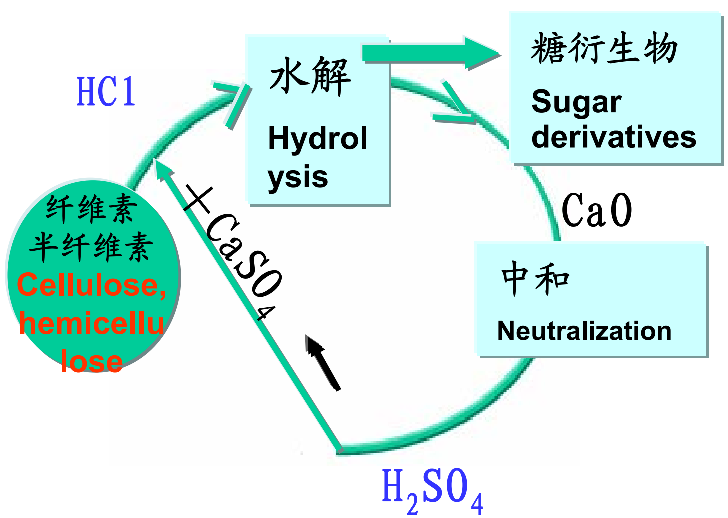


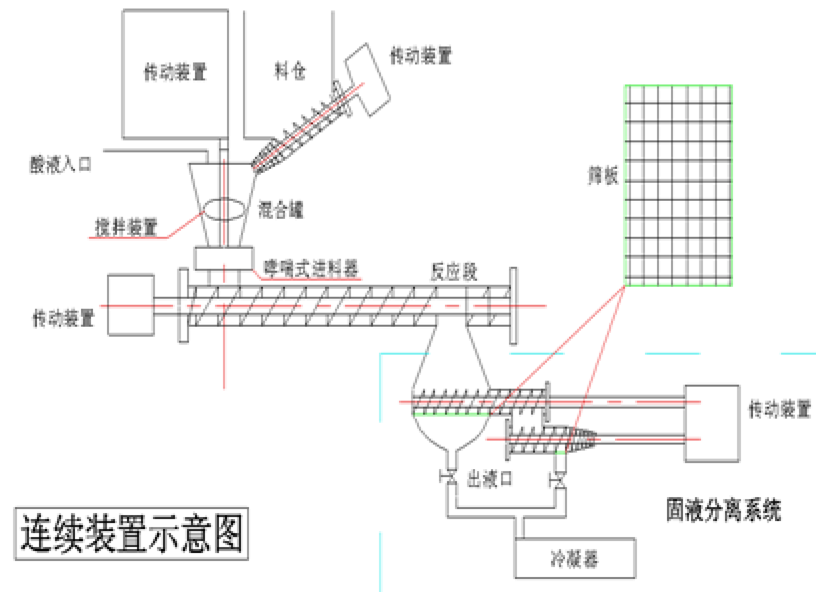
3. 关键技术与工艺 Key Technology and Process

生物质高效水解工艺研究 Biomass hydrolysis technology

高温液态水、超低酸-酶水解、酸-酸耦合水解

**High temperature liquid water,
ultra low acid and enzyme hydrolysis,
bi- acid coupled hydrolysis**





生物质高效水解系统
Biomass efficient hydrolysis system

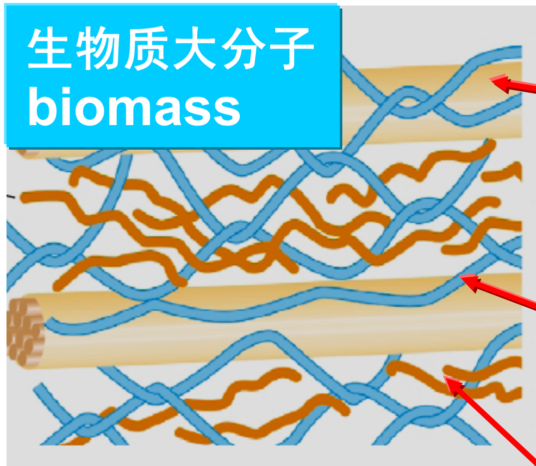
半纤维素-纤维素分级解聚：能耗低、功能单体收率高、选择性高

Depolymerization: low energy consumption, high sugar monomer yield and high selectivity

3. 关键技术与工艺 Key Technology and Process

生物质酸-酸水解 Bi-acid coupled hydrolysis

生物质大分子
biomass



纤维素
Cellulose

半纤维素
Hemicellulose

结晶度、结构
Crystallinity , structure

聚合度、形态
Polymerization, shape

糖类衍生物
sugars

酸浓度、温度、液固比、渗滤速度
Acid concentration, temperature, ratio of liquid/solid, and infiltration speed

水解工艺
Hydrolysis process

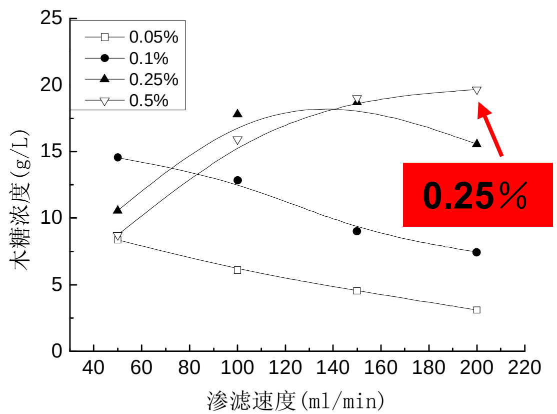
金属盐助催化
Metal salt auxiliaries

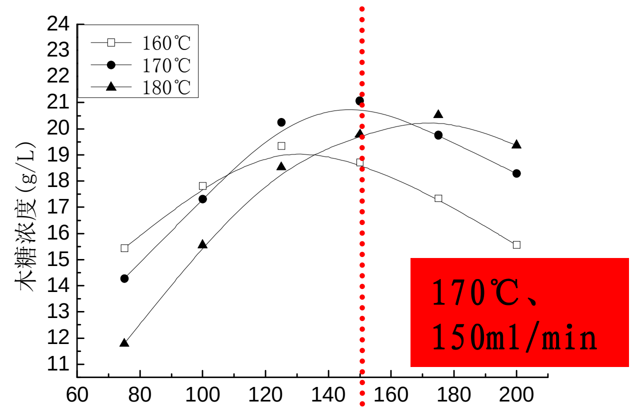
辅助工艺
Aided process

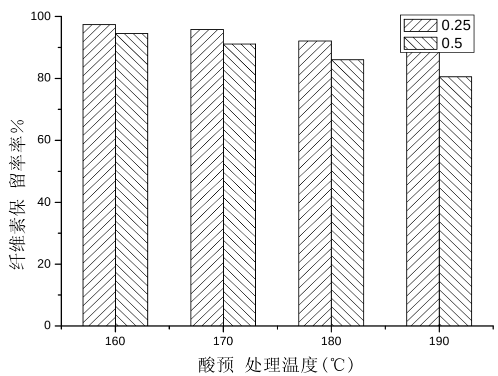
技术难点
Technical difficulties

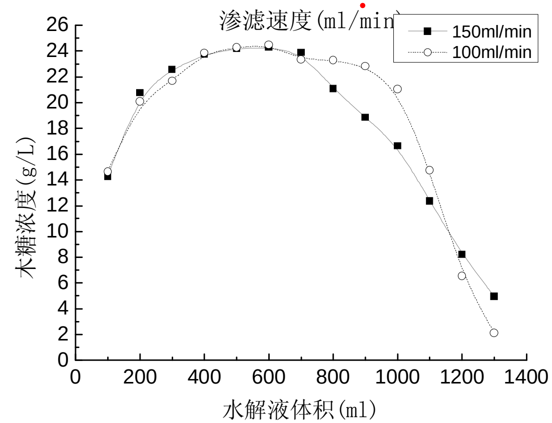
- 有效的预处理水解技术
  Efficient pretreatment
- 水解反应器的设计
  Hydrolysis reactor design

