



GREEN CHEMISTRY

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GREEN CHEMISTRY

DEFINITION

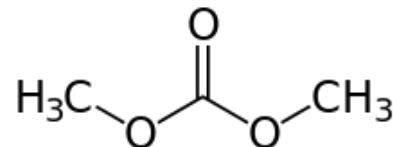
Green Chemistry is the utilisation of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products .

GREEN CHEMISTRY IS ABOUT

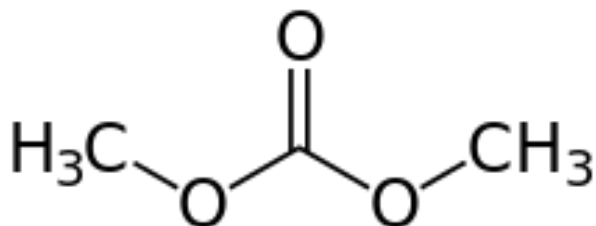
- **Using Non-Toxic Reagents**
- **Use of Catalysts in place of Stoichiometric Reagents**
- **Use of Renewable Resources**
- **Improved Atom Efficiency**
- **Use of Solvent Free or Recyclable Environmentally Benign Solvent systems**
- **Waste Minimisation at Source**

Reactants for green chemistry

- Dimethyl Carbonate
- Carbon Dioxide (CO₂)
- O₂
- Hydrogen Peroxide (H₂O₂)
- Biomass (cellulose, lactic acid, 1,3-propanediol, glycerol)



Dimethyl Carbonate



Boiling point=90.1 °C

Melting point= 4 °C

Density= 1.069 g/cm³

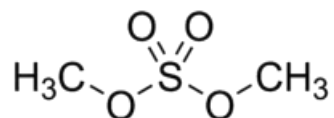
Toxicity (LD₅₀=12900 mg/Kg)

Methanol (LD₅₀=3000 mg/Kg)

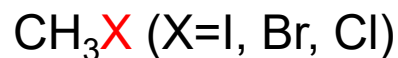
- **Dimethyl carbonate (DMC):** colorless compound with two ester groups, flammable liquid.
- **DMC:** is sparingly soluble in water, but miscible with most organic solvents, particularly polar solvents such as esters, ketones, ethers, and alcohols
- In toxicology, the **median lethal dose, LD₅₀** (abbreviation for "lethal dose, 50%"), is a measure of the dose required to kill half the members of a tested population after a specified test duration.
- DMC: is a green reagent because of its high LD₅₀.
- LD₅₀ figures are frequently used as a general indicator of a substance's acute toxicity.
- A lower LD₅₀ is indicative of increased toxicity.
- **Dimethyl carbonate** contains ester groups, and it is easily decomposed in nature environment.

The application of DMC for methylation Reaction

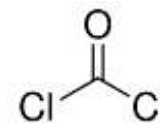
Dimethyl sulfate



Methyl halide

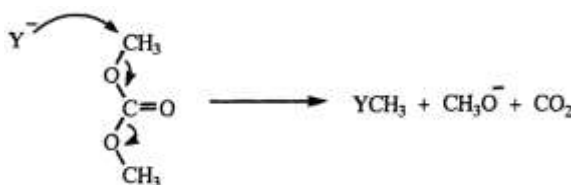


phosgene

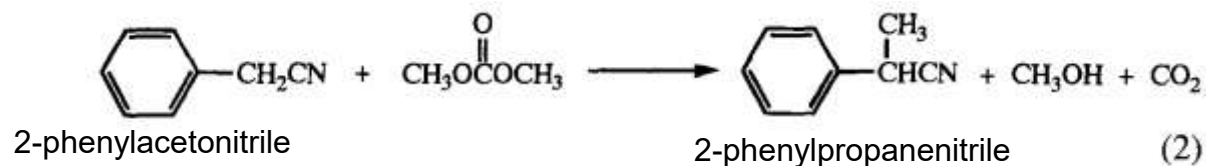


Highly toxic and corrosive

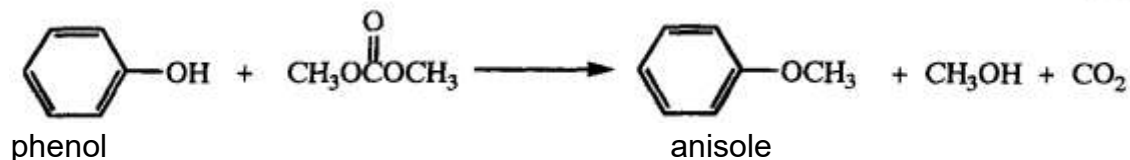
Base- or acid-catalyzed hydrolysis



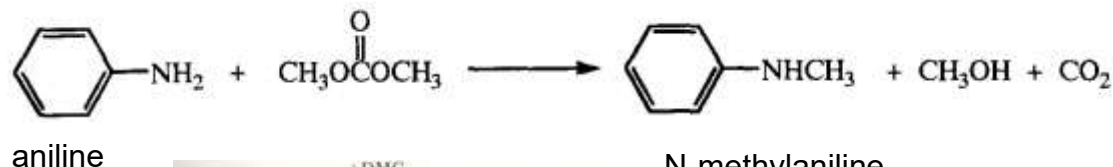
C-methylation with DMC



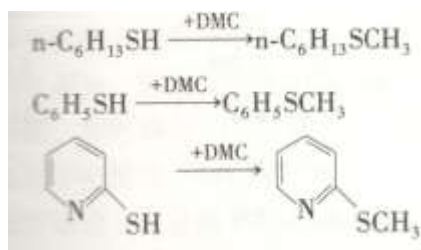
O-methylation with DMC



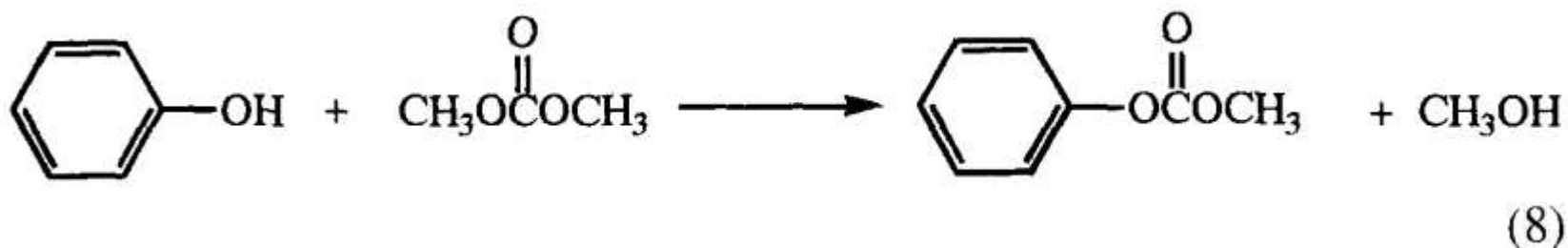
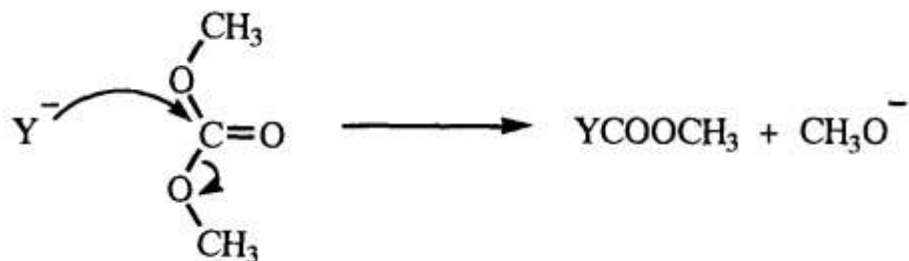
N-methylation with DMC



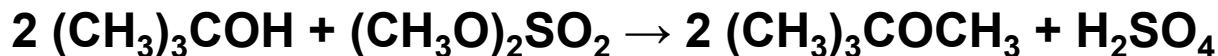
S-methylation with DMC



DMC used as a carboxylating agent

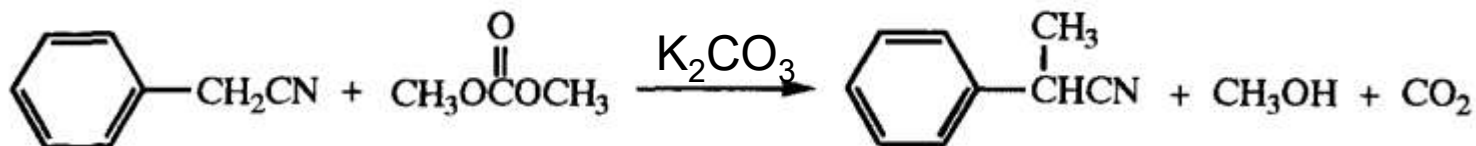


C-methylation with DMC



phenylacetonitrile

- Disadvantages:** (1) **toxic** and **corrosive**;
(2) requiring a stoichiometric amounts of **strong base for neutralization**;
(3) producing a stoichiometric amount of **inorganic solids** such as sodium iodide;
(4) **the mono- to dimethyl derivative ratio was low**, never exceeding 2.4.



- Advantages:** (1) the reaction can proceed with the presence of **weak base**;
(2) these compounds can be effectively **mono-C-methylated** with an unprecedented selectivity of **>99%** at complete conversions.
(3) when a mixture of phenyl acetonitrile, DMC, and K_2CO_3 in a 1:20:2 molar ratio, respectively, was allowed to react at 180°C for 3.75 h, 2-phenylpropionitrile was obtained in a **95% yield** with a **purity >99%**.

C-methylation with DMC



Mono-methylation of arylacetonitriles and methyl arylacetates by dimethyl carbonate [19]

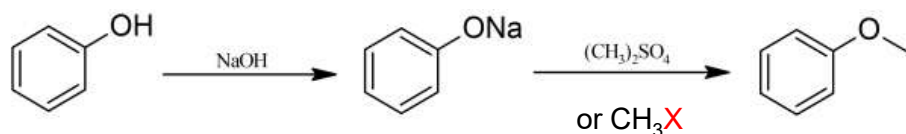
	Substrate Ar in ArCH_2X	X	Reaction time (h)	Conversion ^a (%)	Product $\text{ArCH}(\text{CH}_3)\text{X}$ yield ^b (%)
1	Ph	CN	3.75	100	90
2	<i>o</i> -MeOC ₆ H ₅	CN	14.5	100	85
3	<i>m</i> -MeOC ₆ H ₅	CN	3.5	100	80
4	<i>p</i> -MeOC ₆ H ₅	CN	4.75	99	88
5	<i>o</i> -MeC ₆ H ₅	CN	7.5	99	82
6	<i>p</i> -MeC ₆ H ₅	CN	7.5	98	80
7	<i>p</i> -ClC ₆ H ₅	CN	2.25	100	89
8	<i>p</i> -FC ₆ H ₅	CN	2.75	100	81
9	<i>m</i> -MeO ₂ CC ₆ H ₅	CN	8.00	100	91
10	Ph	COOMe	8.00	99	80
11	2-(6-MeOC ₁₀ H ₆)	COOMe	6.00	100	90

All reactions were carried out in an autoclave and using substrate, DMC and K_2CO_3 in a 1 : 18 : 2 molar ratio, respectively. Entries 1–9: reactions carried out at 453 K; entries 10–11: reactions carried out at 493 K.

^a Conversions determined by GC.

^b Yields based on distilled (entries 1–10) or recrystallized (entry 11) products.

O-methylation of phenols



苯甲醚: anisole



Yields=40%

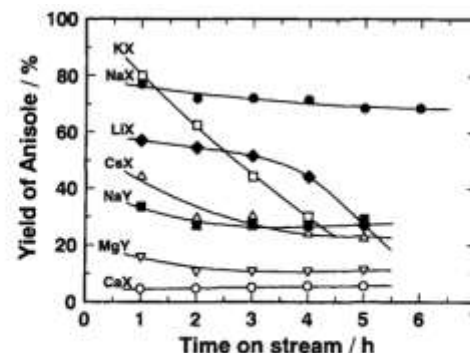
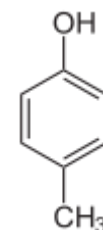
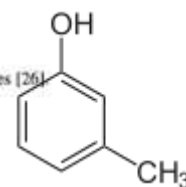
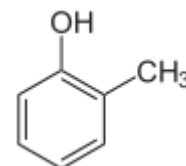


Fig. 3. Change in the anisole yield with time on stream in the methylation of phenol over various zeolites [26].
Reaction temperature: 553 K, phenol: 24.7 kPa, DMC/phenol: 1.0, WHSV = 3.70 h⁻¹.



cresols

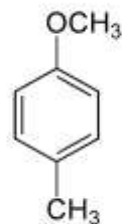
M. Lissel, S. Schmidt and B. Neumann, Synthesis, (1986) 382.

Products distribution in the methylation of phenol with DMC over zeolites

Catalyst	Phenol conversion (%)	Selectivity				Selectivity (based on DMC)
		Anisole	Cresols	Methyl tolyl ether	Others ^a	
NaX	81	93.6	1.5	4.9	—	76
KX	86	94.5	1.1	4.3	—	82
CsX	51	89.9	5.9	4.3	—	75
CaX	12	39.5	42.0	3.4	15.2	16
MgY	42	32.9	30.9	5.3	30.9	25

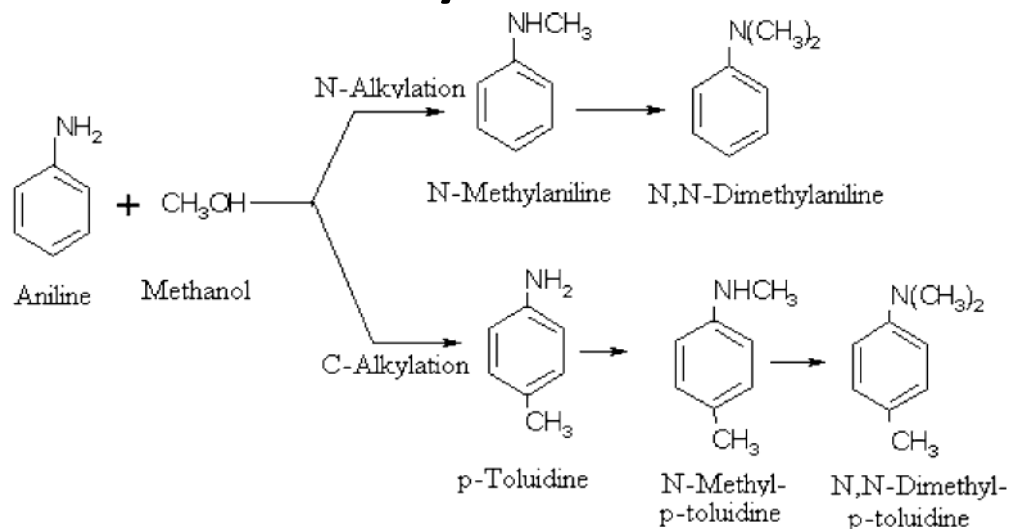
553 K, phenol=24.7 kPa, DMC/phenol=1.0, WHSV = 3.70 h⁻¹.

^a Mainly xylenols.

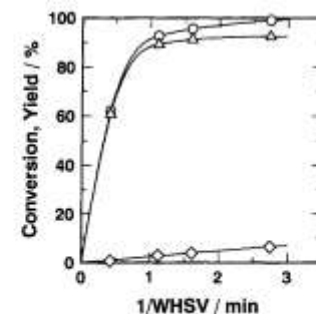
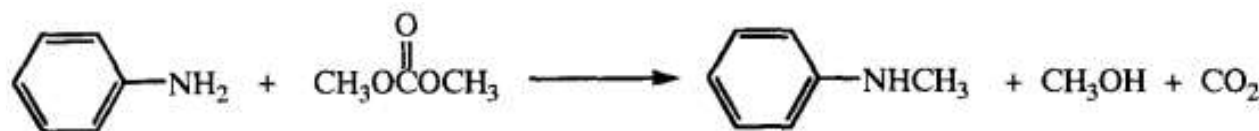


methyl tolyl ether

N-methylation with DMC



Catal Lett (2009) 133:175–184

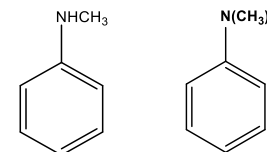


Conversion of aniline (○) and the yields of N-methylaniline (Δ) and N,N-dimethylaniline (□) in the methylation of aniline with DMC over KY [33]. Reaction temperature: 453 K, [aniline]: 1.25.

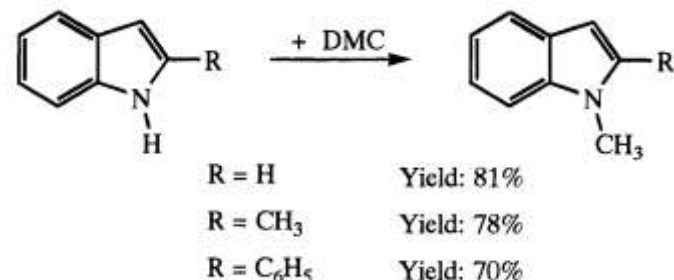
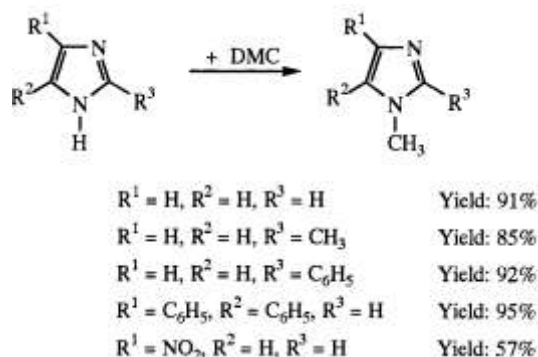
The reaction of aniline with DMC over alkali-exchanged zeolites

Catalyst	Temperature (K)	DMC/AN ratio	WHSV (h ⁻¹)	AN conversion (%)	Selectivity	
					1	2
KY	453	1.25	0.37	99.6	93.5	6.5
	478	1.25	0.37	100	86.8	13.2
NaX	508	2.0	0.10	100	11.5	88.5
	513	2.5	0.13	100	4.4	95.6

Z.-H. Fu and Y. Ono, Catal. Lett., 22 (1993) 277.



N-methylation of heterocycles

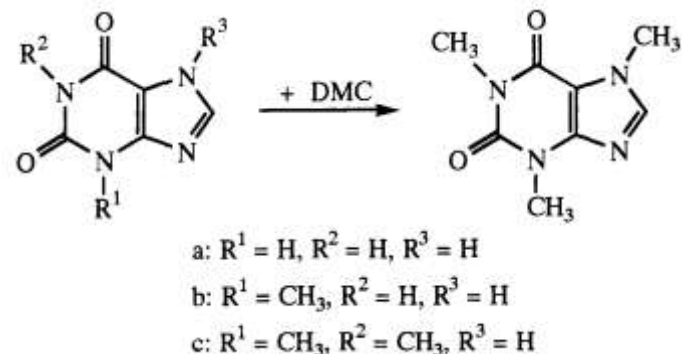
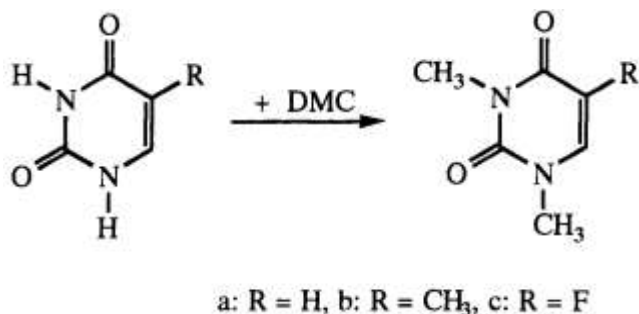


M. Lissel, Liebigs Ann. Chem., (1987) 77.

H. Jansen in der War and M. Lissel, Z. Naturforsch., 44b (1989) 863.

H. Jansen in der War and M. Lissel, Z. Chem., 29 (1989) 253.

M. Lissel and A.R. Rohani-Dezfuli, Chem. Ztg., 111 (1987) 83.

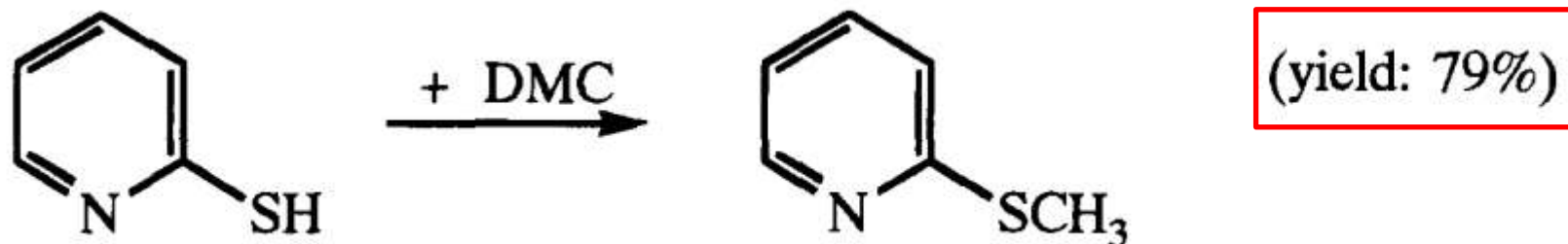
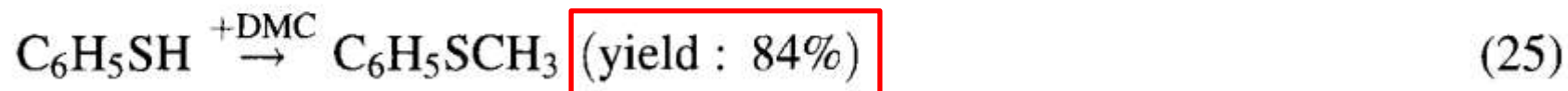
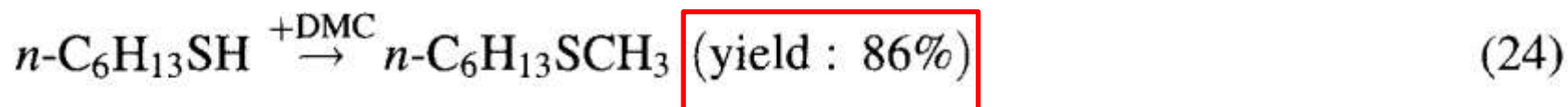


H. Jansen in der War and M. Lissel, Z. Naturforsch., 44b (1989) 863.

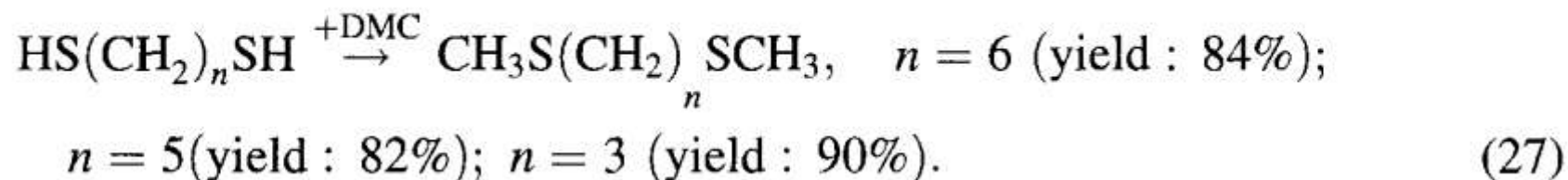
H. Jansen in der War and M. Lissel, Z. Chem., 29 (1989) 253.