半纤维素水解工艺研究 Hemicellulose hydrolysis









水解优化工艺：0.25%硫酸、温度170℃、液固比10：1、渗滤速度150ml/min 木糖浓度：21 g/l

Optimized hydrolysis process:

0.25% of sulfuric acid concentration, 170 ℃,

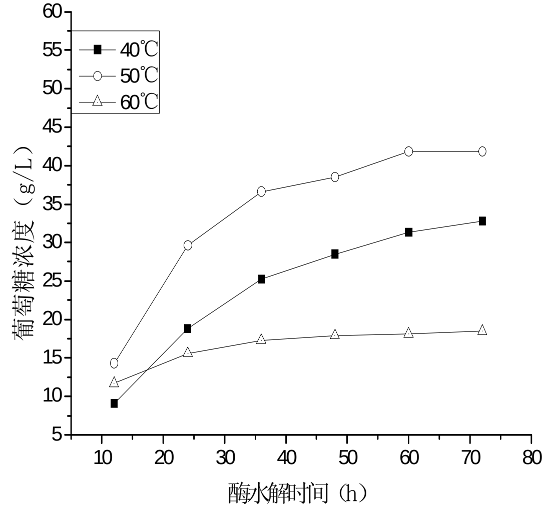
10:1 of liquid to solid ration,150 ml/min of infiltration speed

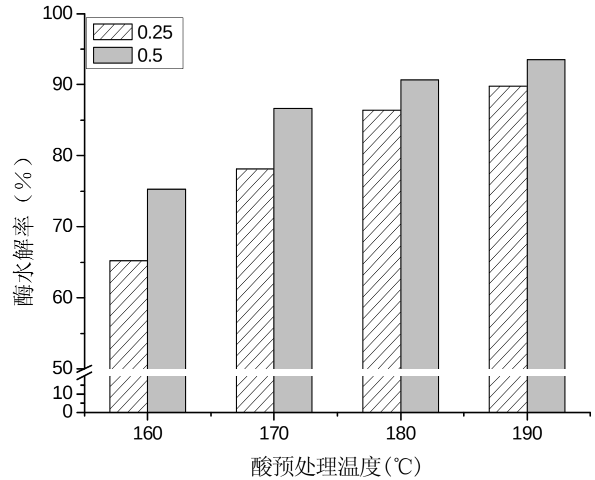
Xylose concentration: 21 g/l

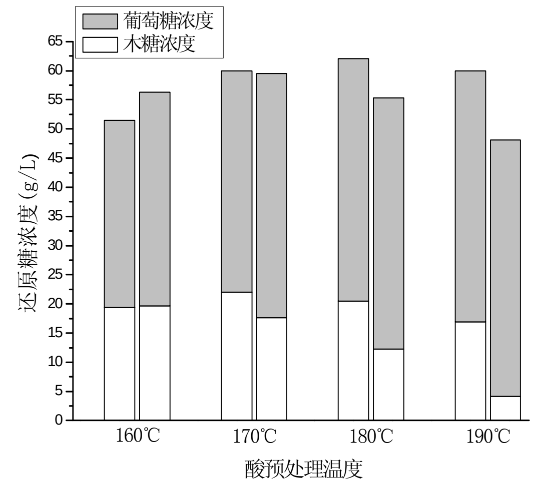
纤维素酸酶水解工艺研究

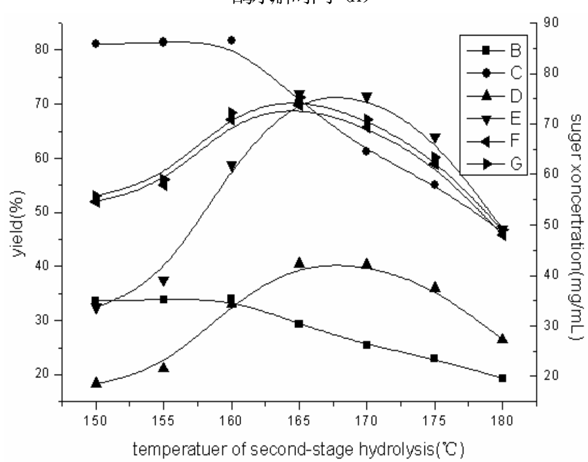
Acid-enzyme cellulose hydrolysis

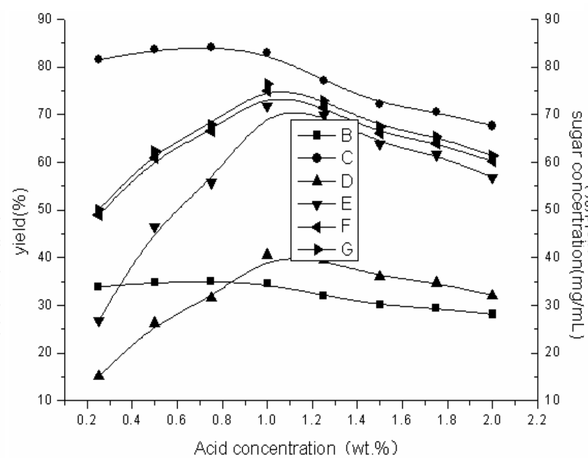
可溶-不可溶互变载体
纤维素固定化酶
Soluble-insoluble support
Cellulose immobilized enzyme

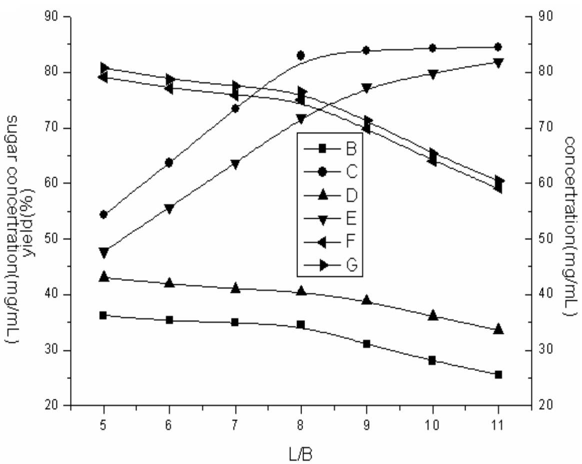










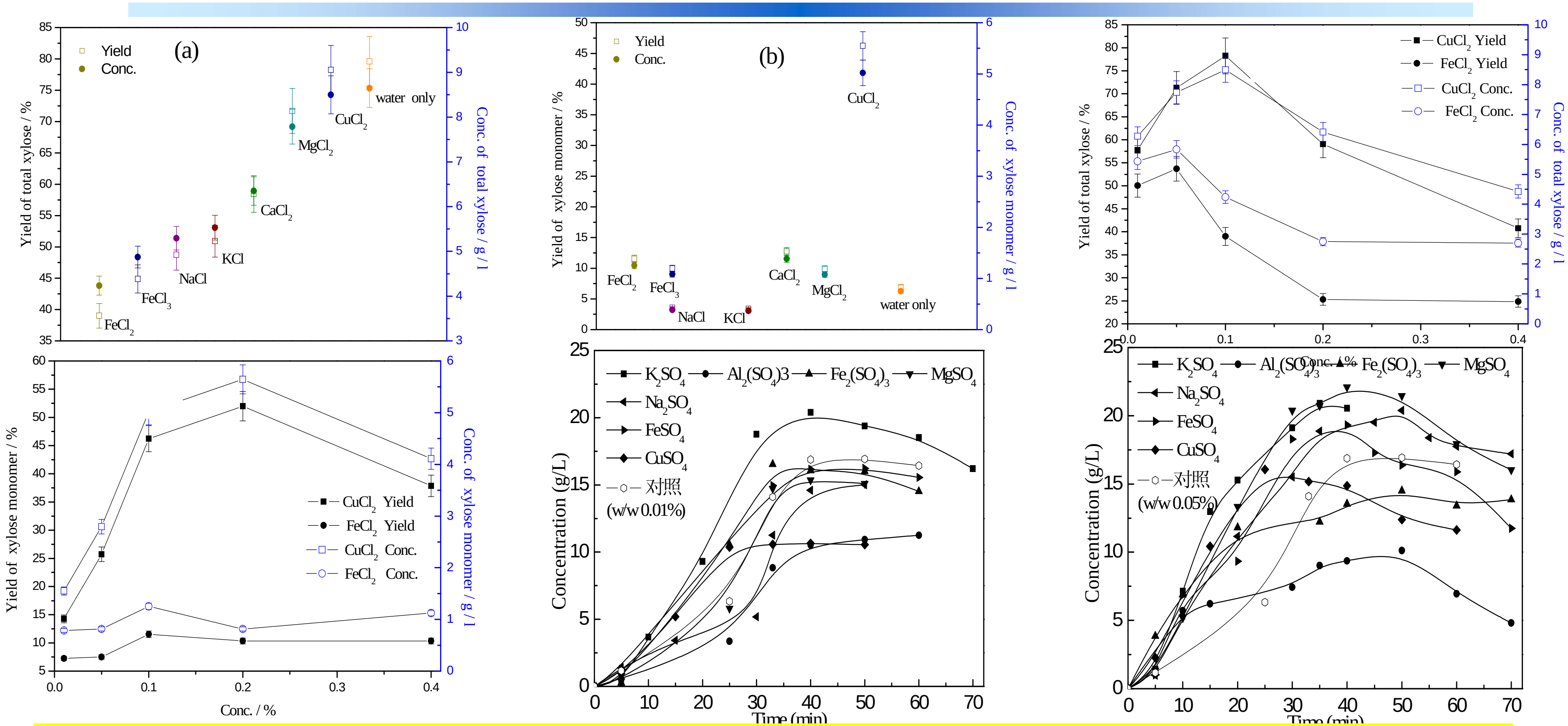


纤维素水解优化工艺：硫酸浓度为**0.25%**；酶水解温度为**50**℃；处理时间**60h**；葡萄糖浓度: **40.5 g/l**。

Optimized hydrolysis process: 0.25% of sulfuric acid concentration, 50 ℃, 60 h of treating time. glucose concentration: 40.5 g/l.

金属盐助催化预处理工艺研究

Metal salts catalyzed pretreatment process



考察了FeCl2 、CuCl2、 NaCl、KCl 和K2SO4 等金属盐对水解工艺的影响, 结论:

1. FeCl2和CuCl2有利于木聚糖生成,总木糖收率最高为78.3%;
2. K2SO4对纤维素酸水解有催化作用且催化效果稳定，优化浓度为0.05%;
3. NaCl、KCl则不利于木聚糖的生成。

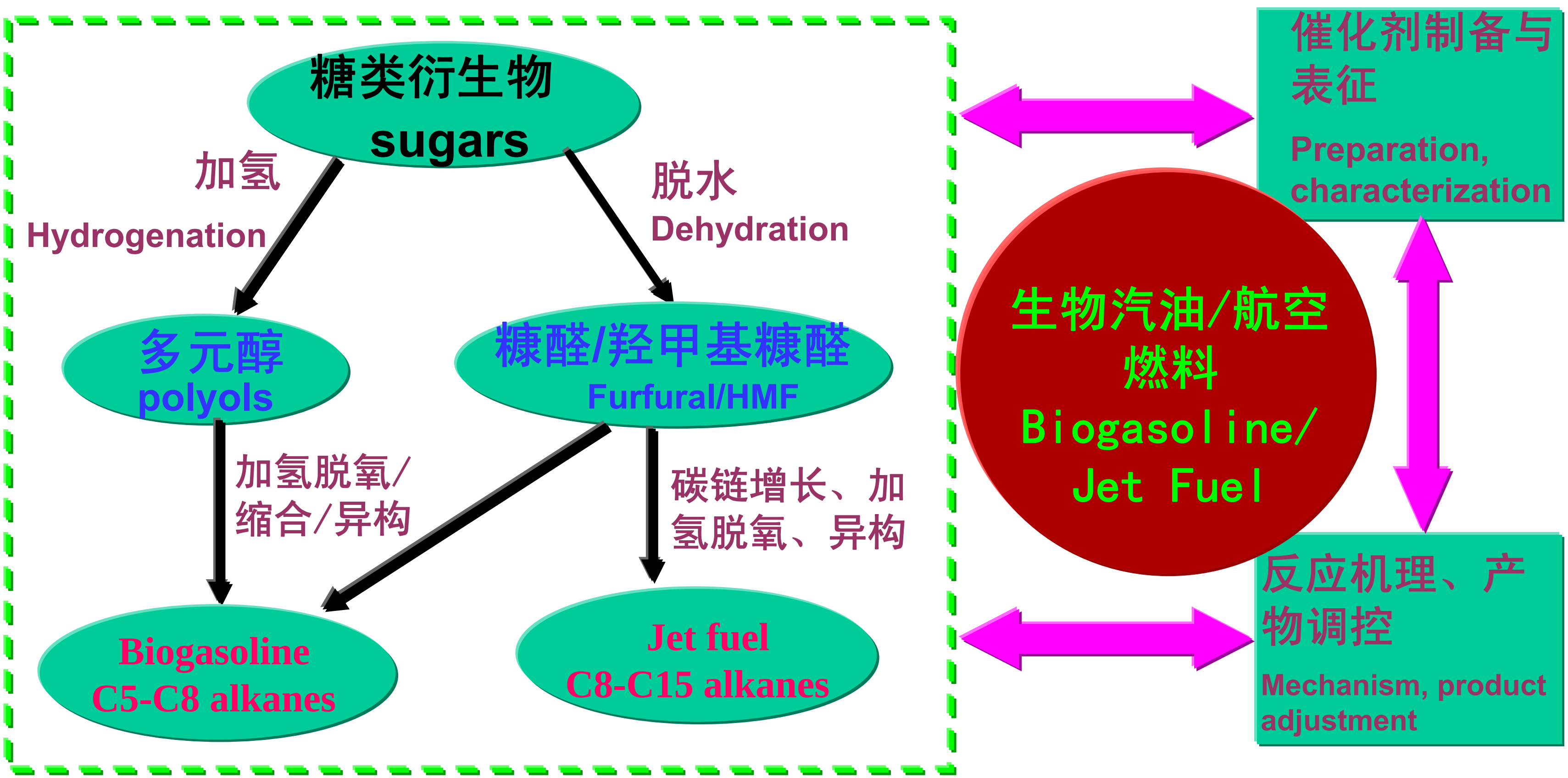
Effects of some metal salts on the hydrolysis process, FeCl2, CuCl2, NaCl, KCl and K2SO4 :

1. FeCl2 and CuCl2 enhanced the formation of xylan with a total xylose yield up to 78.3%;
2. K2SO4 favored the acid hydrolysis of cellulose with a stable activity, the optimized concentration of K2SO4 was 0.05%;
3. NaCl or KCl was negative to the formation of xylan.