Catalysis: K_2CO_3 and 18-crown-6, dimethylaminopyridine (DMAP) or N,N,N',N'-tetramethylethylenediamine (TMEDA).

S-methylation with DMC



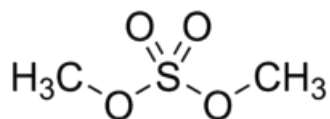
Pyridine-2-Thiol (26)



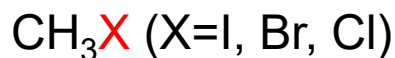
Y. Tamura, T. Saito, H. Ishibashi and M. Ikeda, Synthesis, (1975) 641.

The safety issues with traditional methylation agents

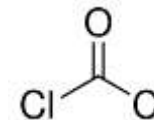
Dimethyl sulfate



Methyl halide



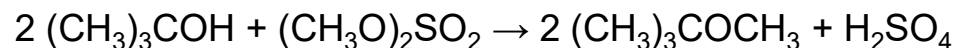
phosgene



Highly toxic and corrosive



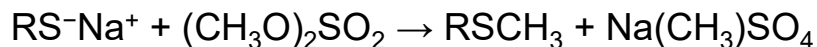
O-methylation with dimethyl sulfate



N-methylation with dimethyl sulfate

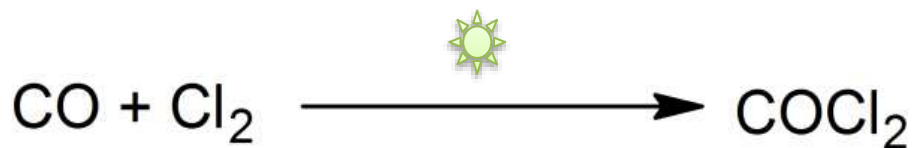
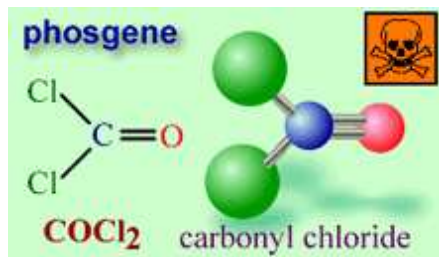


S-methylation with dimethyl sulfate



- Dimethyl sulfate is **carcinogenic** and **mutagenic**, **highly poisonous**, **corrosive**, **environmentally hazardous** and **volatile**.
- It can be absorbed through the skin, mucous membranes, and gastrointestinal tract, and can cause a fatal delayed respiratory tract reaction.
- **In water**, the compound is ultimately hydrolyzed to **sulfuric acid** and **methanol**.

The safety issues with phosgene



John Davy, in 1812

Effects of phosgene (COCl_2) on health

Phosgene concentration
(expressed in ppm)

Effects on human health

200

► Lethal within minutes

50

► Increase of the breathing rate, respiratory distress and pulmonary edema

30

► Irreversible effects threshold after 1 minute

3

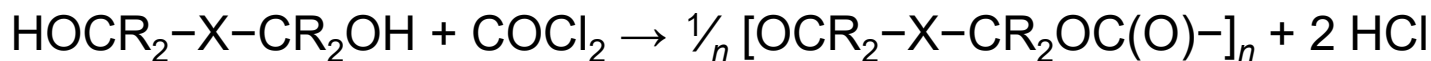
► Slight breathing difficulties, chest tightness

1

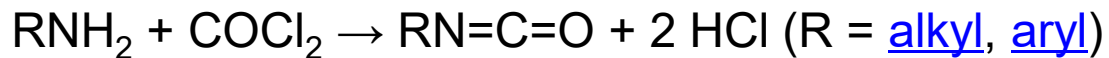
► Irreversible effects threshold after 30 minutes



Synthesis of carbonates



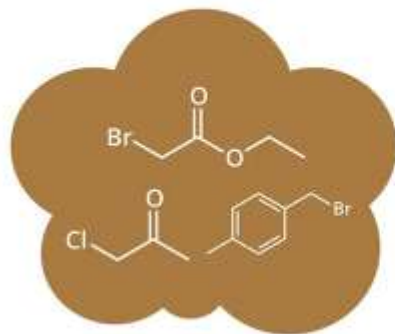
Synthesis of isocyanates



Sodium bicarbonate may be used to neutralise liquid spills of phosgene. Gaseous spills may be mitigated with ammonia.

CHEMICAL WARFARE WORLD WAR I

WORLD WAR I IS SEEN AS THE DAWN OF MODERN CHEMICAL WARFARE. SOME 50 DIFFERENT CHEMICAL AGENTS WERE DEPLOYED ON THE BATTLEFIELDS, AND 3,000 CHEMICALS WERE INVESTIGATED AS POTENTIAL WEAPONS. THEIR USE CAUSED APPROXIMATELY 1.3 MILLION NONFATAL CASUALTIES, AND 90,000–100,000 FATALITIES. HERE, WE SUMMARIZE THE MOST PREVALENT OF THE CHEMICALS USED.



TEAR GASES

(ethyl bromoacetate, chloroacetone & xylol bromide)

SMELL & APPEARANCE

Both ethyl bromoacetate and chloroacetone are colorless to light yellow liquids with fruity, pungent odors. Xylol bromide is a colorless liquid with a pleasant, aromatic odor.

EFFECTS

Tear gases are what are known as lachrymatory agents: They irritate mucous membranes in the eyes, mouth, throat, and lungs, leading to crying, coughing, breathing difficulties, and temporary blindness.

FIRST USED

1914 In August, the French used tear gas grenades against the German Army, to little effect.

ESTIMATED CASUALTIES

0 These gases were used to incapacitate enemies rather than to kill; the symptoms commonly resolved within 30 minutes of leaving the affected area.

fatalities in World War I



CHLORINE

SMELL & APPEARANCE

Chlorine is a yellow-green gas with a strong, bleachlike odor. Soldiers described its smell as "a distinct mix of pepper and pineapple."

EFFECTS

Chlorine reacts with water in the lungs, forming hydrochloric acid. Coughing, vomiting, and irritation to the eyes occur at low concentrations. At concentrations of 1,000 parts per million, it leads to rapid death.

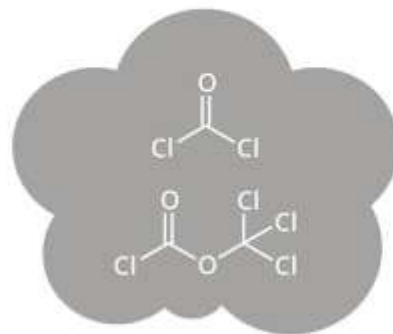
FIRST USED

1915 German forces used chlorine near Ypres, Belgium, in April. British forces retaliated in September, at Loos, France.

ESTIMATED CASUALTIES

>1,100 Chlorine was devastating because troops were initially unequipped to deal with it. Later, gas masks limited its effectiveness.

estimated fatalities in first use of chlorine at Ypres



PHOSGENE & DIPHOSGENE

(carbonyl dichloride & trichloromethane chloroformate)

SMELL & APPEARANCE

Phosgene is a colorless gas with a musty odor comparable to that of newly-mown hay or grass. Its density is four times that of air. Diphosgene is a colorless, oily liquid.

EFFECTS

They react with proteins in lung alveoli, causing suffocation. They cause coughing, difficulty breathing, and irritation to the throat and eyes. Have delayed effects, not evident for 48 hours, leading to death.

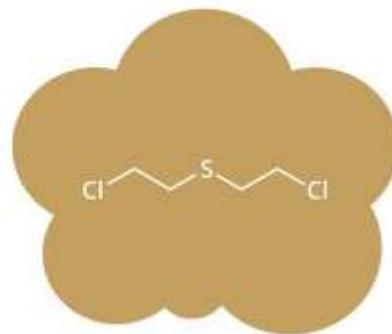
FIRST USED

1915 In December 1915, German forces used phosgene against the British at Ypres.

ESTIMATED CASUALTIES

85% It's estimated that this pair caused a majority of gas-related fatalities. Phosgene was primarily deployed from gas canisters. Both chemicals were used to fill artillery shells.

of all gas-related fatalities in WWI



MUSTARD GAS

(bis[2-chloroethyl]sulfide)

SMELL & APPEARANCE

When pure, mustard gas is a colorless and odorless liquid. In its impure form, it's used as a chemical agent. Then, it's yellow-brown in color and has a variable odor resembling garlic, horseradish, or rubber.

EFFECTS

Irritant and blistering agent that damages the eyes, skin, and respiratory tract. It causes chemical burns on contact with skin. Effects are delayed by hours, and repeat exposure increases sensitivity and blistering.

FIRST USED

1917 On July 12, 1917, German forces used mustard gas against the British at Ypres.

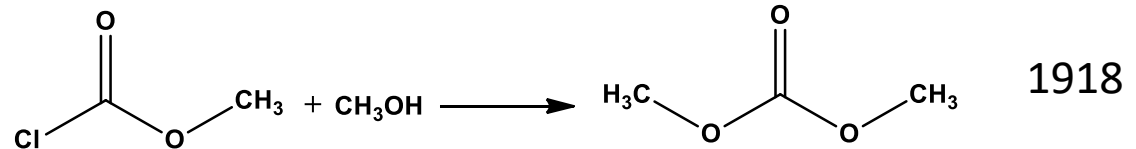
ESTIMATED CASUALTIES

2–3% The mortality rate of mustard gas casualties was low, but the gas's effects were debilitating, and patients required elaborate care.

of mustard gas casualties died in WWI

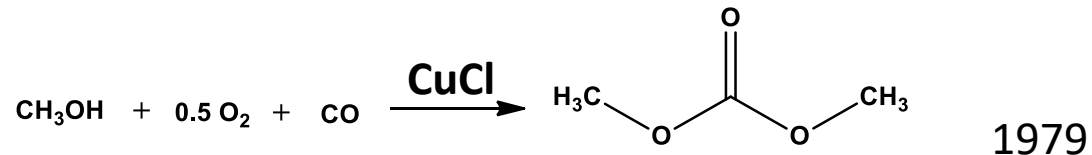
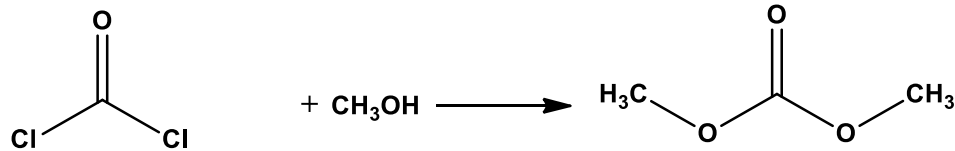
The preparation of DMC

Methyl chloroformate



Phosgene

Highly toxic and corrosive

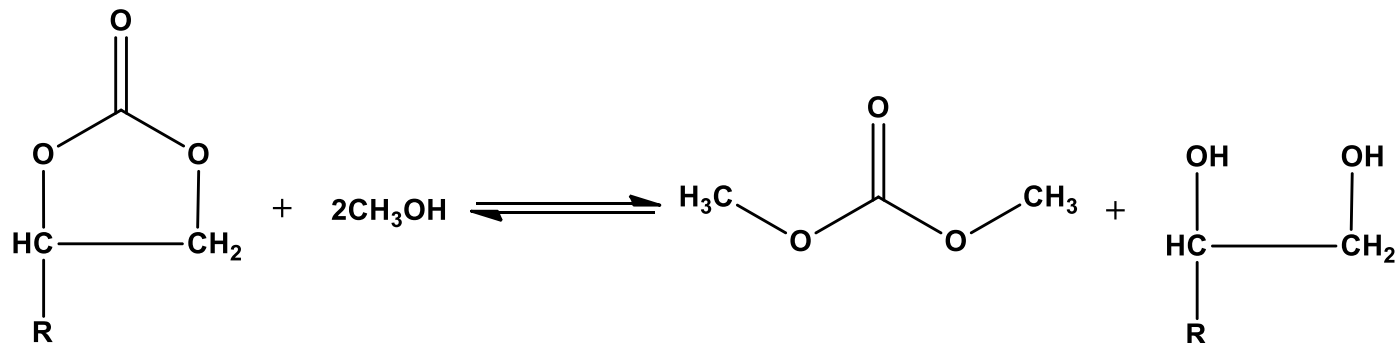


Methanol worked as both solvent and reactant , 120-130 °C, pressure on 2.0-3.0 MPa.

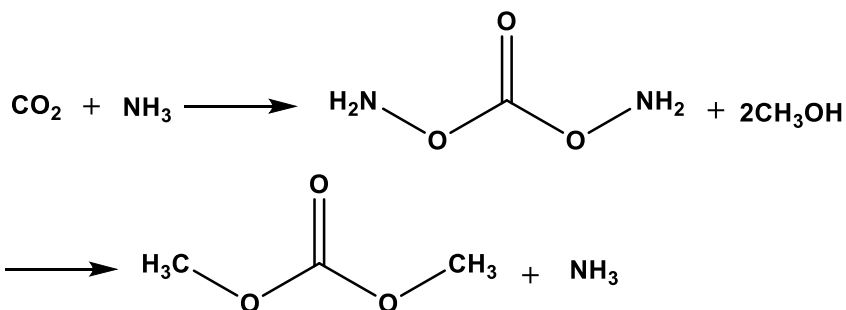
Shortcoming: Corrosive and short life time of catalyst (**CuCl**).

The preparation of DMC

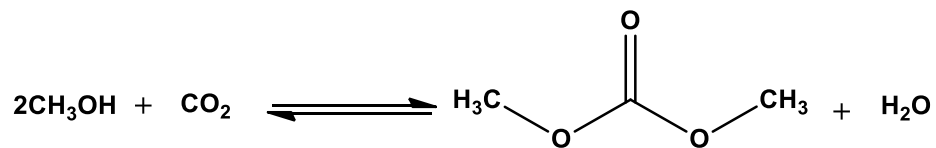
(1)



(2)



(3)

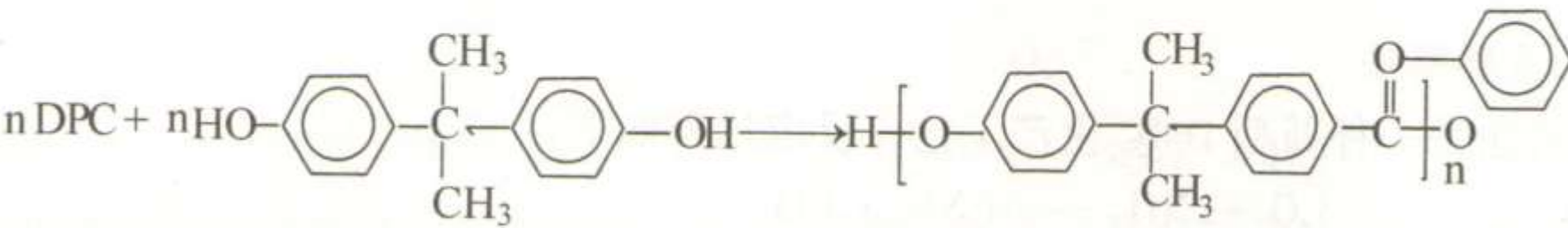
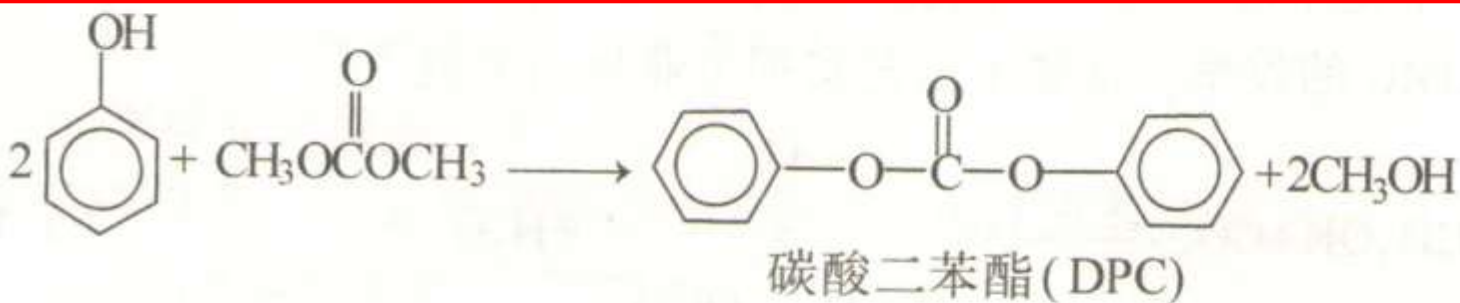
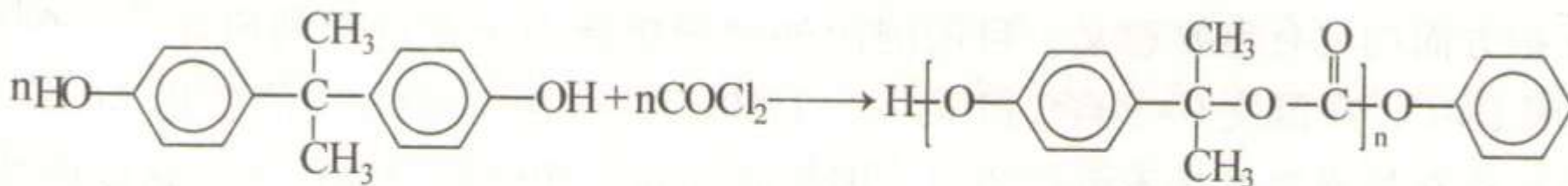


800 °C and 1 Mpa.

The application of DMC for carbonylation

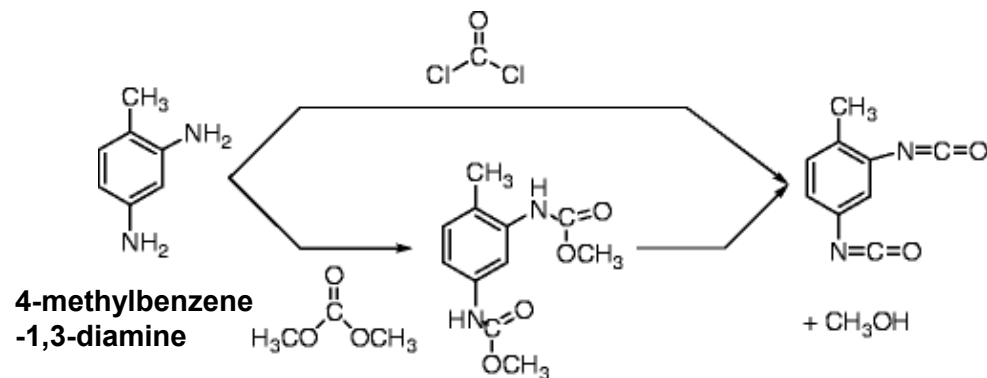
1. Synthesis of polycarbonate via trans-esterification with DMC and phenol

Polycarbonate as an important engineering plastic, was normally synthesized by using **phosgene and bisphenol**.