3. 关键技术与工艺 Key Technology and Process

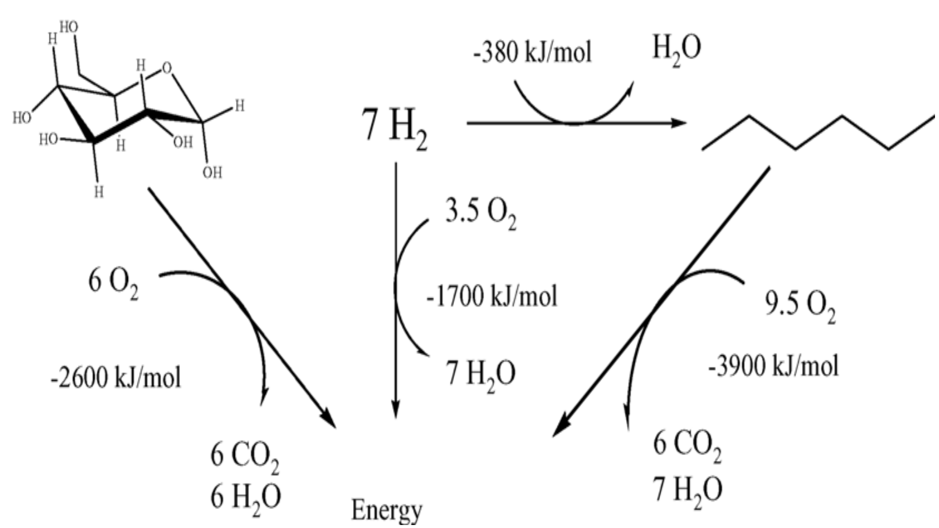
糖平台水相催化合成液体燃料研究

Liquid fuels from sugars by aqueous catalysis



水相催化制取生物汽油研究
Synthesis of biogasoline by aqueous phase catalysis

C_5-C_8 多元醇（木糖醇）（山梨糖醇） → 脱水、增碳、加氢 / Pt/SiO_2-Al_2O_3 → 生物汽油 (Biogasoline)（C5-C8 alkanes）



液态烷烃保留了糖原料约90%的能量

90% energy of sugar reserved in liquid alkanes

单元反应

$$C_{12}H_{24}O_{12} + 2H_2 = 2C_6H_{14}O_6$$
$$C_6H_{12}O_6 + 7H_2 = C_6H_{14} + 6H_2O$$
$$C_5H_{10}O_5 + 6H_2 = C_5H_{12} + 5H_2O$$
$$C_6H_{12}O_6 + 6H_2O = 6CO_2 + 12H_2$$
$$C_5H_{10}O_5 + 5H_2O = 5CO_2 + 10H_2$$

技术难点
Technical difficulties

- 催化剂设计与制备
  Catalysts design and preparation
- 水相加氢工艺
  Aqueous phase hydrogenation
- 催化剂稳定性
  Catalyst stability

水解液水相催化重整制备C5-C8烷烃（汽油）

Gasoline production from hydrolyzate by aqueous phase catalysis

单糖加氢醇化反应

Monosaccharide hydrogenation to polyols

Ru/C催化剂上不同水解液加氢醇化反应

Hydrogenation of different hydrolyzate to polyols over the Ru/C catalyst

原料 Materials	pH	总糖浓度 Total sugar concentration（g/L）	糖类 Sugar（g/L）				呋喃类 Furan（g/L）	产物 (Product)		X(C) (%)
			葡萄糖 Glucose	木糖 xylose	阿拉伯糖 Arabinose	甘露糖 Mannose		木糖醇 xylitol	山梨醇 sorbitol	
浓酸水解液 Concentrated acid hydrolyzate	1.98	0.20	0.14	0.06	0	0	30.58	4.89	2.34	17.34
稀酸水解液 Diluted acid hydrolyzate	3.34	7.78	2.38	4.91	0.49	0	2.34	3.26	0.98	49.78
酶水解液 Enzyme hydrolyzate	6.72	23.10	3.56	17.32	1.84	0.38	1.84	12.74	1.69	58.36

Reaction condition：T=100 ℃，P=2 MPa

工艺优化 Process optimization

木糖醇制C5-C6 烷烃
C5-C6 alkanes production from xylitol

Catalysts			Alkane selectivity (%)					X_C (%)	Isoparaffin (%)
Pt loading (%)	Ni loading (%)	Support	C1 C2	C3	C4	C5	C6		
0.10	0.00	HZSM	4.35	2.81	10.52	71.96	10.35	25.70	36.62
0.10	1.00	HZSM	9.24	2.72	9.15	72.58	3.75	56.92	15.19
1.00	0.50	HZSM	11.31	3.96	5.29	71.91	4.34	83.92	14.85
1.00	1.00	HZSM	3.81	2.35	4.27	87.76	4.50	98.09	10.11
0.50	1.00	HZSM	23.98	9.14	3.44	57.22	4.59	98.70	12.69
0.10	1.00	HZSM	9.24	2.72	9.15	72.58	3.75	56.92	15.19
0.00	0.50	HZSM	0.18	0.40	4.19	93.22	1.19	71.10	5.86
0.00	1.00	HZSM	0.57	0.44	2.95	95.37	0.66	93.90	11.25
0.00	1.00	MCM22	0.00	0.00	1.04	99.00	0.00	93.00	3.00
0.00	2.00	MCM22	0.12	0.00	0.70	93.91	0.78	96.71	4.31
0.00	3.00	MCM22	3.42	2.37	6.84	87.08	0.00	94.88	9.14

Ni基催化剂上C5-C6烷烃收率接近90%；可替代贵金属催化剂
Near 90% C5-C6 alkane yield over Ni-catalyst, a potential substitute for noble catalyst

工艺优化 Process optimization

Ni/HZSM-5催化山梨醇加氢制烷烃

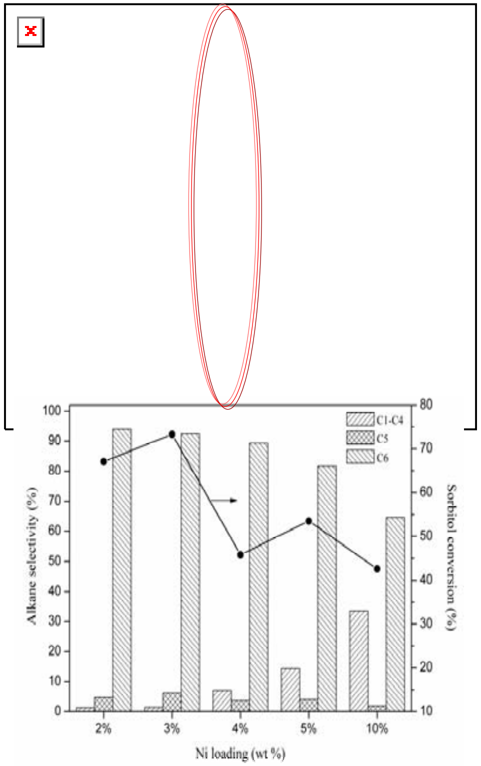
Alkanes production from sorbitol hydrogenation over the Ni/HZSM-5 catalyst

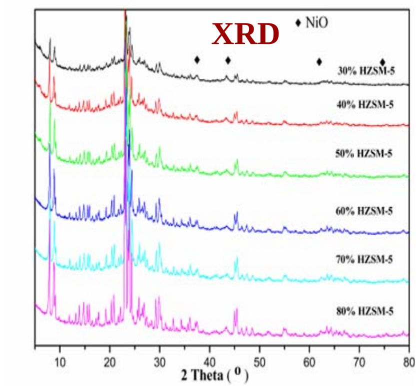
分子筛HZSM-5硅铝比对水相重整和异构化反应的影响 Effect of the Si/Al ratio of HZSM-5 on the catalytic performance and isomerization			
产物分布 Product distribution	硅铝比 (Si/Al) 50	硅铝比 (Si/Al) 38	硅铝比 (Si/Al) 25
C_1-C_4	0.332	0.221	0.281
i-pentane	0.083	0.111	0.082
n-pentane	0.102	0.080	0.121
2,2-DMB	0.101	0.101	0.071
2,3-DMB	0.122	0.160	0.102
2-methy pentane	0.101	0.141	0.101
3-methy pentane	0.102	0.120	0.104
n-hexane	0.071	0.150	0.151
C_{5+} Selectivity	0.668	0. 779	0.719
Total Conversion	0.851	0.951	0.952

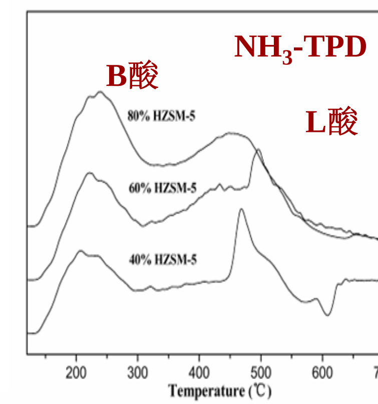
硅铝比为38时碳选择性最好，总转化率达到95.1％,总C_{5+}选择性达到77.9%。

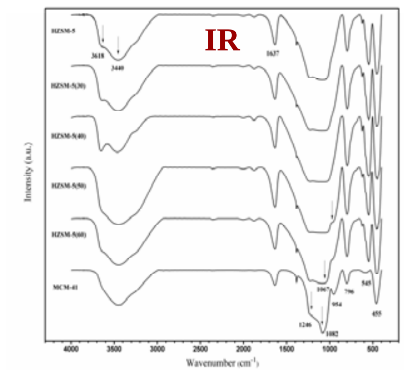
Si/Al =38: 95.1% of the total conversion and 77.9% of $C5^+$ selectivity.

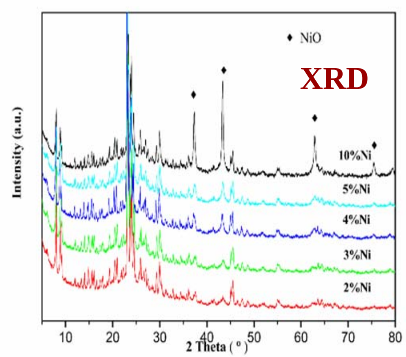
载体优化 Support Optimization

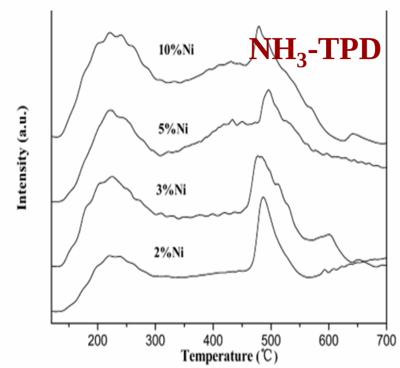


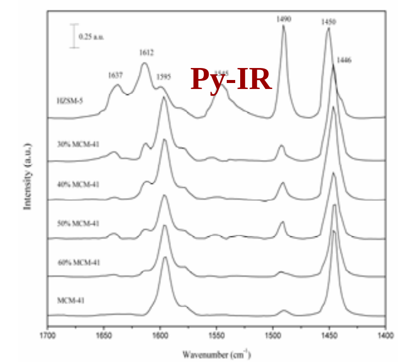












优化复合分子筛：60% HZSM-5+40% MCM-41；优化Ni含量为3%；

Optimized composite support: 60 wt% HZSM-5 +40 wt% MCM-41; Ni loading of 3%.

山梨醇转化率达到73%，C5-C6烷烃选择性达到98%；

The catalyst showed the highest activity with 73% of sorbitol conversion, and 98% of C5-C6 alkane selectivity.

催化剂表征结果：催化剂晶粒较小，L/B酸适中，其中L酸较多，利于加氢。

The catalyst contained smaller grains and moderate L / B acid, where in L acid was positive to hydrogenation.

烷烃异构化 Alkanes isomerization

温度 Temperature/℃	时间 Time /h	转化率 Conversion/%	选择性 Selectivity (%)							异构化程度 Isomerization(%)
			<C3	C4H10		C5H12		C6H14		
				i	n	i	n	i	n	
300	5	86.1%	43.8	2.2	9.3	1.6	1.5	41.8	-	45.6

反应条件： 催化剂：1%Pt/HZSM-5；正己烷流速：0.04ml/min；压力：3.5MPa；H2流量：70ml/min。

Reaction condition: Catalyst: 1%Pt/HZSM-5; N-hexane flow rate: 0.04 ml/min; Reaction Pressure: 3.5 MPa; H2 flow rate: 70 ml/min.

选用1%Pt/HZSM-5催化剂，正己烷转化率为86.1%，异构化程度为45.6%。

Conversion of hexane reached 86.1% and the isomerization degree of 45.6%

催化制取生物航空燃油研究

Synthesis of jet fuel by catalytic process

C_8-C_{15}

葡萄糖
果糖
木糖

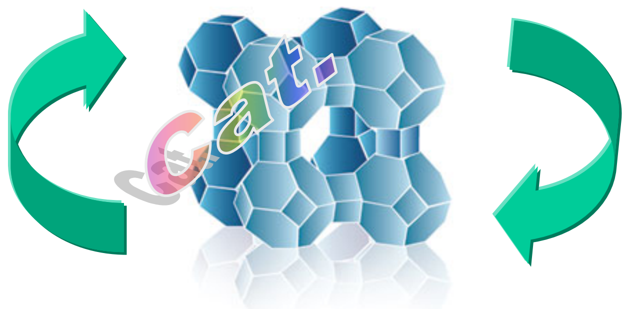
脱水 → Acid

5-HMF
糠醛

羟醛缩合
加氢/脱水 → Base/metal

航空燃油（C8-C15烷烃）

反应工艺
Reaction process



系统耦合
System combination

水相脱氧增碳 加氢异构

Aldol condensation,hydrogenation and isomerization

航空燃油
Jet fuel

技术难点
Technical difficulties

- 糖脱水工艺
Sugar dehydration
- 缩合催化剂设计
Catalysts design
- 碳链增长工艺
Aldol condensation
- 加氢异构
Hydrogenation and isomerization
- 反应器设计
Reactor

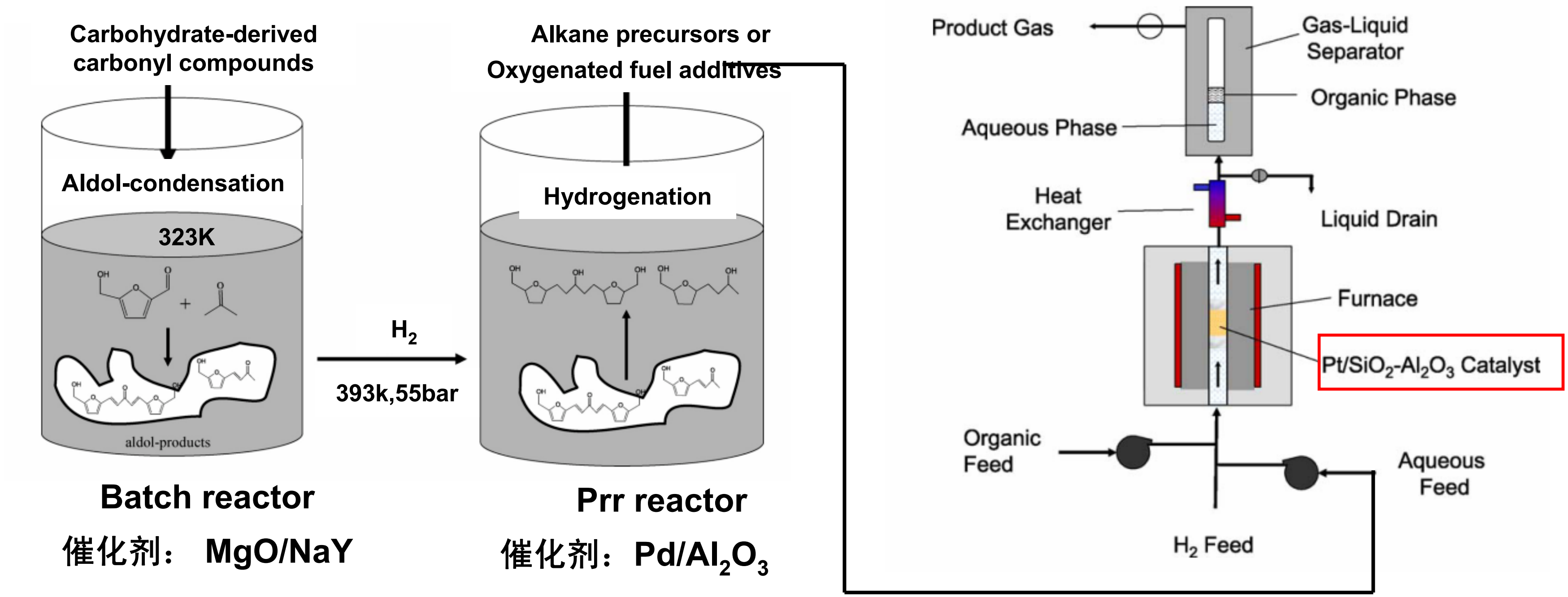
催化制取生物航空燃油研究

Synthesis of jet fuel by catalytic process

羟醛缩合

Aldol condensation

（HMF和丙酮）



羟醛缩合 Aldol condensation	催化加氢 Hydrogenation	加氢-异构 Hydrogenation and isomerization
分子碳链增长 C chain increase	水溶性中间化合物 Soluble intermediates	正构/异构长链烃 Long /heterogeneous chain alkanes