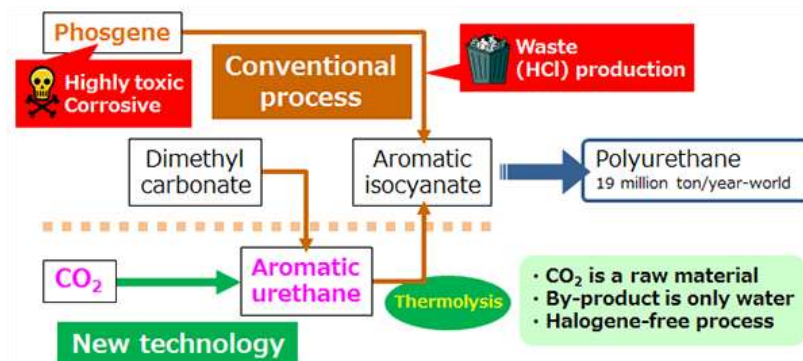
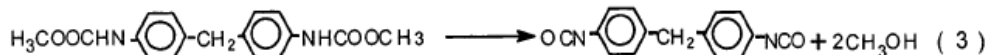
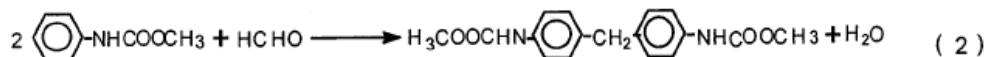
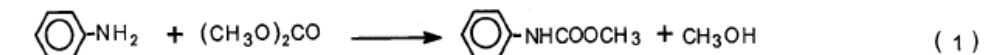


The application of DMC for carbonylation

2. The synthesis of isocyanate: Isocyanate includes **toluene diisocyanate** (TDI, 甲苯二异氰酸酯) and **diphenylmethane diisocyanate** (MDI, 二异氰酸酯), which can be used to synthesize plastics and elastomer (**polyurethane**).



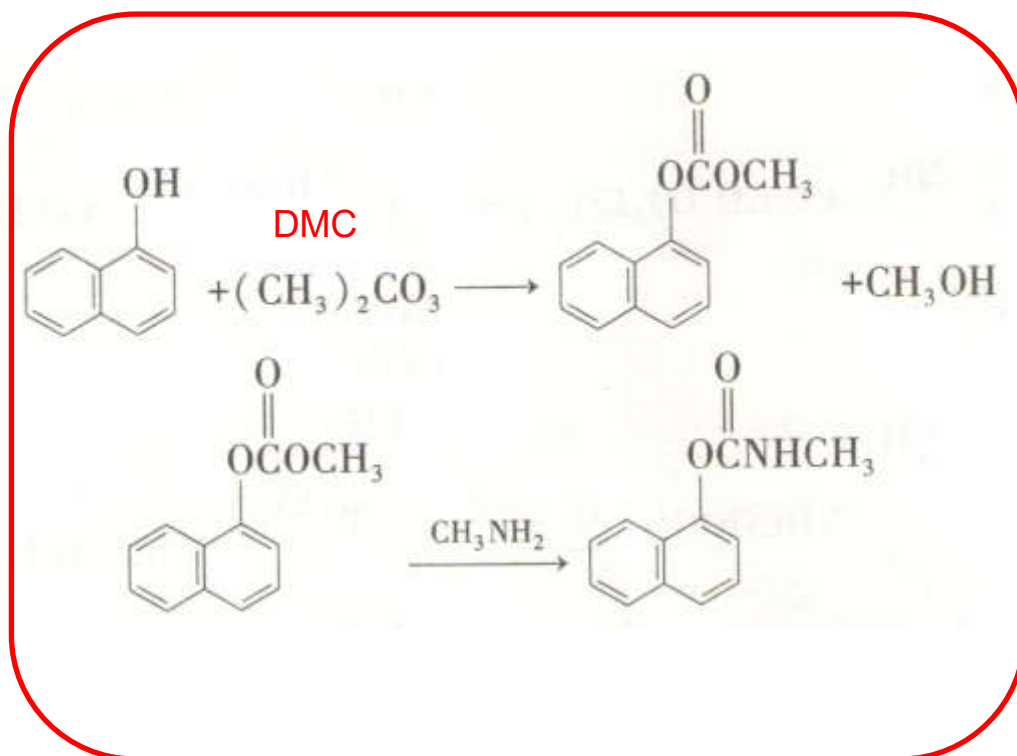
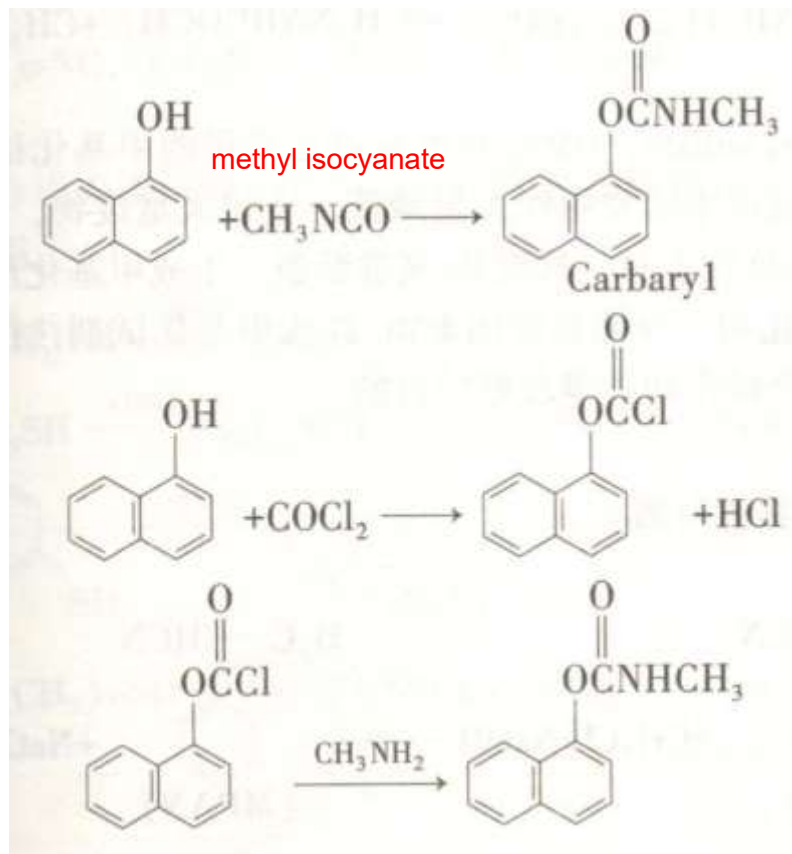
Toluene diisocyanate (TDI): 4-methylbenzene-1,3-diamine reacted with DMC to afford the formation of **methyl N-phenyl carbamate** first, and then undergo thermolysis to lose methanol and form **toluene diisocyanate**.



Diphenylmethane diisocyanate (MDI): phenylamine firstly reacted with DMC to form **methyl N-phenyl carbamate**, and then further reacted with **formaldehyde** to form **Diphenyl methane-4,4' diurethane**, which further undergo thermolysis to afford MDI.

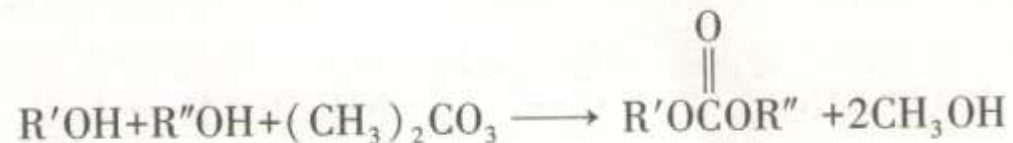
The application of DMC for carbonylation

3. The synthesis of carbaryl: carbaryl (胺甲萘) worked as a pesticide, was prepared from **naphthol** and **methyl isocyanate**, or using **phosgene** and **methylamine**.

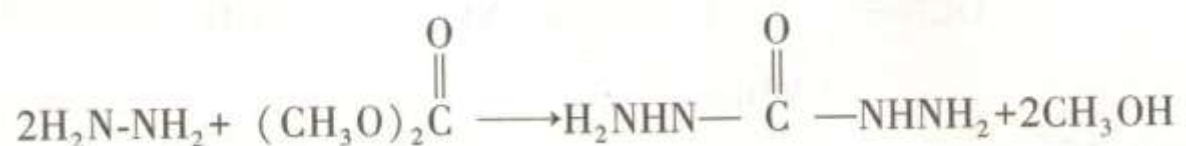


The application of DMC for carbonylation

4. The synthesis of aliphatic carbonate: aliphatic carbonate was normally used as **lubricant**.

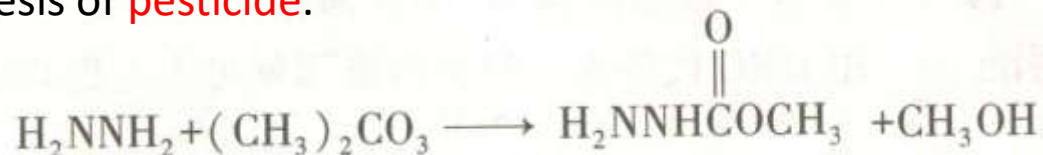


5. The synthesis of semicarbazide(二氨基脲)



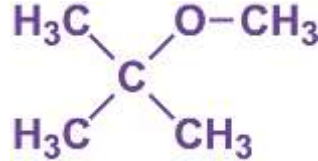
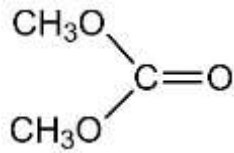
hydrazine

6. The synthesis of N-methyl-carbazole: N-methyl-carbazole (甲基呋唑) as intermediate for the synthesis of **pesticide**.



DMC worked as additive of gasoline

Dimethyl carbonate (DMC) has been of interest as **an oxygenate** additive to diesel fuel because of its high oxygen content (53%) than methyl tert-butyl ether (MTBE).



- **MTBE** has been used as an octane enhancer of gasoline fuel to reduce the exhaust emissions from gasoline engines. Because of an environmental effect on the ground-water and surface-water contamination, MTBE has been prohibited or limited in premium gasoline fuel in many countries.
- **DMC** has excellent features such as: (1) non-toxic production, environmentally friendly, non-corrosive, and safe handling ; (2) high oxygen content, 53.28% by weight, which plays an important role in suppressing the soot precursor concentration in fuel-rich combustion zone; (3) 100% miscibility in fossil fuels (diesel and gasoline) ; (4) relatively high hydrogen to carbon (H/C) ratio; (5) absence of carbon-carbon links in its molecular structure ;(6) low boiling point, which is important in spray atomization and mixing;and (7) low carbon to oxygen (C/O) ratio.

By using of oxygenates to gasoline, DMC alters the physiochemical properties of **density, volatility, octane rating and enthalpy** of combustion, makes gasoline **burn more cleanly**, thereby significantly **reducing toxic tailpipe pollution**, and produces higher compression ratios inside the engines without knocking and increase in horse power due to increase in the **octane number**.

Global Dimethyl Carbonate (DMC) market

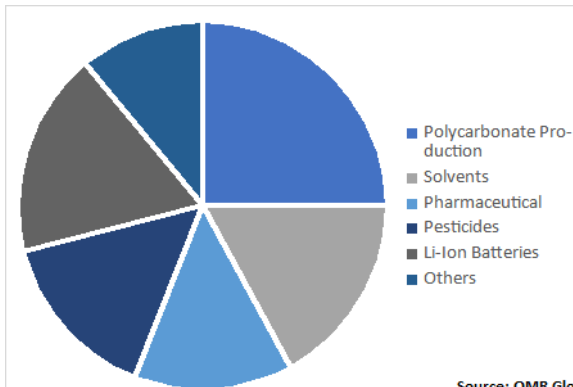
The global Dimethyl Carbonate (DMC) market was valued at **USD 849 million in 2020** and it is expected to reach **USD 1348.6 million by the end of 2027**, growing at a CAGR (Calculate Compounded Annual Growth Rate) of **6.8%** during 2021-2027.

Global Dimethyl Carbonate Market:
Dimethyl Carbonate Market, by Grade

- o Industrial
- o Battery
- o Pharmaceutical

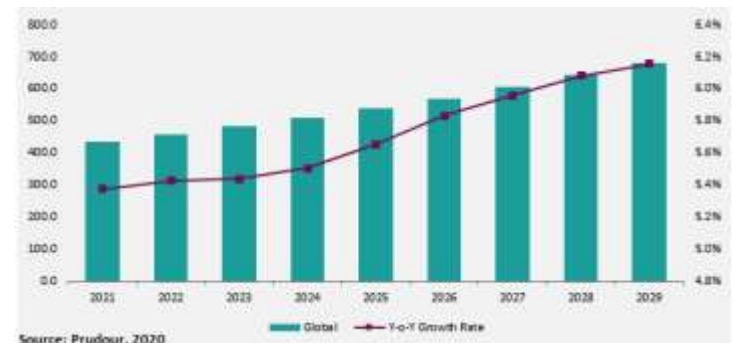
Dimethyl Carbonate Market, by End Use

- Solvents
 - o Paints & Coatings
 - o Adhesives
 - o Cleaning Agents & Others
- Alternative Fuel Additives
- Polycarbonate Production
- Pharmaceuticals
- Pesticides
- Lithium-ion Batteries
- Others



Source: OMR Global

Major Factors Driving The Growth Of The Dimethyl Carbonate (Dmc) Market Are Increasing end-user applications such as **Polycarbonate, Battery Solvent, Other Solvent, and Pesticides** is expected to drive the growth of the Dimethyl Carbonate (DMC) Market.



Source: Prudour, 2020

Carbon Dioxide

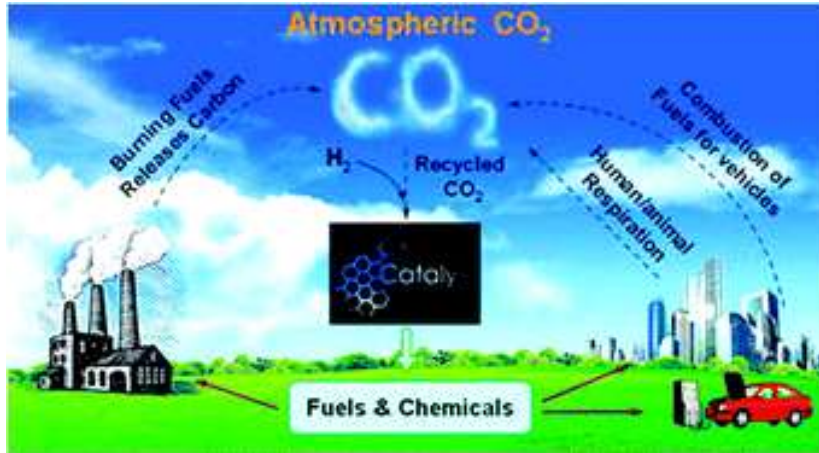
Carbon dioxide (CO_2) is a colorless and odorless gas vital to life on Earth.

Atmospheric carbon dioxide is the primary source of **carbon** in life on Earth.

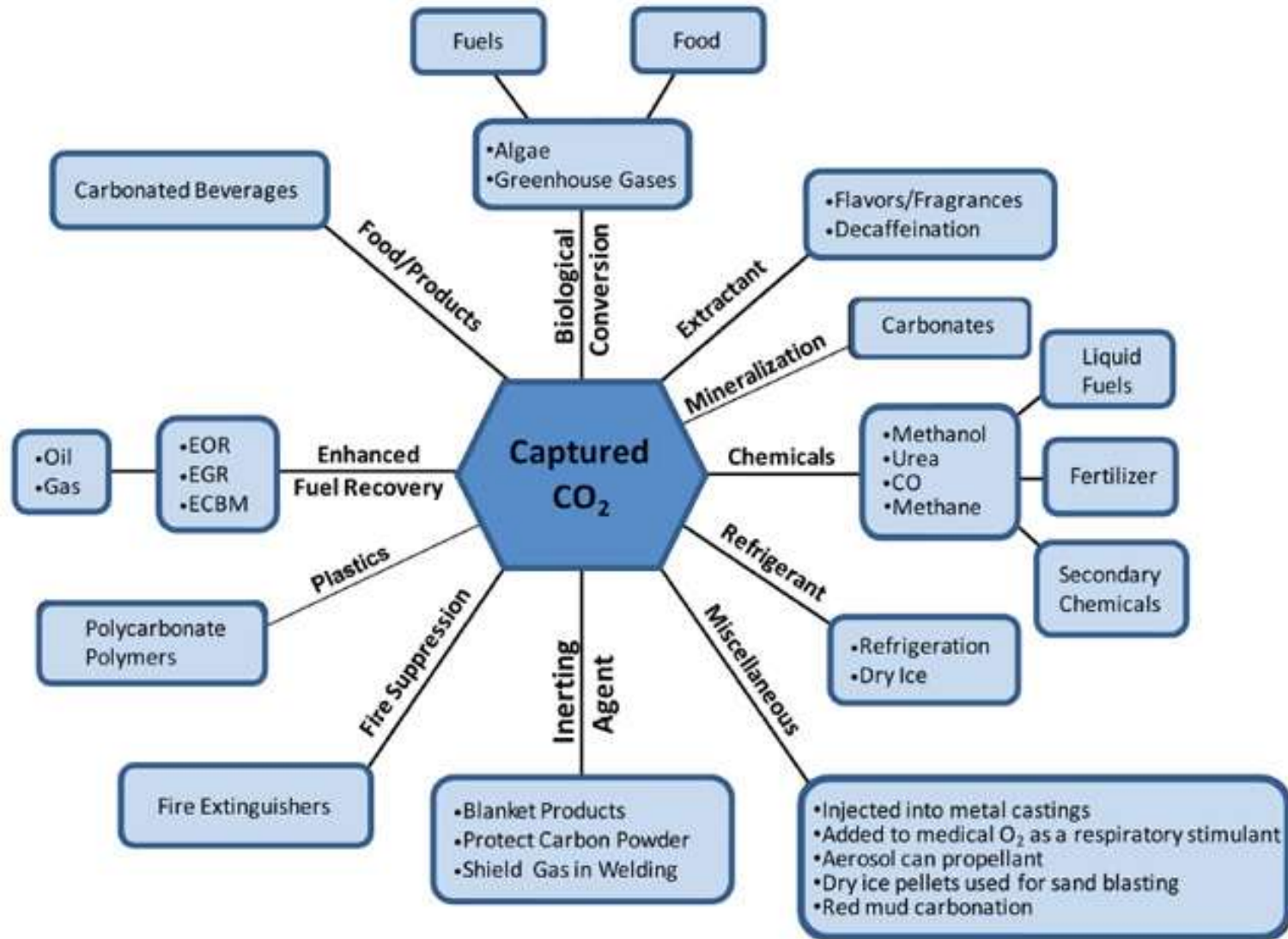
In nature, CO_2 is produced by all aerobic organisms when they metabolize carbohydrate and lipids to produce energy by respiration.

It is a versatile industrial material, used, for example, as **an inert gas in welding** and **fire extinguishers**, as a **pressurizing gas** in air guns and oil recovery, as a **chemical feedstock** and in liquid form as **a solvent** in decaffeination of coffee and supercritical drying.

Carbon dioxide is a significant greenhouse gas.