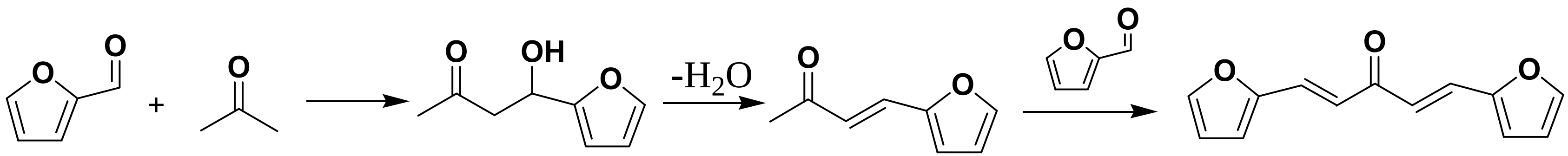
糠醛-缩合源头
Furfural - the source of condensation

$$\text{Cellulose} \xrightarrow[NaHSO_4]{\text{Hydrolysis}} \text{Glucose} \xrightarrow[ZnSO_4]{\text{Isomerization}} \text{Fructose} \xrightarrow[NaHSO_4]{\text{Dehydration}} \text{HMF}$$

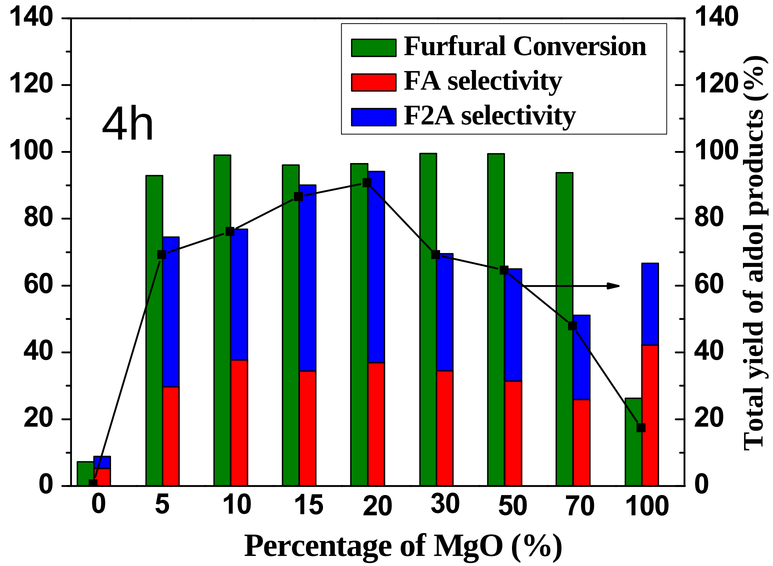
Run no.	Catalyst (mmol)		HMF yield（mol%）
	$NaHSO_4$	$ZnSO_4$	
1	1.8	-	19.7
2	1.8	1.4	41.5
3	1.8	2.1	44.4
4	**1.8**	**2.8**	**53.2**
5	1.8	3.5	48.1
6	1.8	4.2	47.8
7	2.7	2.8	46.1
8	3.6	2.8	17.3

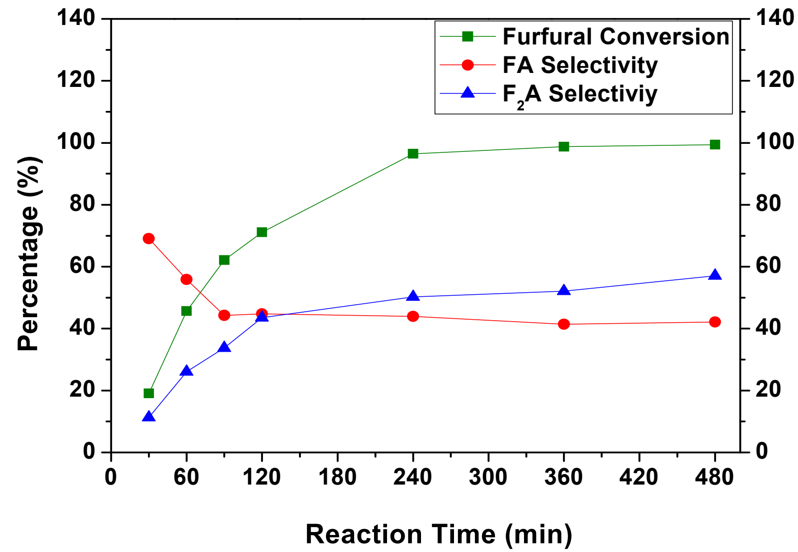
Cellulose 1.0g, Water 4ml, THF 40ml, T=160℃， t=60min

羟醛缩合-中间体
Aldol condensation - intermediates



F A FA-OH FA F_2A





- 20%MgO/NaY催化剂表现出较好的催化性能；
  Better catalytic performance： 20% MgO/NaY
- 反应8h后糠醛转化率和总选择性都达到98%。
  Furfural conversion and selectivity: 98% in 8h reaction

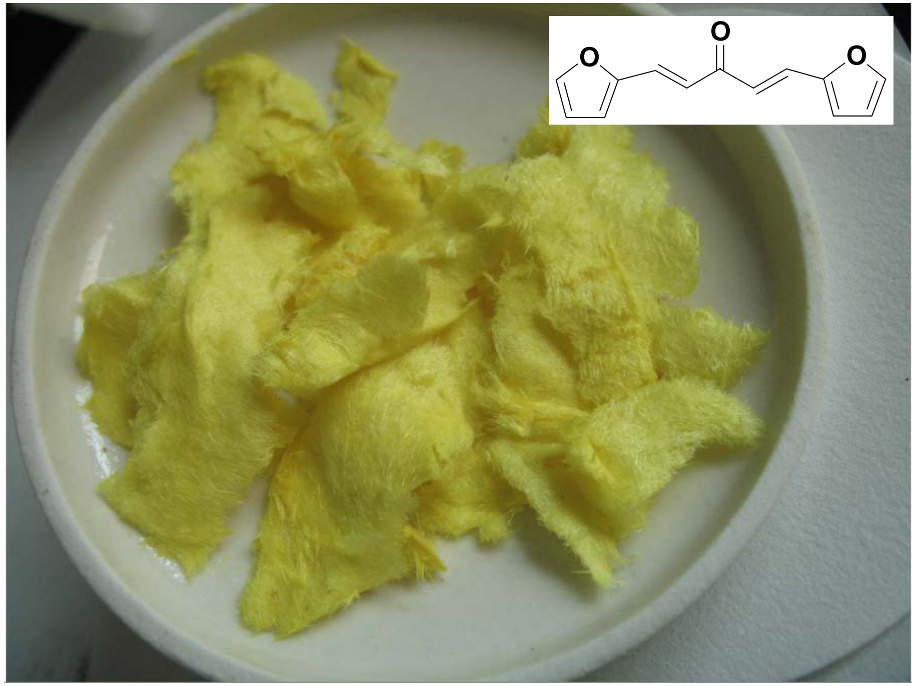
缩合中间体-分离
Condensation intermediates - Separation

亚糠基丙酮 C8 (FA)

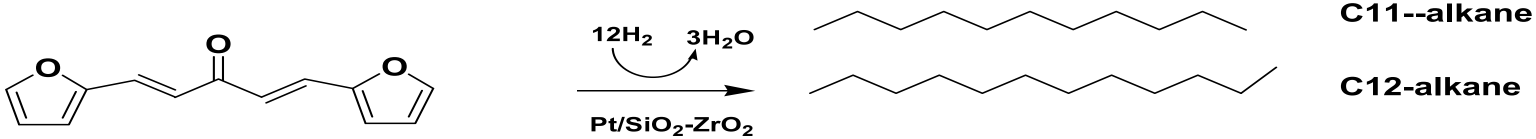
4-(2-furyl)-3-buten-2-one

二亚糠基丙酮 C13 (F2A)

1,5-di-2-furanyl-1,4-pentadien-3-one

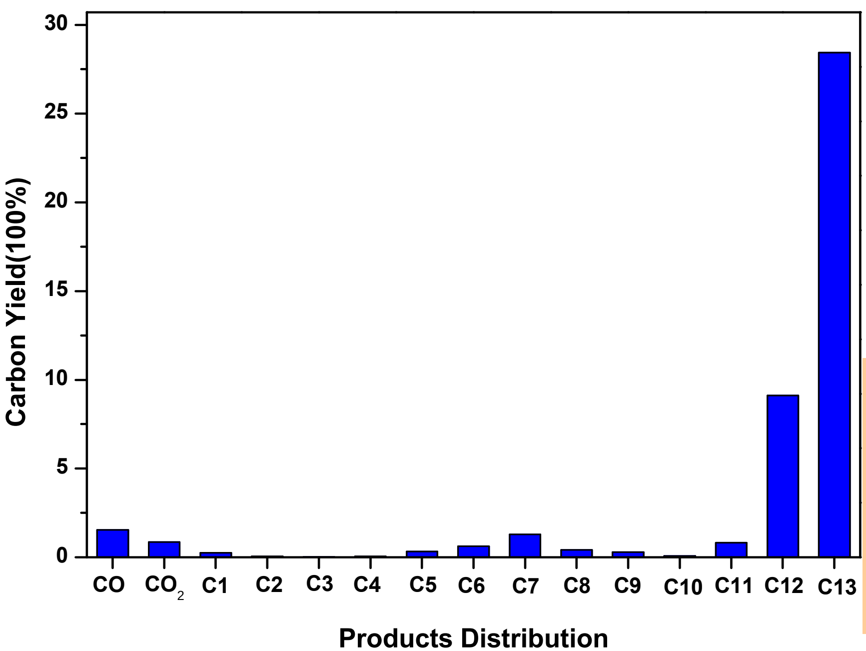


中间体加氢异构
Intermediate Isomerization



二亚糠基丙酮(F2A)
1,5-di-2-furanyl-1,4-pentadien-3-one

反应温度（℃）		C摩尔得率（%）														
	CO	CO2	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C8-C13
260	1.54	0.86	0.26	0.05	0.01	0.048	0.33	0.62	1.29	0.41	0.28	0.08	0.82	9.12	28.43	39.14

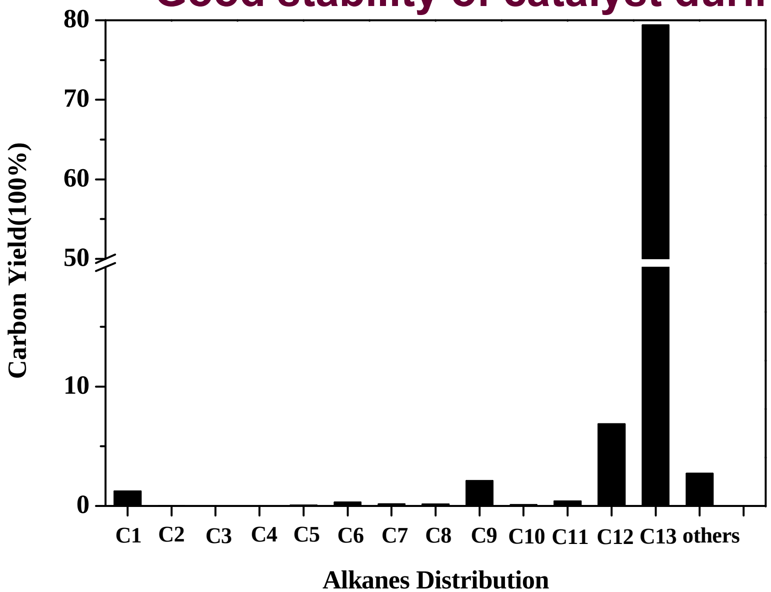


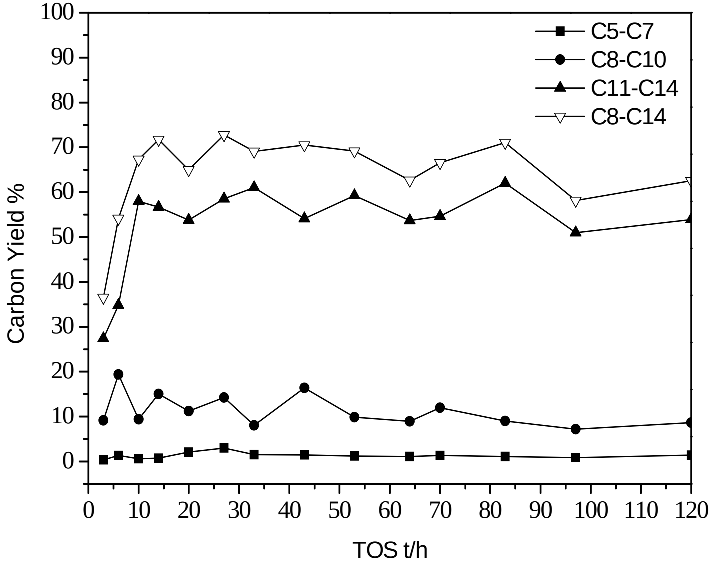
C11-C13 alkanes
（航空燃油, Jet fuel）

- 采用浆态床对中间体C13进行HDO初步探索。
  HDO of C13 intermediate (F2A) in a slurry bed.
- 产物以C12和C13烷烃为主，收率为40%。
  The product was dominated by C12 and C13 alkanes with the total yield of 40%.

中间体加氢异构
Intermediate Isomerization

- 采用固定床对航空燃料中间体C13进行HDO初步探索。
  HDO of C13 intermediate (F2A) in a fixed bed.
- 产物以C13烷烃为主，收率近90%。
  The product was dominated by C13 alkanes with the total yield of 90%
- 催化剂反应120 h，催化活性保持稳定。
  Good stability of catalyst during 120 h

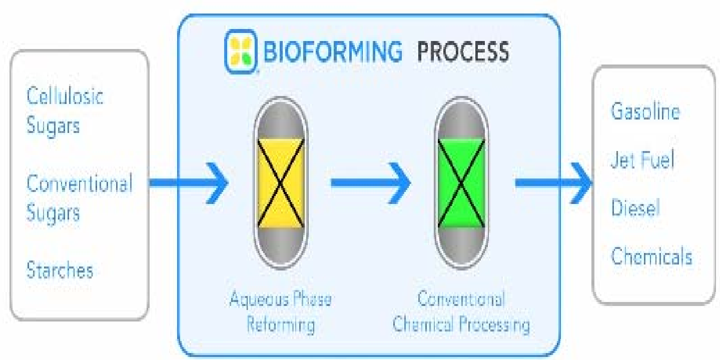




反应温度/°C	C摩尔得率（%）													
	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	others	C8-C13
300	0.26	-	-	-	0.05	0.32	0. 16	0.13	2.10	0.01	0.41	6.86	79.39	2.73	88.90

技术对比
Technical comparison

2008 - (pilot plant) USA



2010 - (pilot plant) CHINA

原料：纤维素糖、单糖类、淀粉（Feedstocks：cellulose, sugars, or starches）

2004年美国提出水相催化转化生物质生产运输燃料（贵金属催化体系）(Noble metal catalysts)