CO₂ Can Be A Resource Rather Than A Waste Product



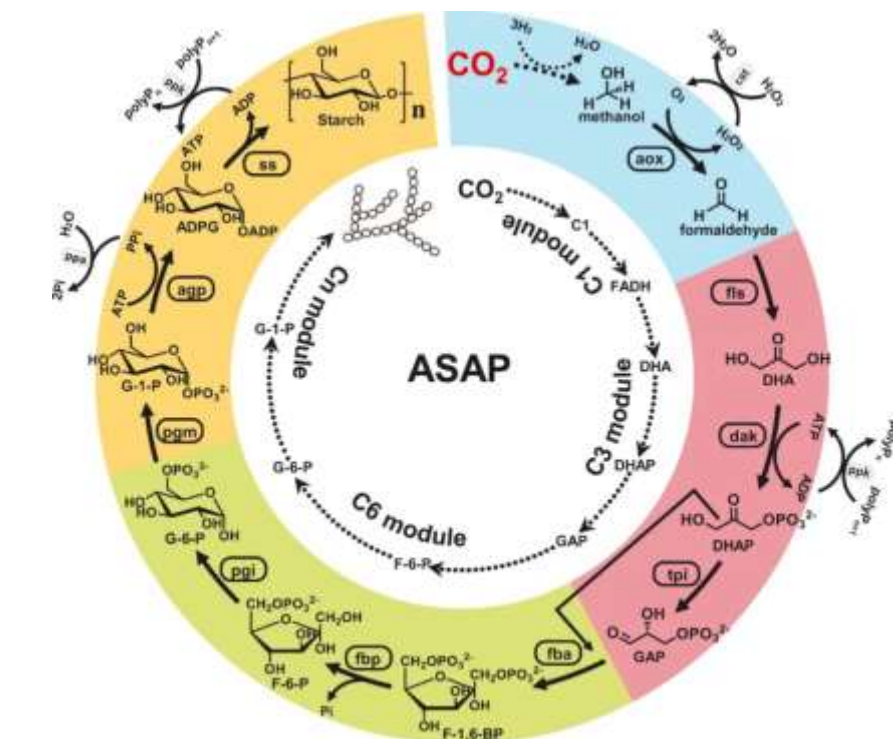
Cell-free chemoenzymatic starch synthesis from carbon dioxide

TAO CAI · HONGBING SUN · JING QIAO · LEILEI ZHU · FAN ZHANG · JIE ZHANG · ZIJING TANG · XINLEI WEI · JIANGANG YANG · QIANQIAN YUAN

WANDYIN WANG · XUE YANG · HUANYU CHU · QIAN WANG · CHEN YU · HONGWU MA · YUANXIA SUN · YUE LI · CAN LI · HUIFENG JIANG

QIN-QING WANG · AND YANHE MA · fewer Authors Info & Affiliations

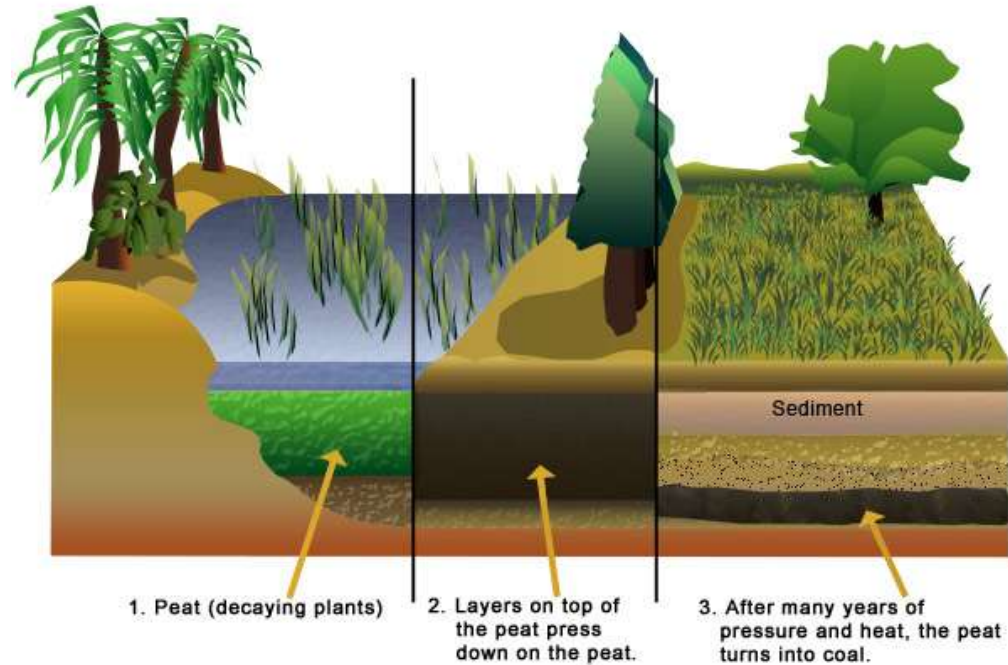
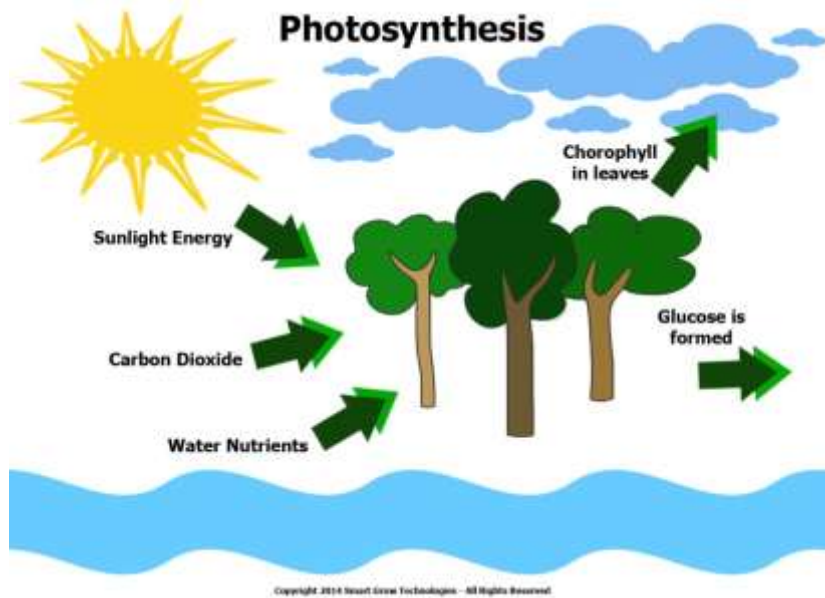
SCIENCE · 24 Sep 2021 · Vol 373, Issue 6562 · pp. 1523-1527 · DOI: 10.1126/science.abb4549



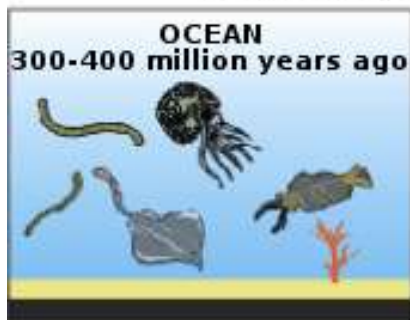
The scientists from the Chinese Academy of Sciences report a chemical-biochemical hybrid pathway for starch synthesis from carbon dioxide (CO₂) and hydrogen in a cell-free system. The **artificial starch anabolic pathway (ASAP)**, consisting of **11 core reactions**, and converts CO₂ to starch at a rate of **22 nanomoles** of CO₂ per minute per milligram of total catalyst, an **~8.5-fold higher rate** than **starch synthesis in maize**. This approach opens the way toward future chemo-biohybrid starch synthesis from CO₂.



Carbon recycling under nature process



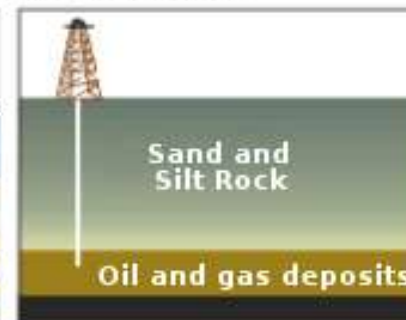
Petroleum and natural gas formation



Tiny sea plants and animals died and were buried on the ocean floor. Over time they were covered by layers of silt and sand.

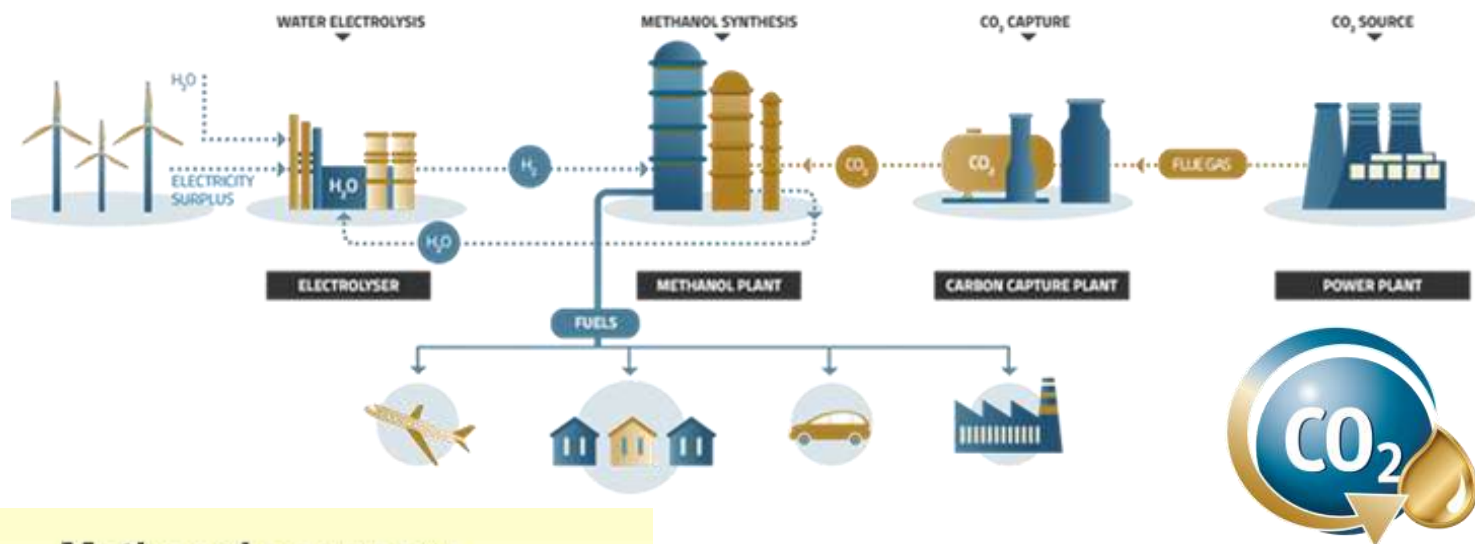
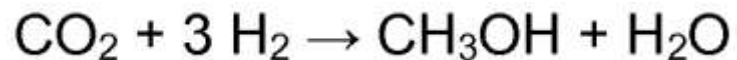


Over millions of years, the remains were buried deeper and deeper. The enormous heat and pressure turned them into oil and gas.

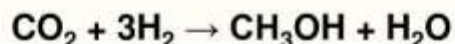


Today we drill down through layers of sand, silt and rock to reach the rock formations that contain oil and gas deposits.

Synthesis of methanol from carbon dioxide



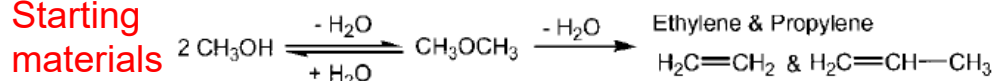
Methanol economy



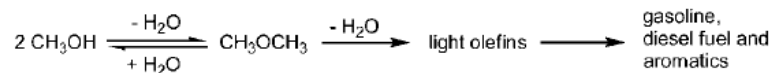
Methanol is a fuel for heat engines and fuel cells. Methanol is a liquid under normal conditions, allowing it to be stored, transported and dispensed easily. It can also be readily transformed into diesel fuel. Methanol is directly prepared from CO_2 .

The term **methanol economy** was coined by George Oláh (2006).

Starting materials



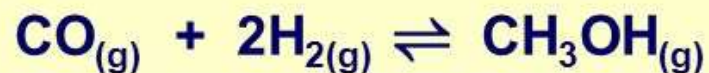
Fuel storage



Formation of methanol

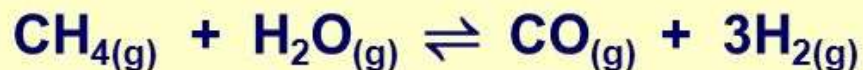


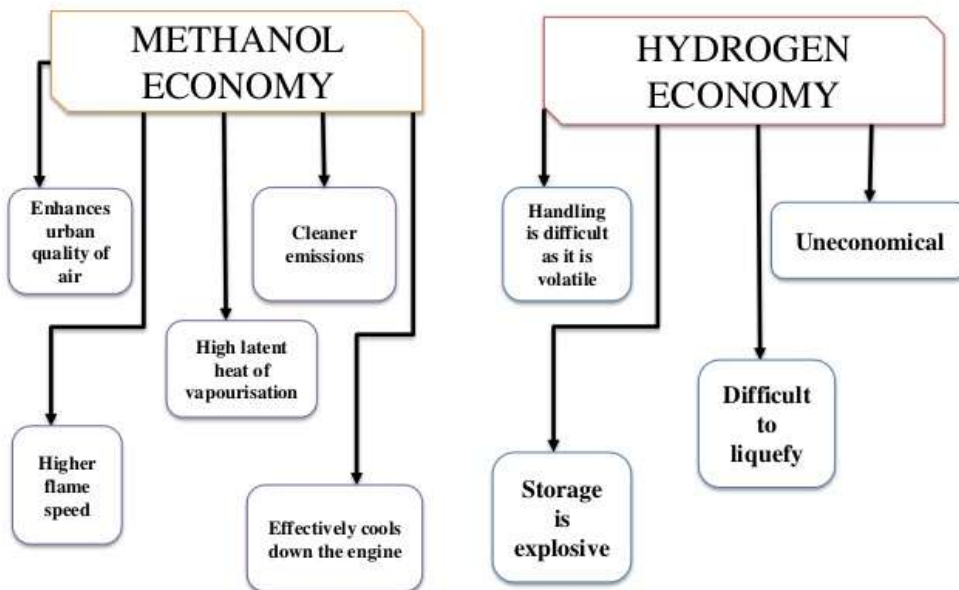
Methanol is an important chemical used in the manufacture of other chemicals. Methanol is made industrially by the reaction of carbon monoxide and hydrogen.



A mixture of **copper**, **zinc oxide** and **aluminium oxide** is used as a catalyst.

The mixture of carbon monoxide and hydrogen is called **synthesis gas**. It is made from methane and water by a process called **steam reforming**.

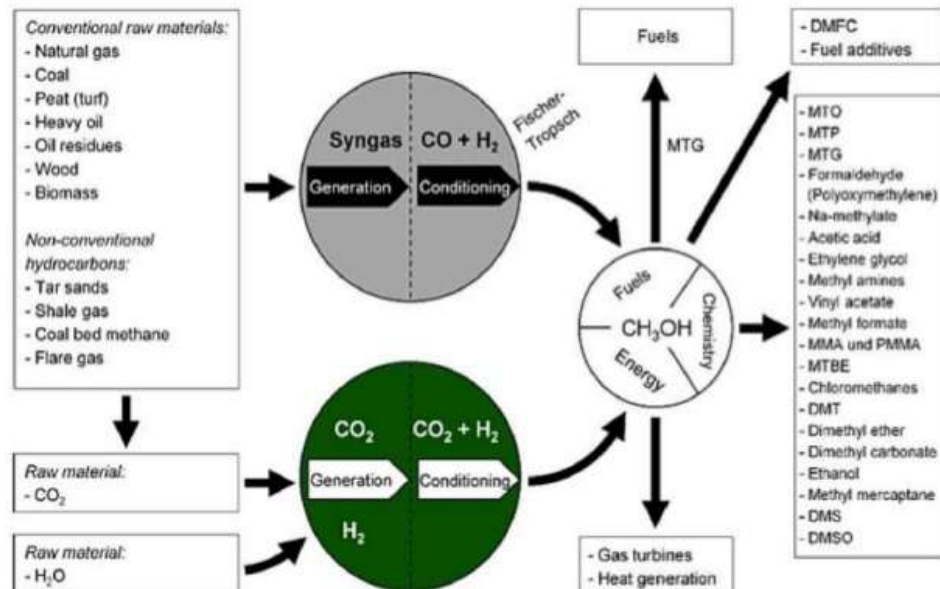




The Methanol Economy

- Broad range of sources:
 - Methane, bio-methane, organic wastes
- Useable in both Spark Ignition Engines and Diesels
- Can be mixed with ethanol and gasoline
- Higher octane
- Burns cooler
- Higher Flash point
- Burns cleaner
 - Emissions
- Fuel for furnaces, turbines
- Fuel for fuel cells

The cheapest liquid fuel, with the largest number of non-food sources

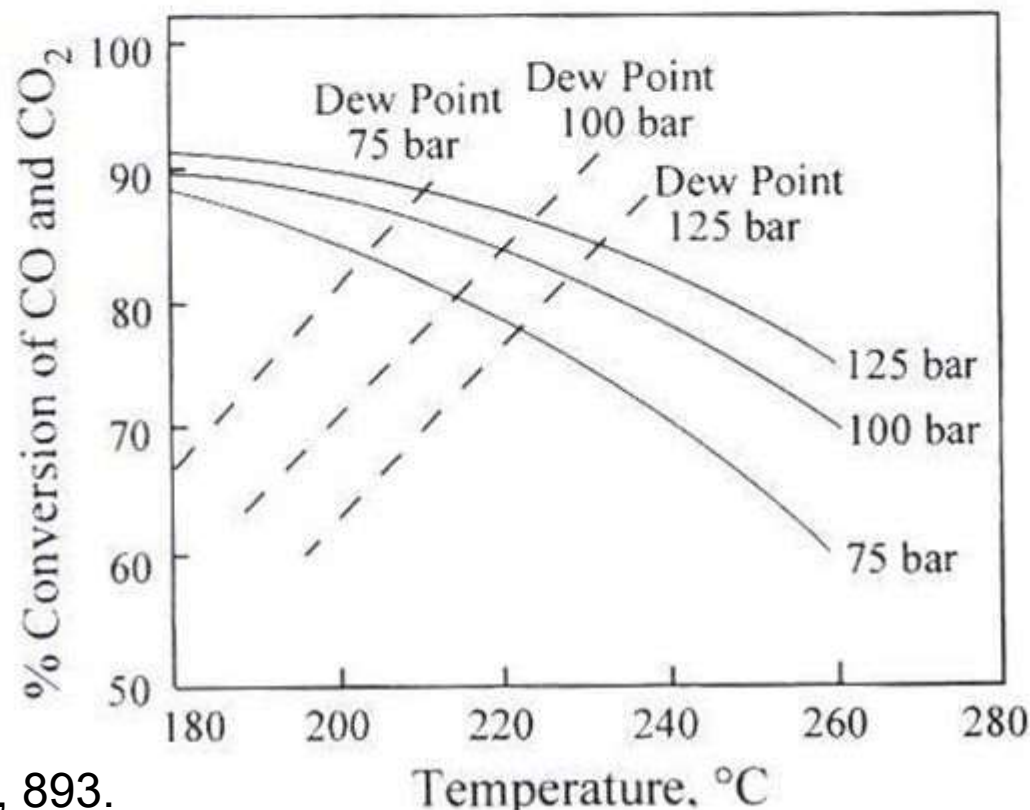


- Methanol can be efficiently produced from a wide variety of sources including still available fossil fuels (**coal, oil shale, tar sands**, etc.) and varied **agricultural products, municipal and industrial waste, wood, and varied biomass**.
- Methanol can be used as an alternative fuel to gasoline** for conventional transportation fuels due to its low cost of implementation, low risk of flammability and toxicity, and potential to reduce pollution emissions and dependence.
- In addition, methanol serves as raw material for synthetic hydrocarbons, as it can be converted into **ethylene or propylene** in the methanol-to-olefins process.

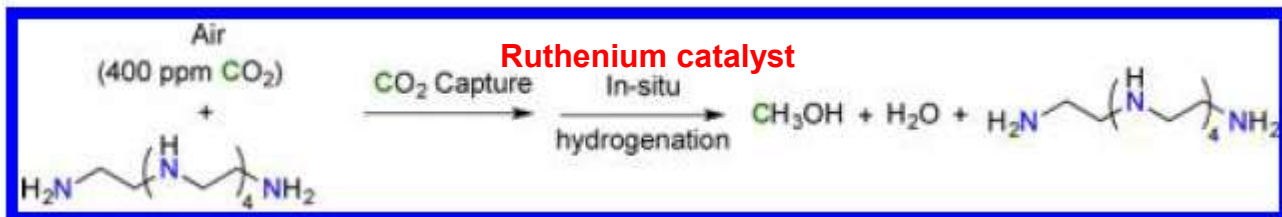
C.- SYNTHESIS GAS: Production of Methanol



Operated with Cu/ZnO/Al₂O₃ at 220~327°C and 50~100atm



Conversion of CO₂ from Air into Methanol Using a Polyamine and a Homogeneous Ruthenium Catalyst



PEHA: **Pentaethylenehexamine**

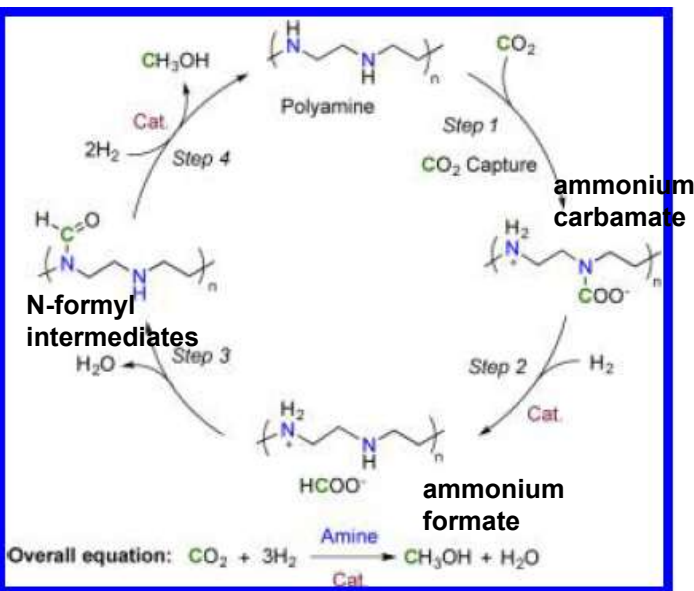
J. Am. Chem. Soc. 2016, 138, 778–781

Table 3. CO₂ Capture from Air and Conversion to CH₃OH^a

entry	amine	CO ₂ captured (mmol)	solvent	CH ₃ OH (mmol)	NMR yield (%)
1	PEHA	5.4	1,4-dioxane	2.1	39
2	PEHA	5.4	triglyme	3.3	61
3 ^b	PEHA	5.4	triglyme	4.3	79

^aReaction conditions: PEHA = 3.4 mmol, catalyst **1** = 20 μmol, H₂ = 50 bar, *t* = 40 h, *T* = 155 °C, and organic solvent (10 mL)–H₂O (8 mL). ^b*t* = 55 h.

Advantages : (1) operating at comparatively **low** temperatures, minimum decomposition of the catalyst meant that the researchers were able to repeat the process five times with minimal loss of the **catalyst effectiveness**. (2) using **homogeneous catalyst** resulting in a **simpler and faster** "one-pot" process.



Synthesis of methanol from carbon dioxide

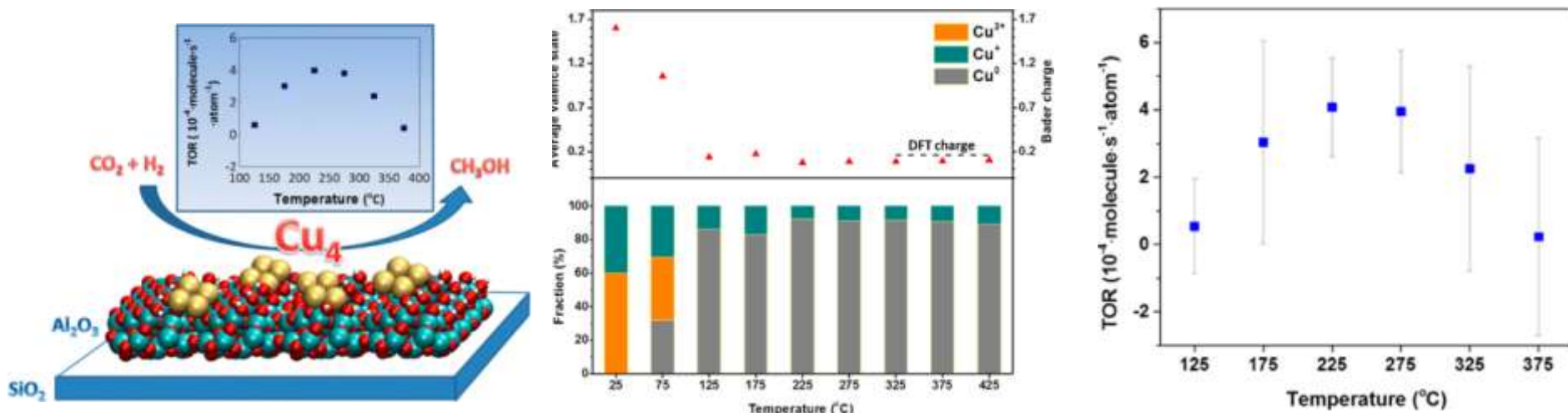


Table 1. Comparison of TOR/TOF of the Present Work and Previous Studies

catalyst	temperature (°C)	total pressure (atm)	partial pressure of H ₂ (atm)	partial pressure of CO ₂ (atm)	max TOR/TOF of CH ₃ OH (molecule.s ⁻¹ .atom ⁻¹)	ref
Cu ₄ /Al ₂ O ₃	225	1.25	0.038	0.013	4.0 × 10 ⁻⁴ (TOR)	this work
Ni ₅ Ga ₃ /SiO ₂	200–220	1	0.75	0.25	6.7 × 10 ⁻⁵ (TOF) ^a	25
Cu/ZnO/Al ₂ O ₃	200–220	1	0.75	0.25	6.7 × 10 ⁻⁵ (TOF) ^a	25
polycrystalline Cu foil	237	5	4.6	0.4	1.2 × 10 ⁻³ (TOR)	26

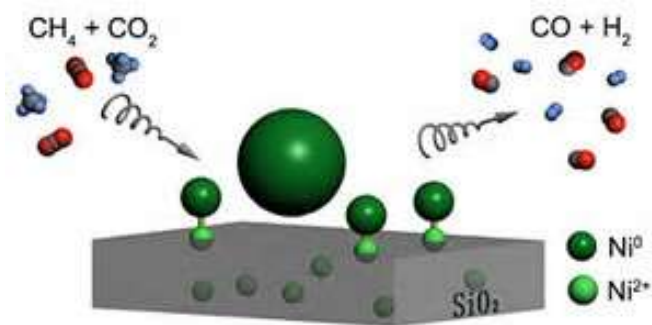
^aThese values were converted from the graphs in ref 25.

CO₂ dry reforming of CH₄

Methanol Synthesis #1 (CO ₂)	$\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$
Methanol Synthesis #2 (Syngas)	$\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$

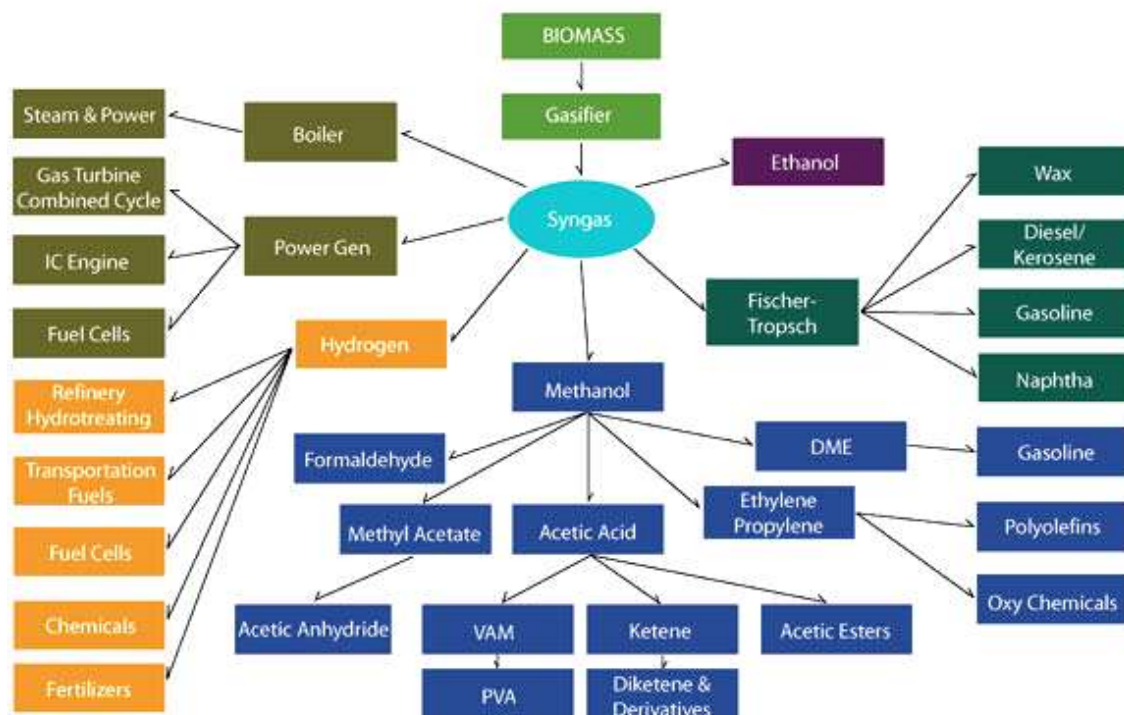
Steam reforming $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$

CO₂ dry reforming of CH₄ $\text{CO}_2 + \text{CH}_4 = 2\text{CO} + 2\text{H}_2$, $\Delta H_{298\text{K}} = 247.3 \text{ kJ/mol}$

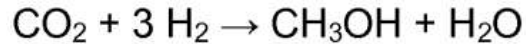


Condition: Nickel, 850 °C

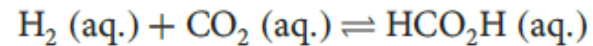
Gasification – Options for Bio-based Products



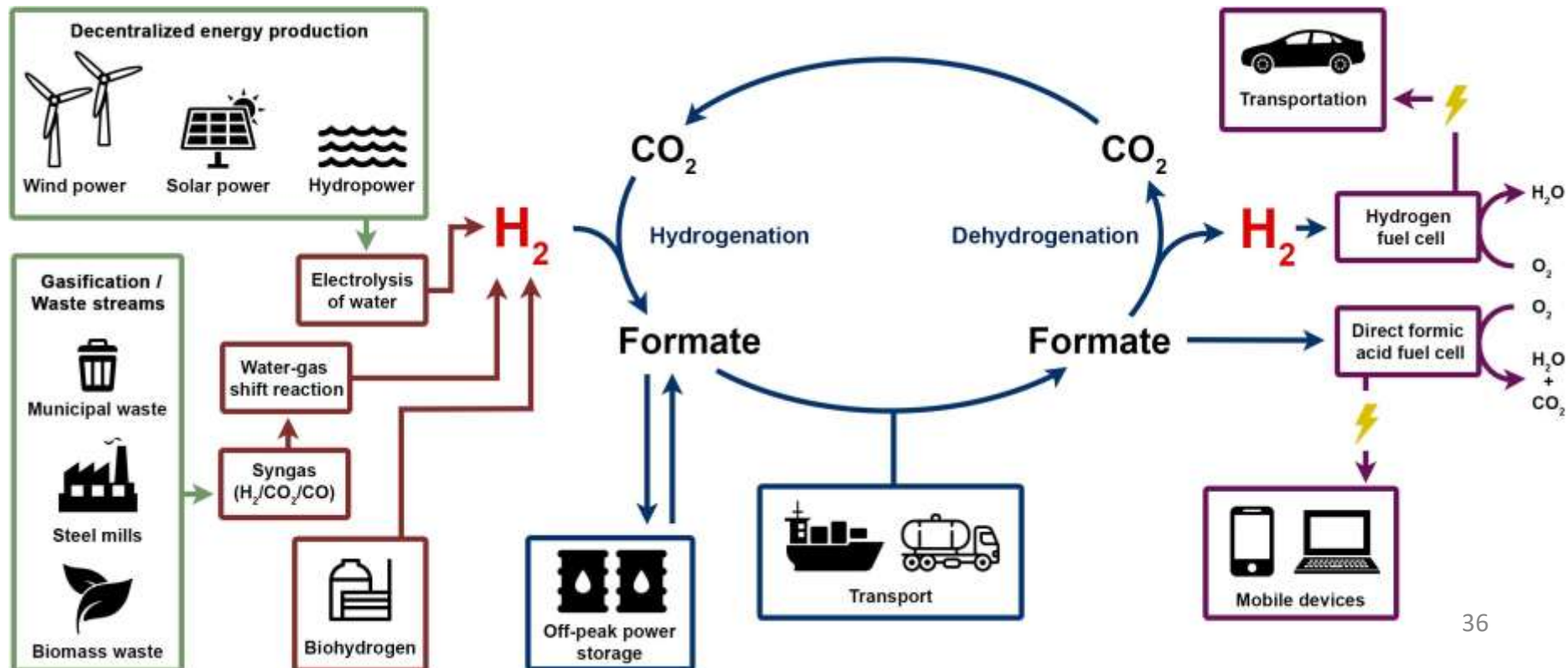
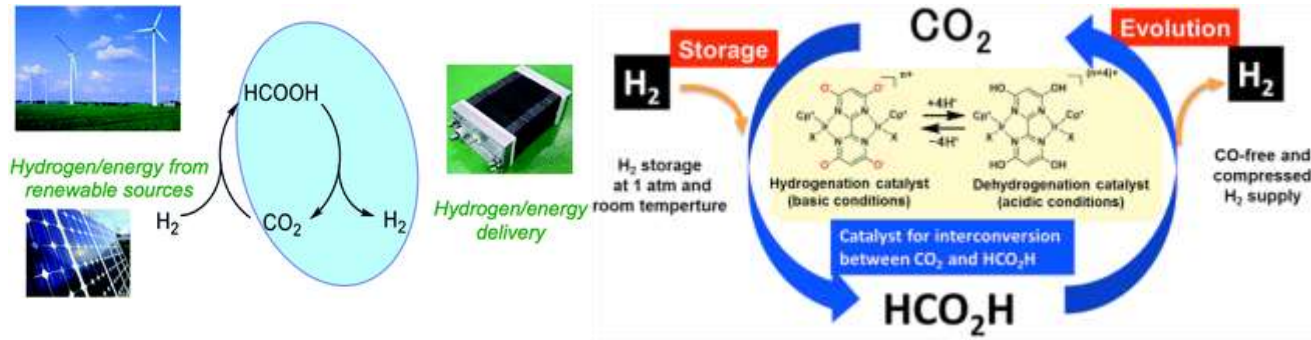
Transformation of Carbon dioxide to formic acid as a hydrogen energy carrier



Atom economy=64%



Atom economy=100%



1. Reduction of carbon dioxide to formic acid by homogeneous catalysts



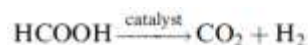
$\text{CO}_2 + \text{H}_2 \xrightarrow{\text{catalyst}} \text{HCOOH}$			
Catalyst	TOF (h^{-1})	$T/^\circ\text{C}$	Ref.
[RuCl(OAc)(PMe ₃) ₄]	95 000	50	22
[RuCl ₂ (TPPMS) ₂] ₂	9600	80	23
RhCl(TPPTS) ₃	7260	81	21 ^c
RuH ₂ (PMe ₃) ₄	1400	50	25
Rh(hfacac)(dcpb)	1335	25	21

[RuCl(OAc)(PMe₃)₄]: turnover frequency (TOF) of 95 000 h^{-1} , under **supercritical conditions** (CO_2 pressure: 190 bar, temperature: 50 $^\circ\text{C}$)

[RuCl₂(TPPMS)₂]₂: non-supercritical conditions (CO_2 -pressure: 95 bar, temperature: 80 $^\circ\text{C}$) **in water**.

Rh(hfacac)(dcpb): 1335 h^{-1} (TOF) at **room temperature** and a low CO_2/H_2 pressure (40 atm).

2. Decomposition of formic acid in the presence of homogeneous catalysts



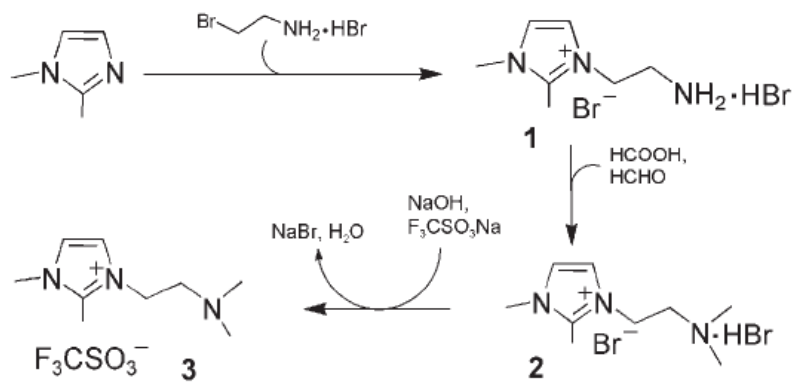
Catalyst	Performance	$T/^\circ\text{C}$	Ref.
[PtCl ₂ (Pbu) ₃]	0.02 mol L ⁻¹ h ⁻¹	118	27
RuHBrCO(Pet ₂ Ph) ₃	2.8 mol L ⁻¹ h ⁻¹	118	27
RuHCl(Et ₂ PC ₂ H ₄ PEt ₂) ₂	2.0 mol L ⁻¹ h ⁻¹	118	27
IrCl ₃ (PEt ₂ Ph) ₃	0.3 mol L ⁻¹ h ⁻¹	118	27
[IrCl ₃ (PBu ₃) ₃]	0.7 mol L ⁻¹ h ⁻¹	118	27
[IrH ₂ Cl(PPh ₃) ₃]	7.4 mol L ⁻¹ h ⁻¹	118	27
[IrH ₃ (PPh ₃) ₃]	80 mol L ⁻¹ h ⁻¹	118	27
[Rh(CO) ₂ Cl] ₂	31 mol L ⁻¹ h ⁻¹	100	28
[Pt{P(iPr) ₃ } ₃]	TOF = 100 h ⁻¹	20	29
[Rh(C ₆ H ₄ PPh ₂)(PPh ₃) ₂]	3.3 × 10 ⁻¹⁰ mol L ⁻¹ h ⁻¹	20	30
[Pt ₂ H ₃ (PEt ₃) ₄][BPh ₄]	TON = 3.3	20	31
[Cp*Mo(PMe ₃) ₂ (CO)H]	—	—	32
[Rh(H ₂)(PMe ₃ Ph) ₄]BF ₄	—	—	33

[IrH₃(PPh₃)₃]: high **decomposition rate** of 80 mol L⁻¹h⁻¹ in refluxing acetic acid as solvent

[Ru ₃ (CO) ₁₂]	TOF = 102 h ⁻¹	75	34
[Ru ₂ (μ-CO)(CO) ₄ (μ-dppm) ₂]	TOF = 500 h ⁻¹	rt	35
[Ru(H ₂ O) ₆](tos) ₂	TOF = 460 h ⁻¹	120	36
[RuCl ₂ (<i>p</i> -cymene)] ₂	TON = 42	40	38
[RuCl ₂ (PPh ₃) ₃]	TOF = 2688 h ⁻¹	40	38
RuBr ₃ ·H ₂ O/3PPh ₃	TOF = 3630 h ⁻¹	40	40
[RuCl ₂ (benzene)] ₂ /dppe	TON = 852	40	40
[RuCl ₂ (benzene)] ₂ /dppp	TON = 1376	40	40
[Rh(Cp*)(bpy)(H ₂ O)]SO ₄	TON = >80	25	42
[Ru ₂ Cl ₂ (DMSO) ₄]	TOF = 17 800 h ⁻¹	120	43
[RuCl ₂ (NH ₃) ₆]	TOF = 18 000 h ⁻¹	120	43
[RuCl ₃]	TOF = 17 400 h ⁻¹	120	43
[Ru ₂ (HCO ₂) ₂ (CO) ₄]	TOF = 17 800 h ⁻¹	120	43

[Rh(Cp*)(bpy)-(H₂O)]SO₄: aqueous solution of formic acid/sodium formate, **at room temperature**

3. Reduction of carbon dioxide to formic acid by heterogeneous catalysts



Scheme 1. Synthesis of the IL [mammim][TfO] (3).

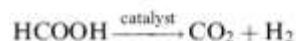
Angew. Chem., Int. Ed., 2008, 47, 1127–1129

Table 1: Turnover frequencies (TOFs) for the hydrogenation of CO₂ to formic acid under different conditions.^[a]

Entry	IL [g]	P _{H₂} [MPa] ^[b]	P _T [MPa] ^[b]	t [h]	AIr ^[c]	TOF [h ⁻¹] ^[d]
1	0.5	1	4	2	0.20	14
2	0.5	3	6	2	0.35	24
3	0.5	9	12	2	0.60	42
4	0.5	3	12	2	0.65	45
4-1 ^[e]	0.5	3	12	2	0.63	44
4-2 ^[e]	0.5	3	12	2	0.61	43
4-3 ^[e]	0.5	3	12	2	0.63	44
4-4 ^[e]	0.5	3	12	2	0.62	43
5	1.5	3	6	2	0.17	36
6	1.5	6	9	2	0.27	57
7	1.5	9	12	2	0.31	65
8	1.5	9	15	2	0.46	96
9	1.5	9	18	2	0.49	103
10	1.5	9	18	5	0.87	73
11	1.5	9	18	10	0.96	40
12 ^[f]	1.5	9	12	2	0.04	8

[a] Reaction conditions: 0.3 g of catalyst (3.8 mg g⁻¹), 5 g of H₂O, 60 °C; [b] P_{H₂} and P_T are the initial partial pressure of hydrogen and total pressure, respectively; [c] AIr is the molar ratio of formic acid formed to IL added; [d] Mols of formic acid per mol of Ru per hour; [e] Entries 4-1, 4-2, 4-3, and 4-4 are the results of recycling the IL and catalyst under the conditions of entry 4; [f] No water was added to the reaction system.

4. Decomposition of formic acid in the presence of heterogeneous catalysts



Catalyst	E _{akt} /kJ mol ⁻¹	Selectivity [% H ₂]	Ref.
Cu(110)	ca. 130	100	54
Cu, polycrystalline	115–130	100	55
Cu, wire, tempered	ca. 98	100	50
Cu, sheet, tempered	ca. 98	100	52
Au, sheet, tempered	ca. 122	93–94	50
Ag, sheet, tempered	ca. 109	100	50
Pd, sheet, tempered	ca. 34	>99	52
Cu ₂₅ Au ₇₅ –Cu ₇₅ Au ₂₅ , sheet, tempered	ca. 101–103	n.s.	50
Pd ₁₇ Cu ₈₃ –Pd ₉₂ Cu ₈ , sheet, tempered	ca. 50–92	n.s.	52
Pd ₁₇ Cu ₈₃ –Pd ₉₂ Cu ₈ , sheet, rapidly solidified	50–68	n.s.	52
Fe ₈₀ B ₂₀ , meltspun	110–160	50–80	59
Fe ₈₀ B ₂₀ , crystalline	ca. 50	10–30	59

Table 2 Heterogeneous catalysts for the decomposition of formic acid

Active phase/support	Solvent/medium	Performance	Temp.
0.61% Au/Al ₂ O ₃	He/gas phase	TOF = 25 600 h ⁻¹ , ~10 ppm CO	353 K
20 wt% Pd/Au/C–CeO ₂	Aqueous	TOF = 832 h ⁻¹ , ~140 ppm CO	375 K
1% Pd/C	He/gas phase	TOF = 255 h ⁻¹ , S _{H2} = 99%	373 K
Mo ₂ C/C	Ar/gas phase	TOF = 437 h ⁻¹ , S _{H2} = 95–98%	423 K
PdAu@Au/C (core-shell)	Aqueous	30 ppm CO	356 K
5% Au/CeO ₂	Ar/gas phase	TOF = 295 h ⁻¹ , S _{H2} = 100% ^a	473 K
Ir/C	Ar/gas phase	TOF = 960 h ⁻¹ , S _{H2} = 99%	373 K
Ag@Pd/C (core-shell)	Aqueous	TOF = 125 h ⁻¹ , S _{H2} = 100%	293 K
		TOF = 626 h ⁻¹ , 84 ppm CO	363 K
Pd–S–SiO ₂	Aqueous	TOF = 803 h ⁻¹ , S _{H2} = 100%	358 K

^a Incomplete FA conversion.