仅美国Virent公司建有生物汽油/航空油生产系统，其生产规模不详。

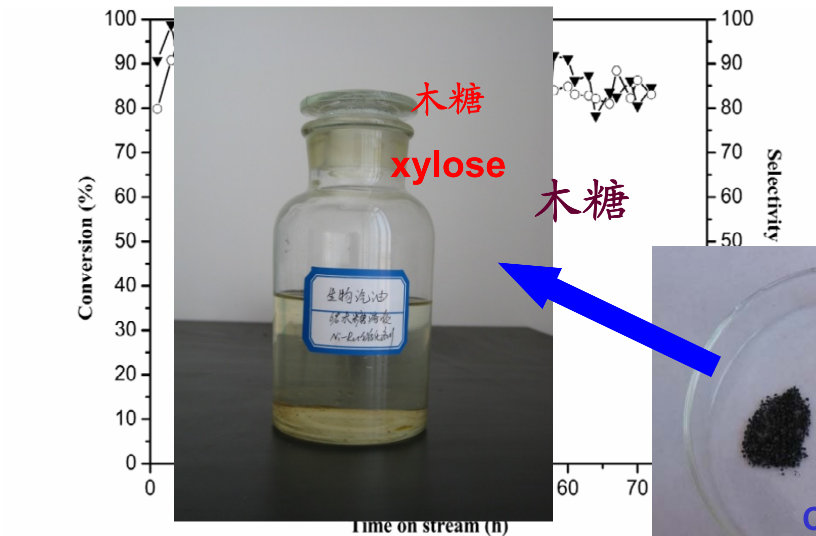
原料：单糖、生物质秸秆 (Feedstocks:sugars or biomass straw)

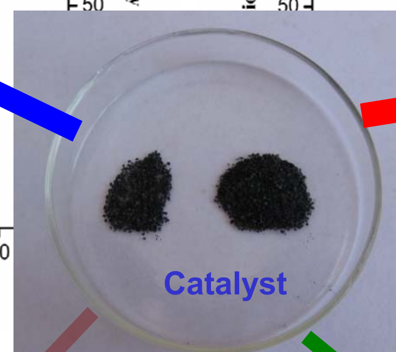
2006年中科院广州能源所开展水相重整技术研究（镍基催化体系）(Ni-based catalysts)

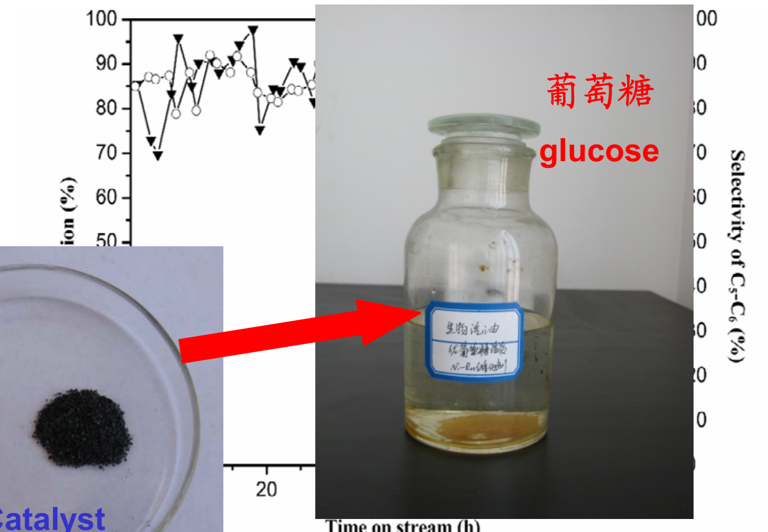
2010年建成国内仅有年产150吨生物汽油示范中试系统。(biogasoline,150 tons per year)

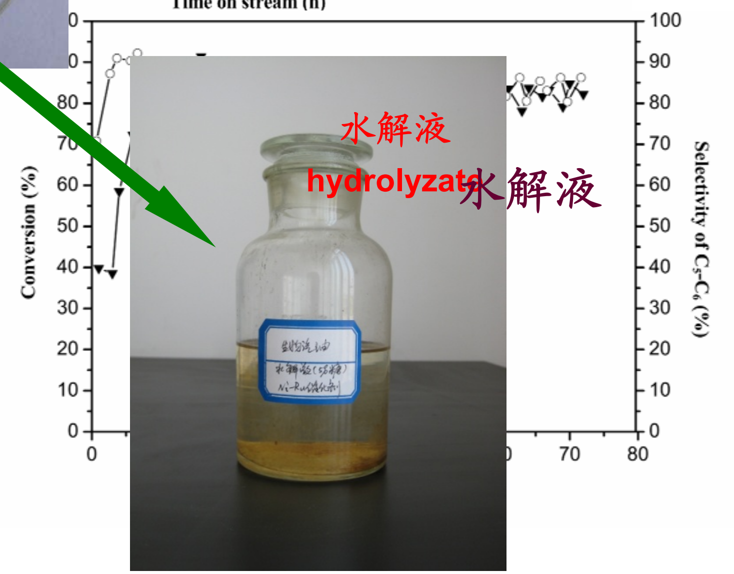
百吨级生物航空燃油中试系统在建设中。

中试系统运行
Pilot plant testing









反应条件 Ni-Ru催化剂

Reaction co ; Ni-Ru catalyst

生物汽油中试

催化剂反应7 总碳转化率维持在80%左 维持在80-90%.

Pilot system ntinuously with 80% of t on and 80-90% of C5 and C6 ring 72 h reaction.

中试系统运行结果(72h)
Results of pilot plant test

水解液 Hydrolyzate	原液（g/l） Before reaction	反应后（g/l） After reaction	单糖转化率 （%） Monosaccharide conversion	总糖转化率（%） Sugar conversion
葡萄糖 Glucose	13.683	3.873	71.6	80.1
木糖 Xylose	38.633	6.162	84.0	
阿拉伯糖 Arabinose	--	0.411	--	
纤维二糖 Cellobiose	0.235	0.065	85.5	
糠醛 Furfural	--	0.034	--	
5-羟甲基糠醛 5-hydroxymethyl furfural	0.024	0.008	66.6	

原料水解液：总糖浓度为4.99%；木糖浓度为3.67%；葡萄糖浓度为1.29%

Hydrolyzate: The total sugar concentration of 4.99%; xylose concentration of 3.67%; glucose concentration of 1.29%.

4.结论 Conclusions

- 采用酸酸耦合水解，半纤维素水解率达到90%；纤维素水解率达到85%以上；总糖浓度达到6%，戊糖和己糖收率达到80%以上；

  Biomass was efficiently hydrolyzed by bi-acid coupled hydrolysis with 90 % and 85% conversion of hemicellulose and cellulose, respectively. Total sugar concentration was 6%, with above 80% yield of pentose and hexose.

- 水相催化重整过程，水解液中糖类转化为以C5-C8烷烃为主的生物汽油组分；糖转化率达到85%； C5-C8选择性达到80-90%；

  Sugar monomers in hydrolyte were efficiently converted into bio-gasoline composed of C5-C8 alkanes by catalytic reforming technology with 85% of sugar conversion and the 80-90% yield of bio-gasoline.

- 通过碳链增长与加氢，水解液中糖类转化为以C8-C15烷烃为主的航空燃油组分；航空燃油收率达到90%；

  By combining carbon chain growth with catalytic hydrogenation, sugar monomers in hydrolyte were efficiently converted into jet fuel composed of C8-C15 alkanes with near 90% yield.

- 生物质水相催化制取烷烃燃料是一条新的技术路线，已建成的百吨级生物汽油中试示范系统,运行数据显示，该项技术具有很强的发展潜力。

  The liquid alkanes from biomass by the aqueous catalysis is a novel technique, and 150-ton of bio-gasoline pilot plant has been built up. The steady operation showed its prospective potentiality.

Thanks for your attention!