Energy Environ. Sci., 2010, 3, 1207–1217

Energy Environ. Sci., 2012, 5, 8171–8181

Using carbon dioxide as a building block in organic synthesis

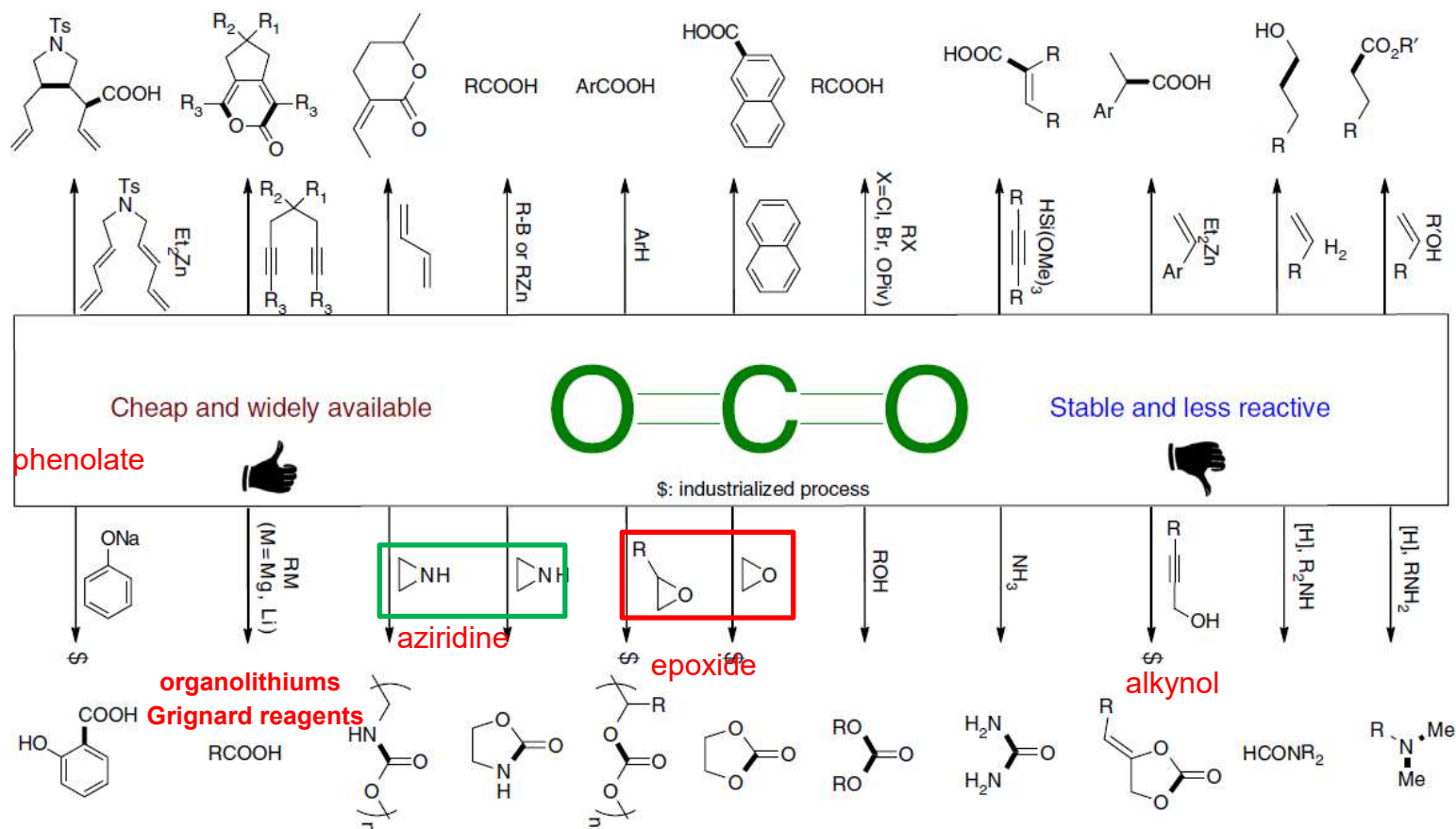


Figure 1 | Representative examples using CO_2 as C1 building block in organic synthesis. Along with the rapid development of organometallic chemistry and catalysis, various types of efficient CO_2 transformations were discovered in the past decades. However, in general, the substrates' scope and efficiency of these reactions are still limited due to the requirement of reactive agents for CO_2 activation. As a result, only a few processes have been industrialized until now (marked by \$).

Synthesis of dimethyl carbonate from CO₂ and methanol

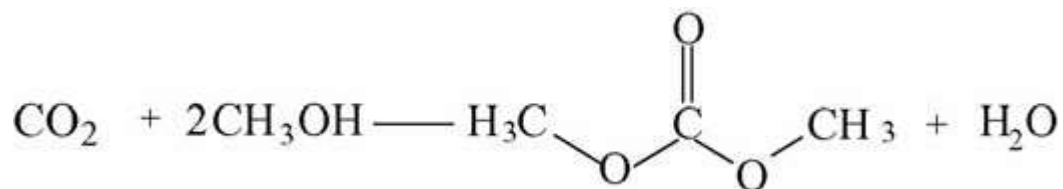


Table 1

Reaction of CO₂, methanol and iodomethane giving dimethyl carbonate (DMC) with base catalysts^a

Entry	Base	DMC/ mmol	DME/ mmol	CH ₃ I consumed/ mmol	Yield%/ mol base
1	no	0	3.5	0.2	0
2	Li ₂ CO ₃	1.3	3.1	1.2	43
3	Na ₂ CO ₃	9.4	4.6	6.4	313
4	K ₂ CO ₃	11.9	5.4	5.2	397
5	K ₂ CO ₃ ^b	11.8	0.9	4.9	395
6	K ₂ CO ₃ ^c	3.2	11.5	3.4	106
7	K ₂ CO ₃ ^d	0	1.1	0	0
8	Cs ₂ CO ₃	8.6	8.1	7.7	287
9	Mg ₂ CO ₃	0	5.4	0	0
10	K ₃ PO ₄	7.7	9.8	4.2	257
11	KH ₂ PO ₄	0	9.0	0.1	0
12	KOH	1.1	20.3	0.5	37
13	Et ₃ N	0.2	4.5	0.1	7
14	Bu ₃ N	0.5	5.6	0.4	17
15	(CH ₃) ₄ NOH	7.3	12.5	4.4	243

^a Carried out at 100°C for 2 h, CH₃OH:CH₃I:base(mol) = 64:8:1.

^b Carried out at 80°C.

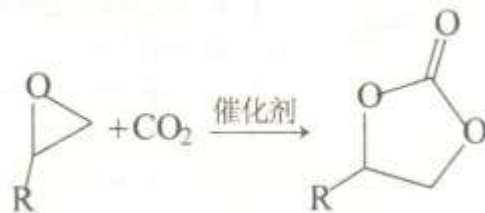
^c Without CO₂.

^d Without CH₃I.

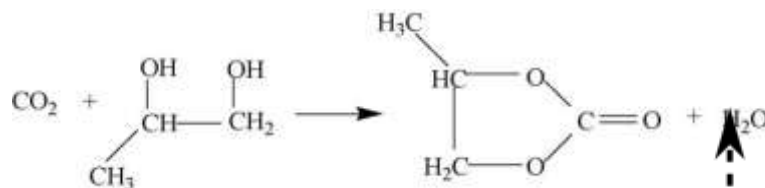
S. Fang, K. Fujimoto / Applied Catalysis A: General 142 (1996) L1–L3

Synthesis of cyclic carbonate from CO₂

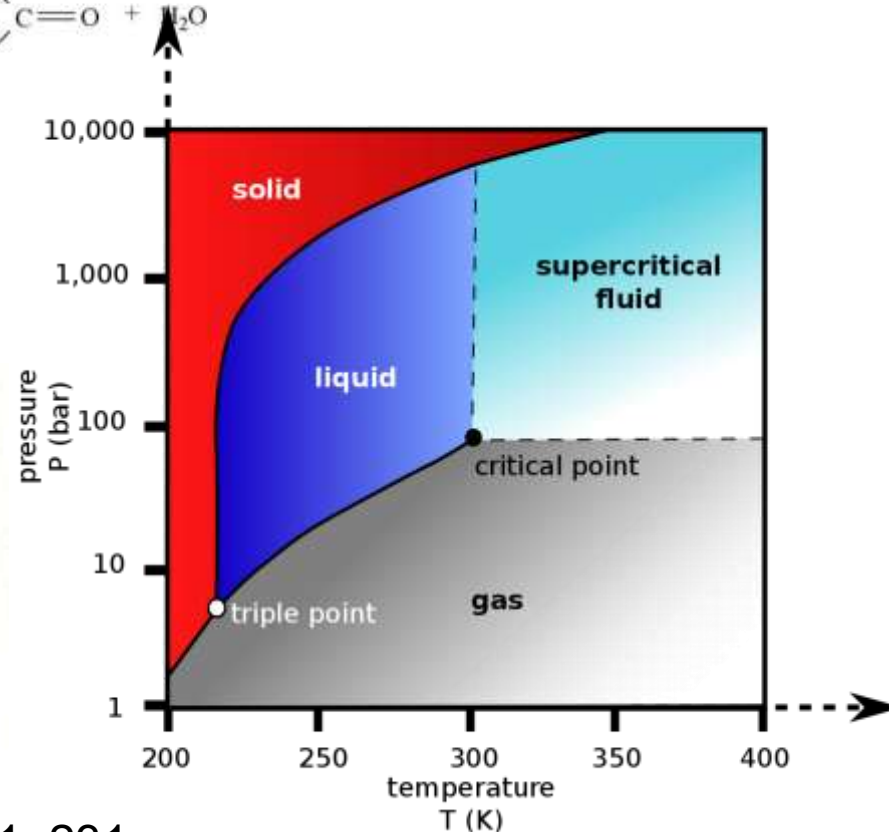
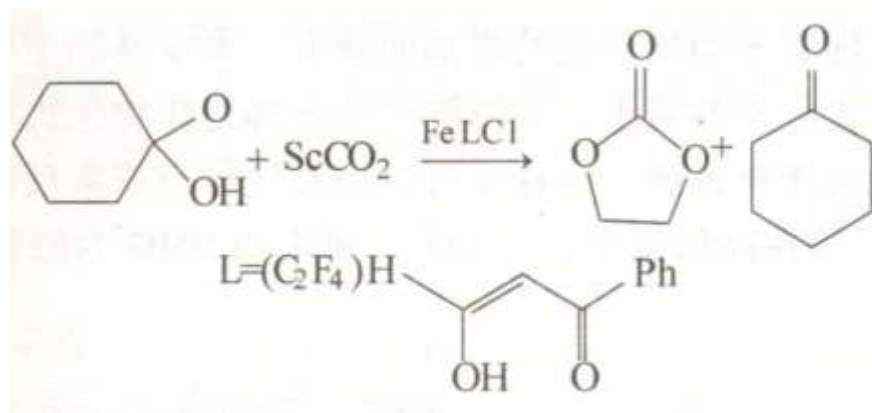
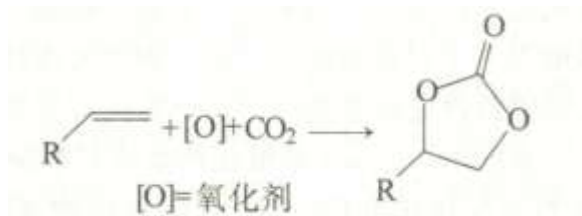
Epoxide



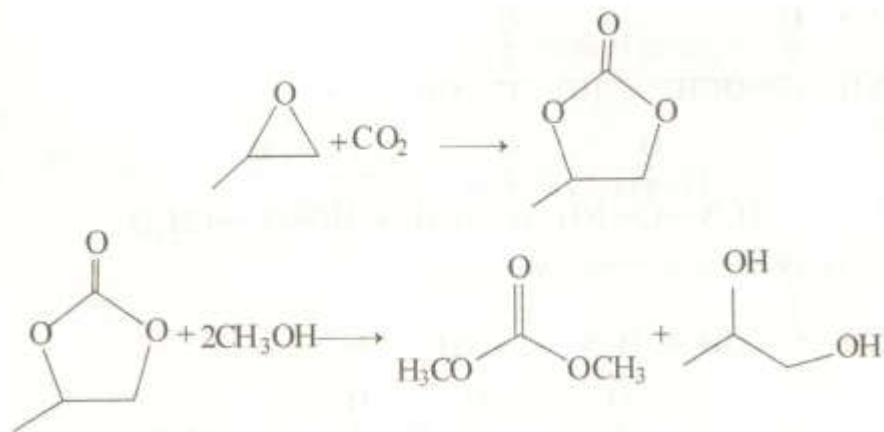
1, 2-propanediol



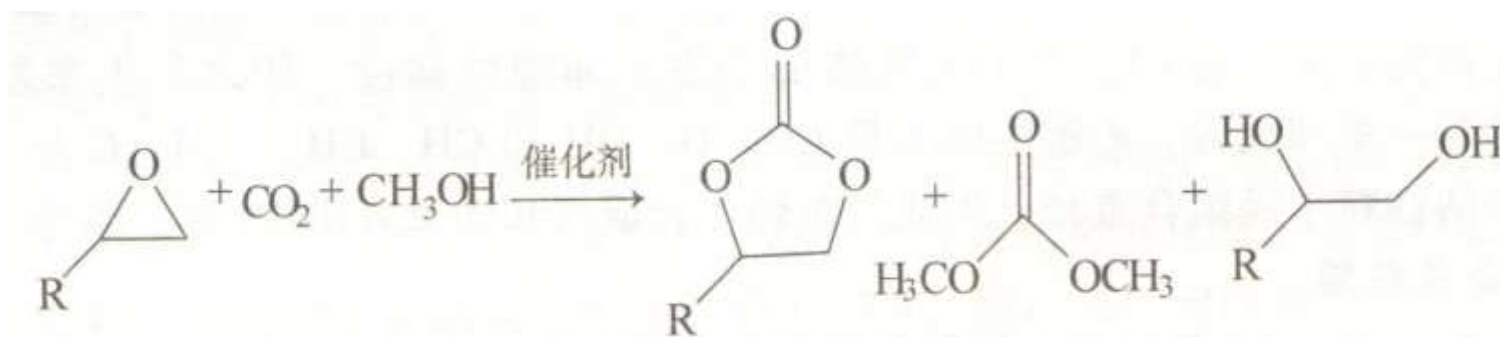
Alkene

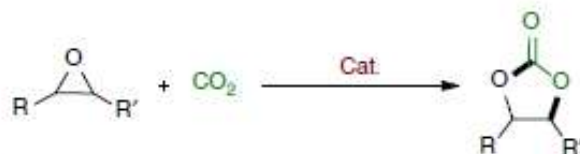


Two step synthesis of DMC from CO₂

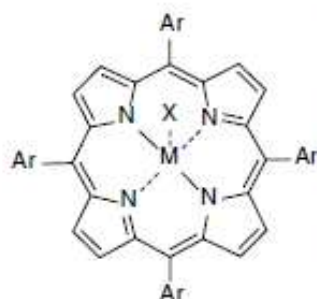


One step synthesis of DMC from CO₂





Solvent-free



M = Al^{III}, X = OMe, Ar = Ph
Inoue *et al.*, 1983

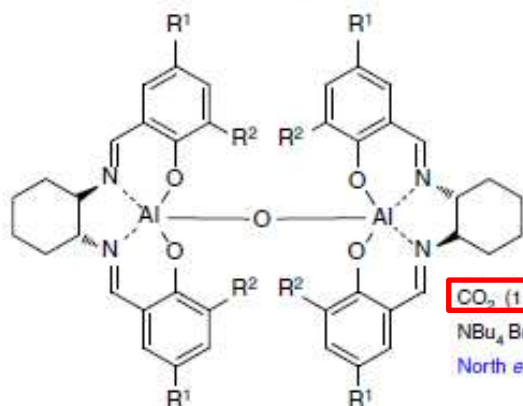
M = Co^{III}, X = OTs, Ar = Ph
CO₂ (7 bar), 20 °C, PTAT
up to 930 TON, 93% yield

Jing *et al.*, 2007

M = Mg^{II}, Ar = 3-O(CH₂)₆N⁺Bu₃Br⁻-Ph
CO₂ (17 bar), 120 °C
up to 103,000 TON, 83% yield

Sakai *et al.*, 2012

Metalloporphyrin catalyst



CO₂ (1 bar), 25 °C

NBu₄ Br, up to 850 TON

North *et al.*, 2010

Bimetallic aluminium(salen) catalyst

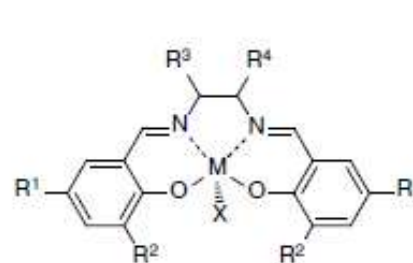


CO₂ (15 bar), 100 °C, KI

Up to 5,580 TON, 5,580 per hour TOF

Xia *et al.*, 2004

Onium salts catalyst



M = Cr^{III}, X = Cl

CO₂ (8 bar), 100 °C,

(4-dimethylamino)pyridine
up to 916 TON

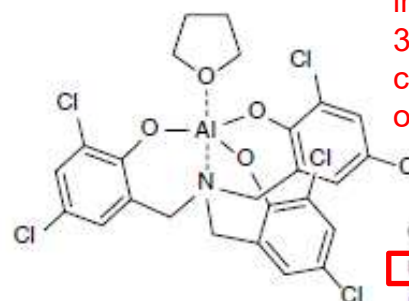
Nguyen *et al.*, 2001

M = Zn^{II}, R₂ = *t*Bu

CO₂ (2 bar), 25 °C, NBu₄I
up to 86% yield

Kleij *et al.*, 2011

Salen catalyst



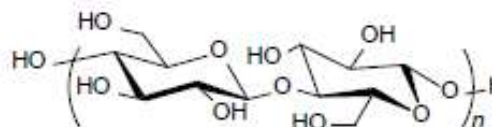
initial turnover frequencies as high as
36,000 per hour during the
cycloaddition of CO₂ to epoxides were
obtained with TONs exceeding 100,000.

CO₂ (10 bar), 90 °C, NBu₄I

Up to 112,000 TON, 36,000 per hour TOF

Kleij *et al.*, 2013

Amino triphenolate aluminium catalyst



CO₂ (20 bar), 110 °C, KI

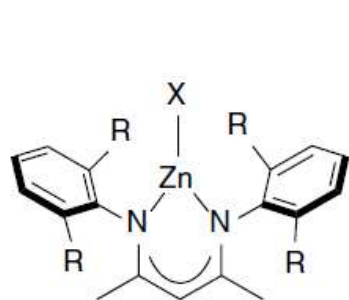
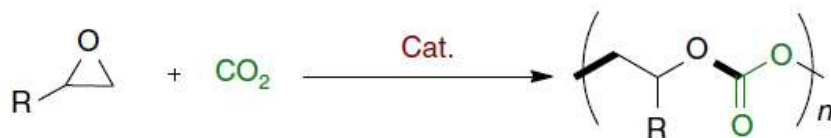
Up to 99% yield

Jiang and Han *et al.*, 2011

Cellulose catalyst

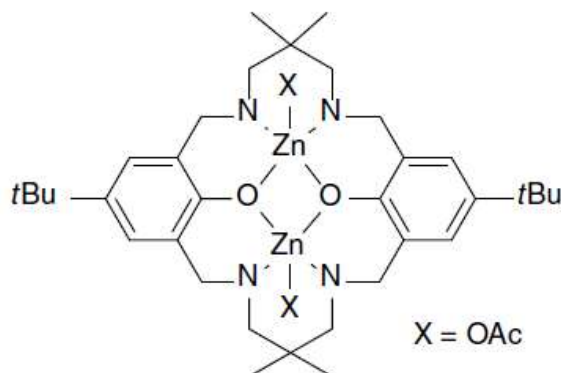
selective and recyclable catalyst
without the assistance of any
transition metal catalyst.

Carbon Dioxide As a Raw Material for polycarbonates



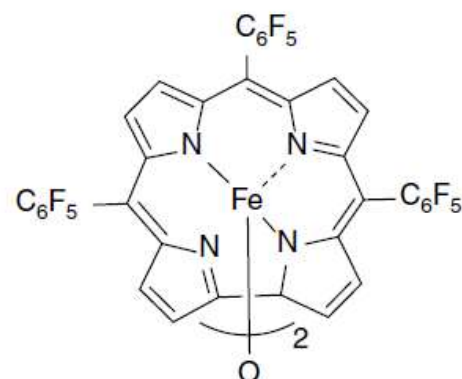
CO_2 (7 bar), 50 °C, TON = 354
 $M_n = 25.5 \times 10^{-3}$, $M_w/M_n = 1.1$
 Coates *et al.*, 2003

Zinc β -diiminate catalyst



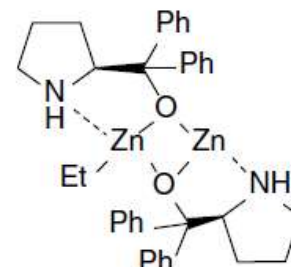
CO_2 (1 bar), 100 °C, TON = 527
 $M_n = 7,360$, $M_w/M_n = 1.2$
 Williams *et al.*, 2009

Dimetallic zinc catalyst



CO_2 (20 bar), 60 °C, TOF = 1,004
 $M_n = 29,000$, $M_w/M_n = 1.3$
 Nozaki *et al.*, 2013

Iron-corrole catalyst



CO_2 (30 bar), 40 °C, 74% ee
 $M_n = 12,000$, $M_w/M_n = 1.3$
 Nozaki *et al.*, 2003

Dimeric zinc catalyst

Green reagents for oxidation reaction



At standard temperature and pressure, oxygen is a colorless, odorless, and tasteless gas with the molecular formula O_2 , referred to as dioxygen.

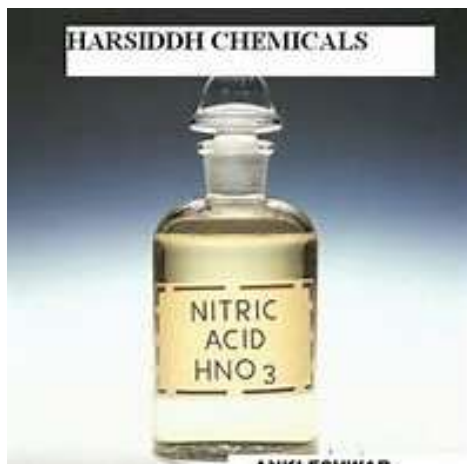
Although both oxygen atoms in O_2 may be utilized for oxidation (100% atom efficiency), only one oxygen atom has been used in most reactions (50% atom efficiency), so the oxidation often requires certain reducing agents to capture the extra oxygen atom during the reaction.



Molecular oxygen is obviously an ideal oxidant, but aerobic oxidation is often difficult to control and sometimes results in combustion and the reaction is performed with a low conversion to avoid over-oxidation.

Other oxidants

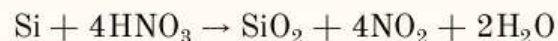
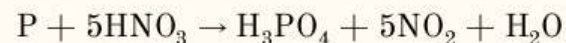
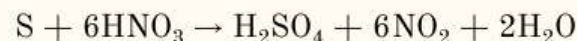
Nitric acid



Nitric acid, the most conventional industrial oxidant, is cheap but unavoidably forms various **nitrogen oxides**.

Reactions with Nonmetals

- HNO_3 oxidizes nonmetals and reduces to NO_2



CrO_3 chromium trioxide

CrO_4^{2-} chromate

$\text{Cr}_2\text{O}_7^{2-}$ dichromate

MnO_4^- permanganate

MnO_4^{2-} manganate

These **heavy metal oxidants** generate **toxic wastes** during oxidation reactions.

O.O

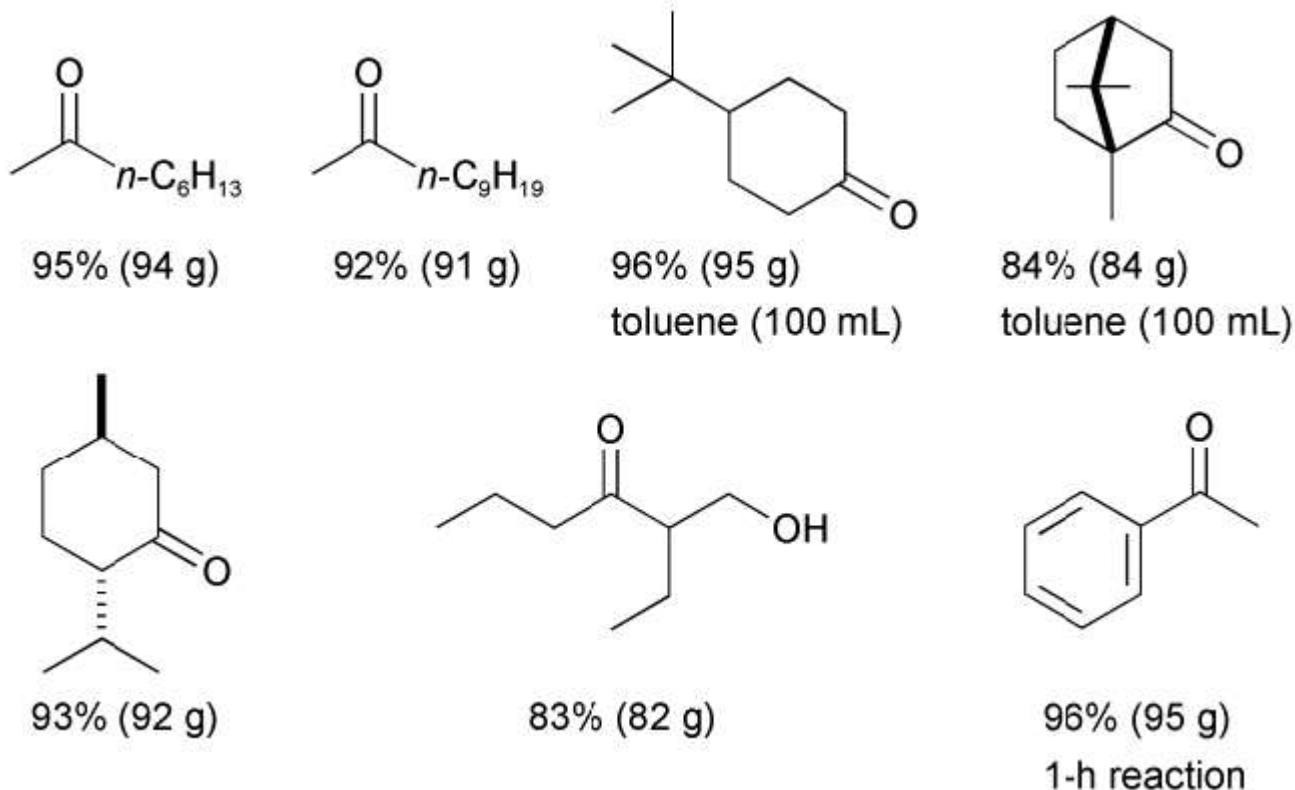
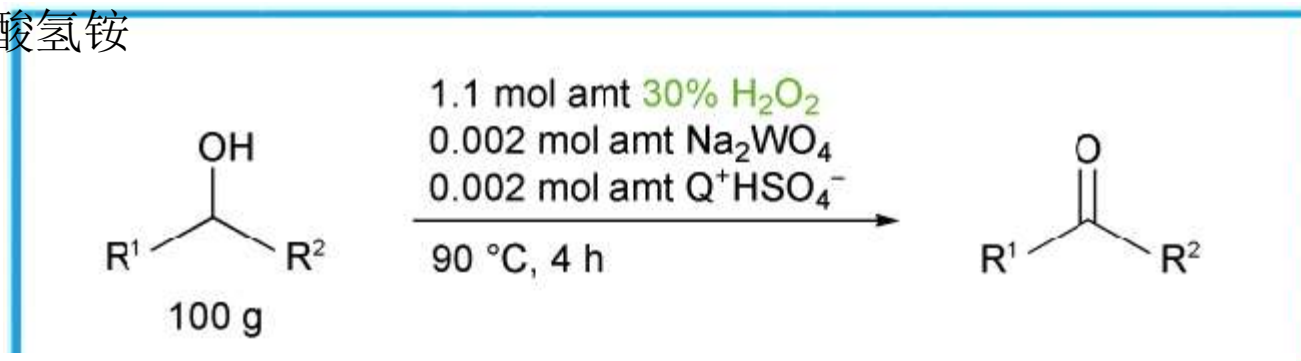
It can oxidize organic compounds with an atom efficiency of 47% and with the generation of **water as the only theoretical co-product**. It is relatively cheap, < 0.7 US dollar kg⁻¹ (100% H₂O₂).

- particularly useful for the synthesis of high-value fine chemicals, pharmaceuticals or agrochemicals, and electronic materials which require high chemical purity.
- improving the environment by oxidative removal of very small amounts of toxic compounds.

Oxidation of secondary alcohols to ketones

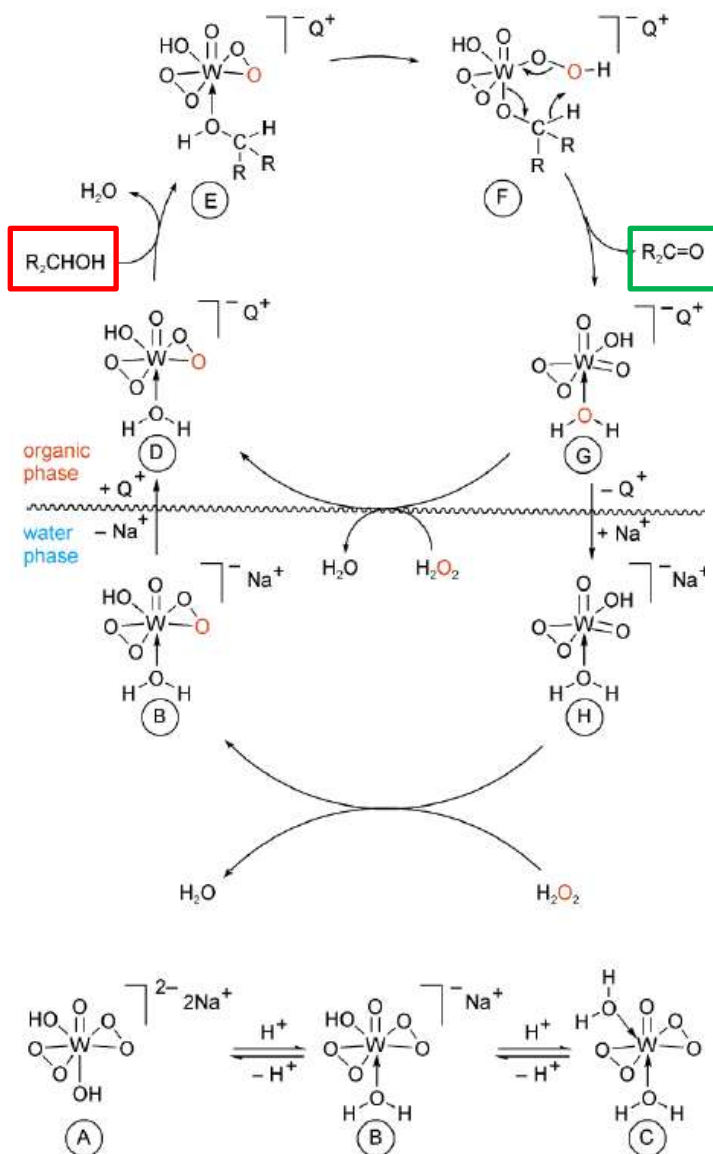
methyltrioctylammonium hydrogen sulfate

三辛基甲基硫酸氢铵



CHEM. COMMUN., 2003, 1977–1986

Oxidation of secondary alcohols to ketones

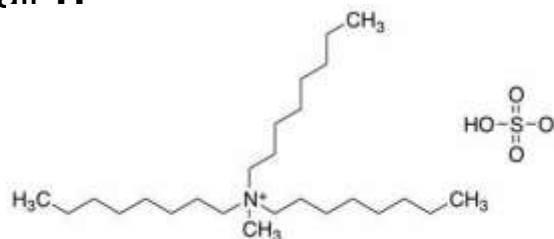


In an **aqueous** phase, **sodium tungstate** is in equilibrium with **B** and **C**, while the mono- and di-protonated forms in **B** and **C** are **sufficiently reactive**.

The mono-protonated species **B** is dominant under reaction conditions with a pH range of 0.4–3. **B** exists mostly as a monomer. Its anion moiety can easily be **transferred** to an **organic phase** by $Na-Q^+$ ion exchange.

In the organic layer, the bisperoxo complex **D** undergoes **water-alcohol ligand exchange** to form **E**. Then **proton transfer** in **E** generates the reactive species **F**, which forms **a ketonic product** and **G**.

The monoperoxo tungstate ion in **G** is **re-oxidized** by H_2O_2 after returning to the **aqueous phase** as the ion pair **H**.

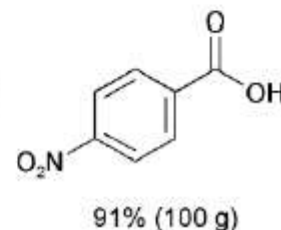
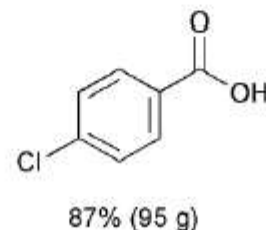
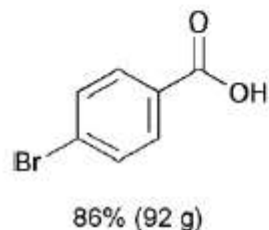
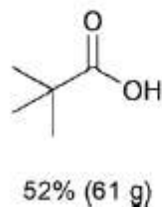
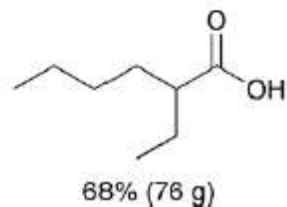
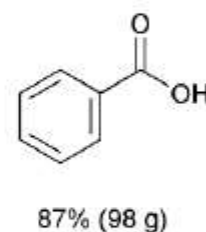
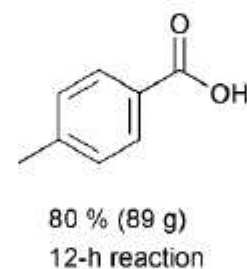
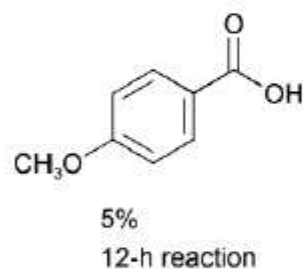
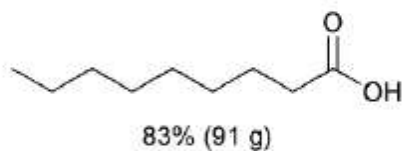
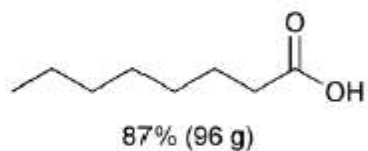
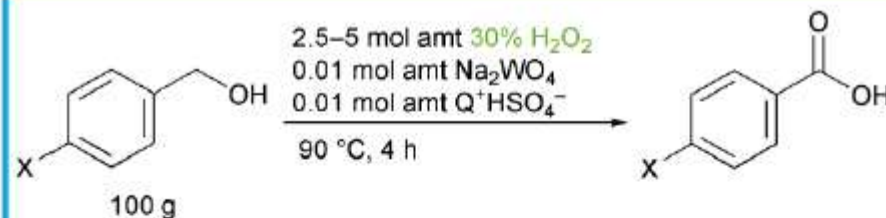
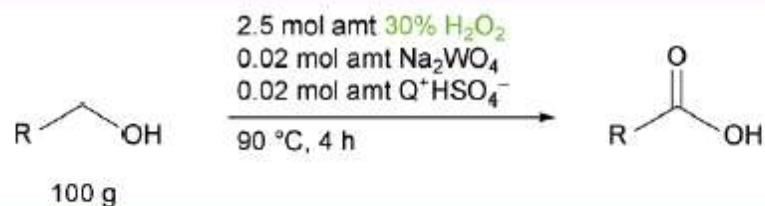


三辛基甲基硫酸氢铵

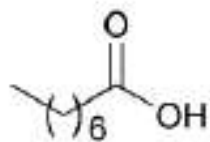
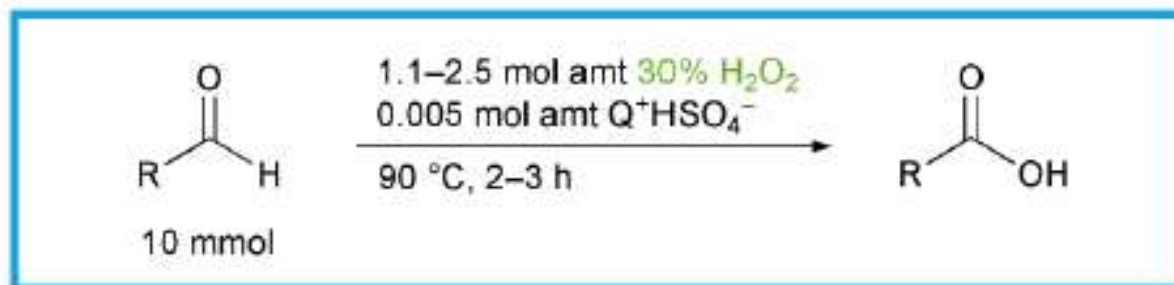
methyltrioctylammonium
hydrogen sulfate

$Q^+HSO_4^-$

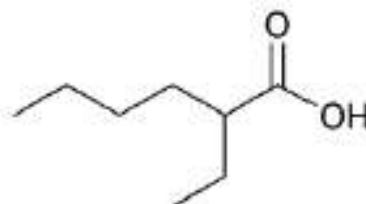
Oxidation of primary alcohols to carboxylic acid



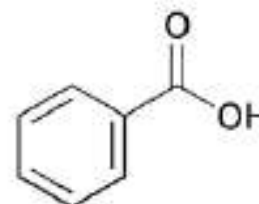
Oxidation of aldehydes to carboxylic acids



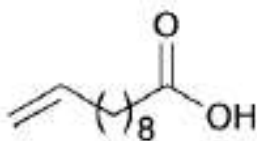
85%
100 g scale



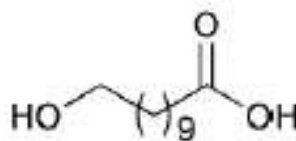
65%



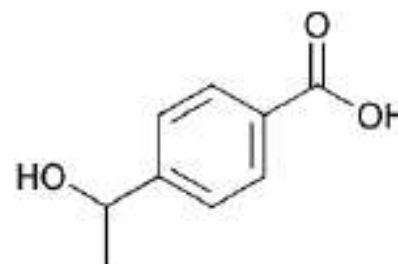
85%
S/C = 100



85%

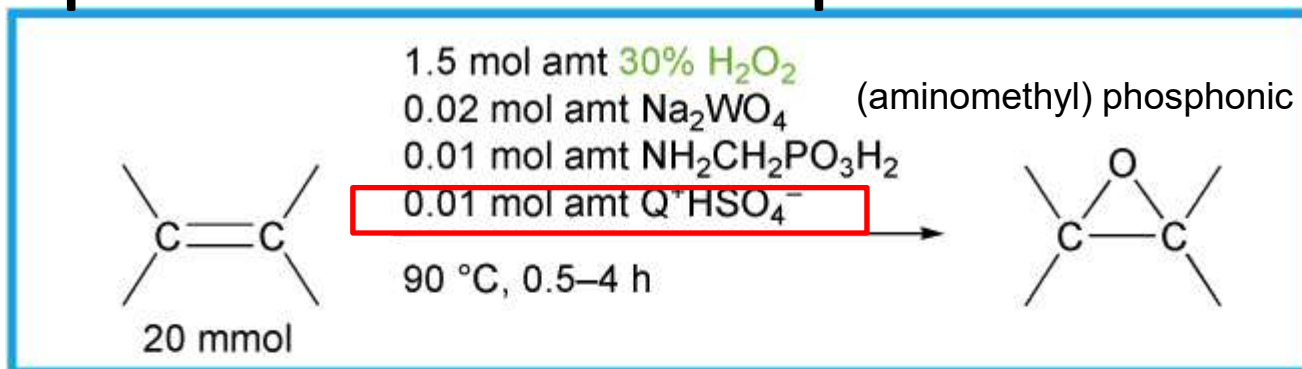


75%

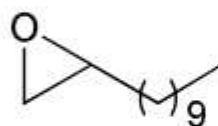


79%
S/C = 100

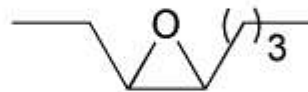
Epoxidation of simple olefins



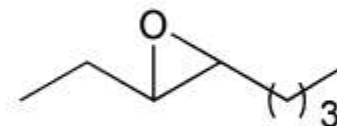
93%



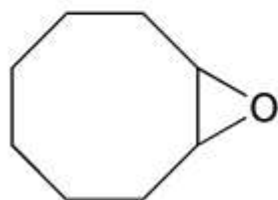
87% (96 g)
100 g scale



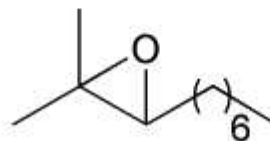
99%



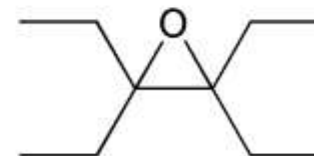
95%



98%
S/C = 500

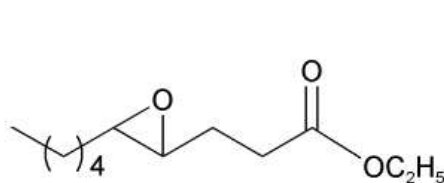
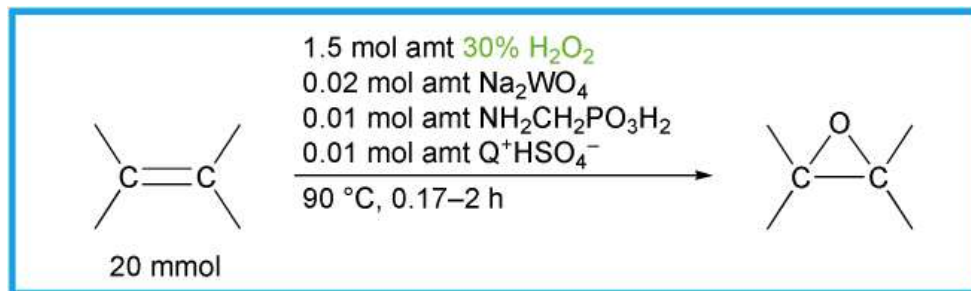


99% (70 °C, 1 h)
S/C = 500



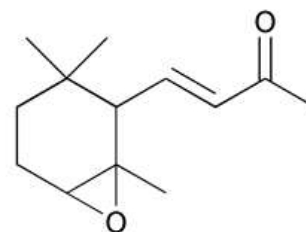
76% (70 °C, 3 h)
S/C = 500

Epoxidation of functionalized olefins



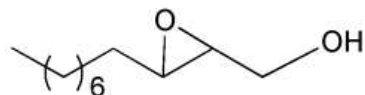
88%

99% (toluene, 4 mL)



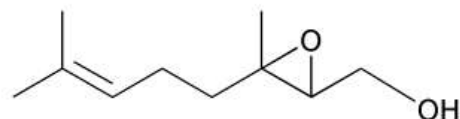
77%

91% (toluene, 4 mL)

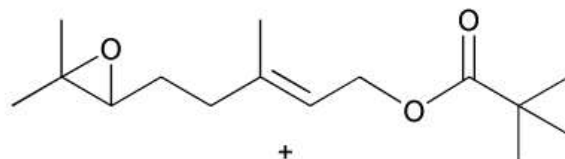


73%

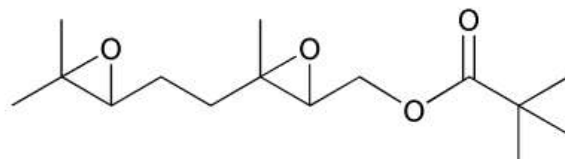
86% (toluene, 4 mL)



82% (0 °C, 2 h)

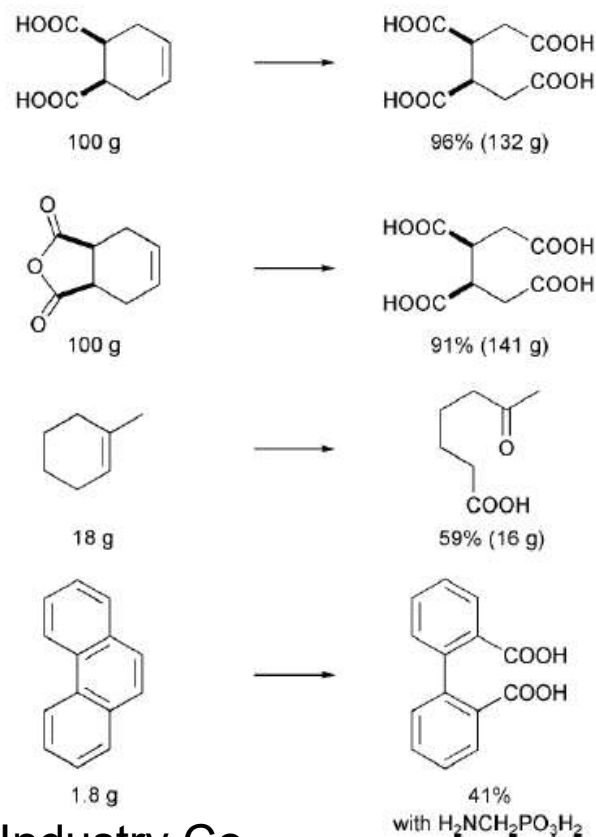
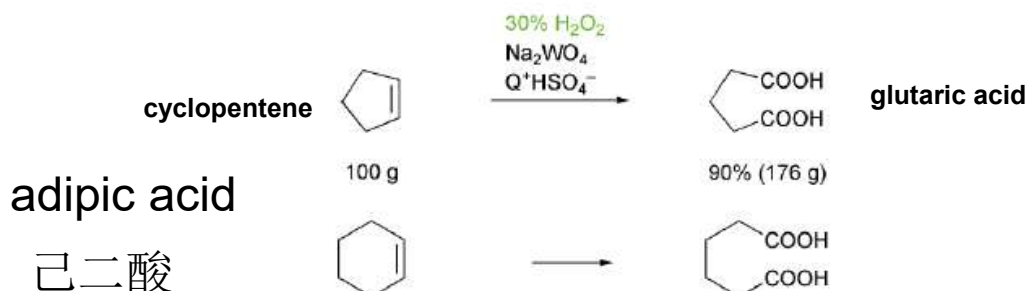
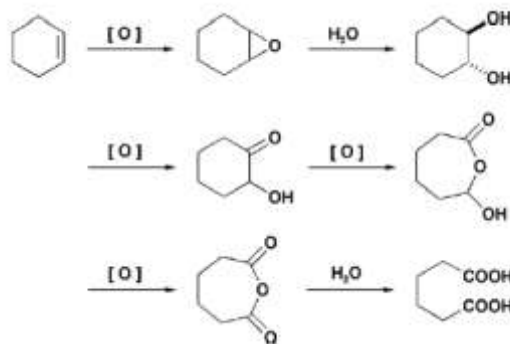
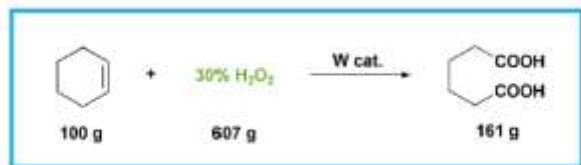
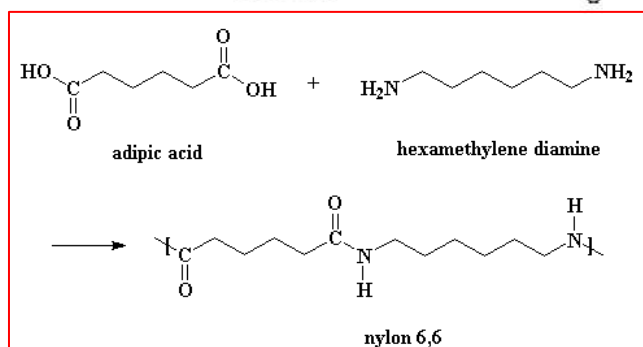
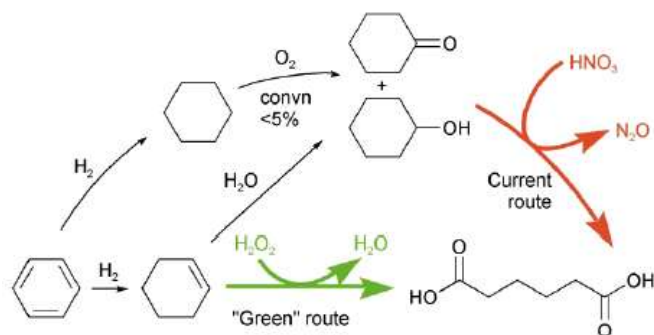


37% (60 °C, 1 h)



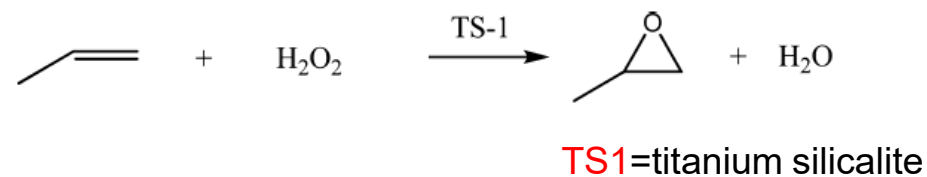
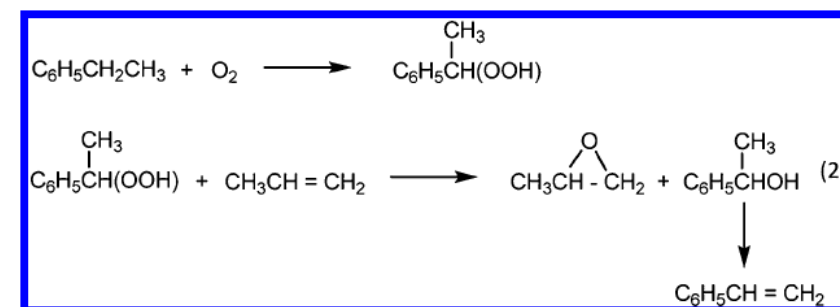
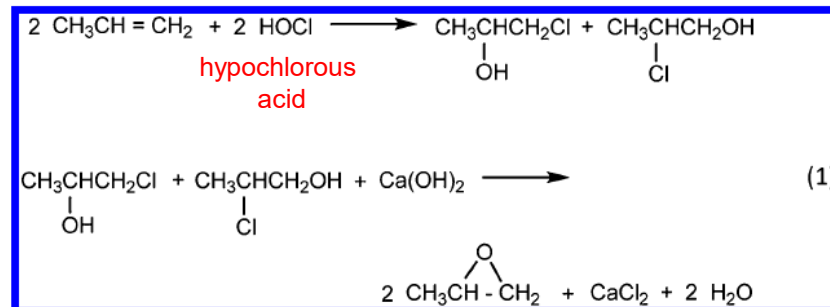
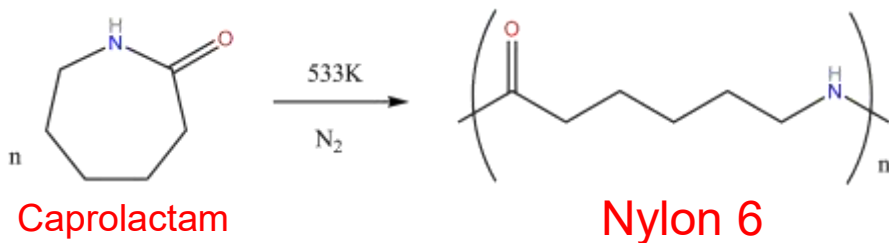
48%

Direct oxidation of cyclohexene to adipic acid



Asahi Chemical Industry Co

Synthesis of Caprolactam and propylene oxidation



BASF and Dow Chemical Co

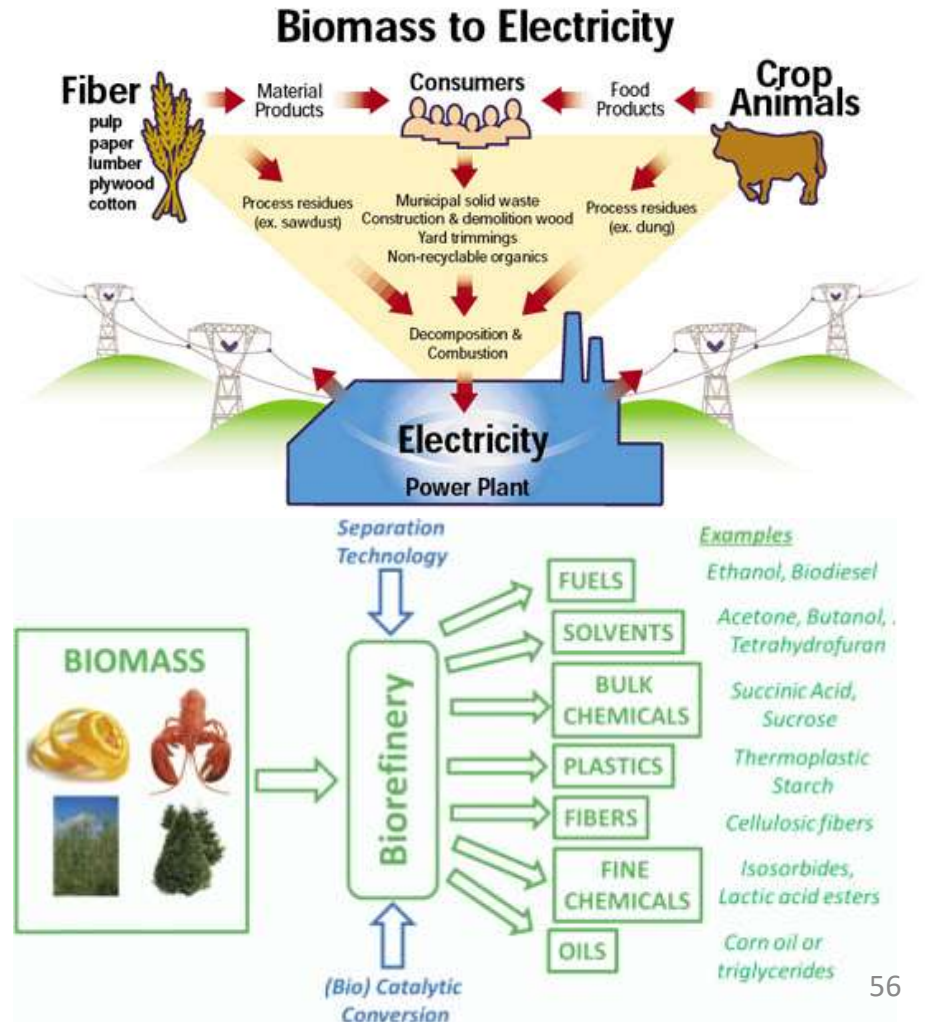
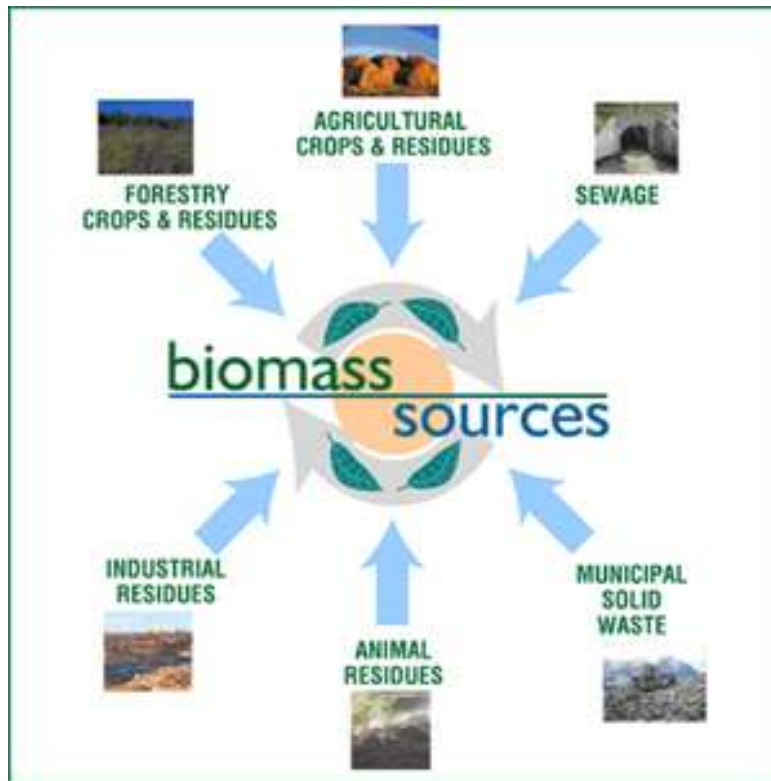
Sumitomo Chemical Co.

Nature **437**, 1243-1244

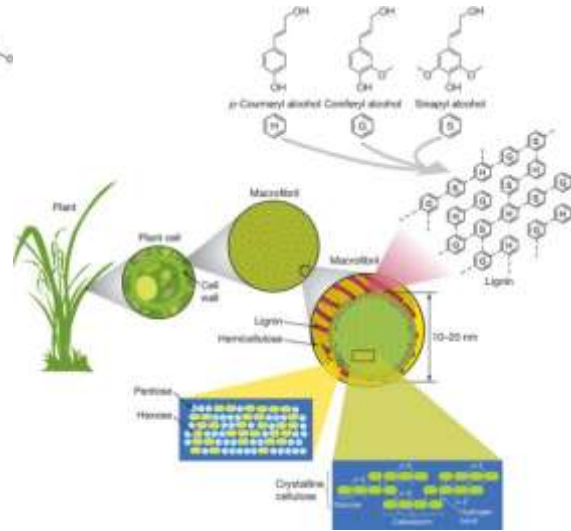
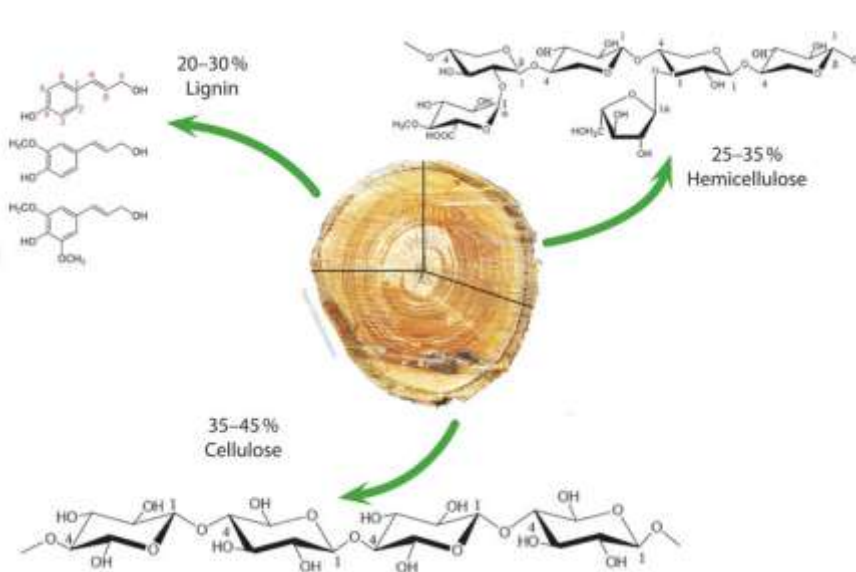
Ind. Eng. Chem. Res. 2013, 52, 1168-1178

Biomass

Biomass(生物质) : refers to organic matter derived from living organisms that has stored energy through the process of **photosynthesis (plants and woods)**, and It may be transferred through the food chain to animals' bodies and their wastes, all of which can be converted for everyday human use through processes such as combustion, or indirectly after converting it to various forms of biofuel.

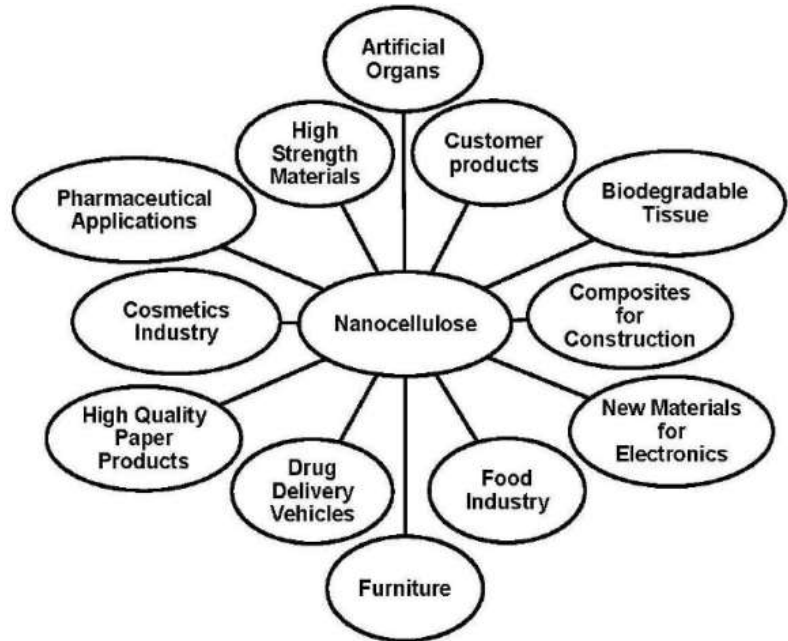
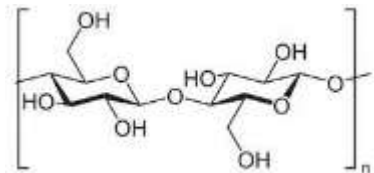


Raw chemicals from biomass



Lignin is a highly aromatic and complex phenolic polymer, particularly important in the formation of cell walls, especially in wood and bark, because they lend rigidity and do not rot easily. Chemically, lignins are cross-linked phenolic polymers.

Cellulose is an important structural component of the primary cell wall of green plants, and it consists of a linear chain of several hundred to many thousands of $\beta(1\rightarrow4)$ linked **D-glucose** units. Cellulose is the **most abundant organic polymer** on Earth. The cellulose content of cotton fiber is 90%, that of wood is 40–50%, and that of dried hemp is approximately 57%



Hydrothermal liquefaction of biomass

Hydrothermal liquefaction: is the thermochemical conversion of biomass into liquid **fuels** by processing in a hot, pressurized water environment for sufficient time to break down the solid biopolymeric structure to mainly liquid components.

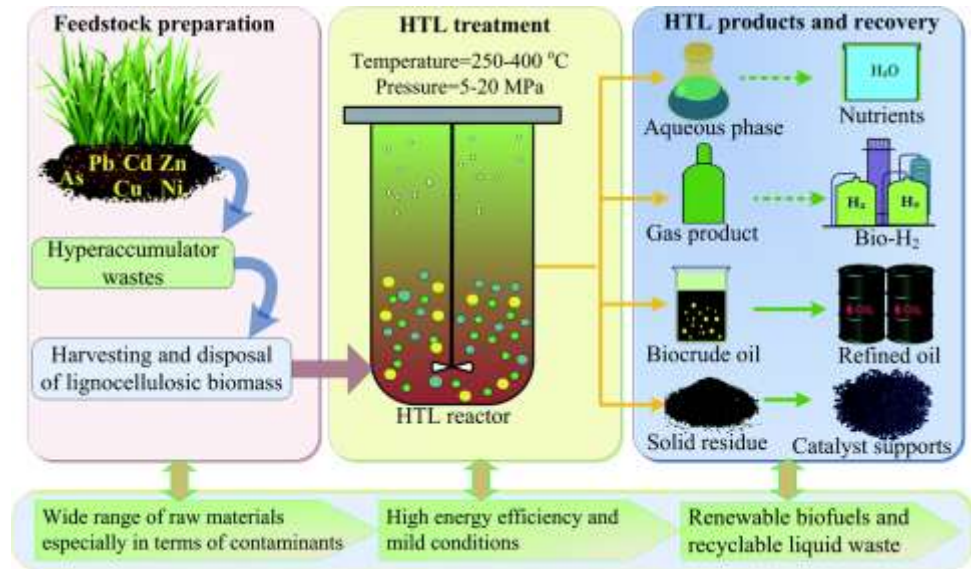
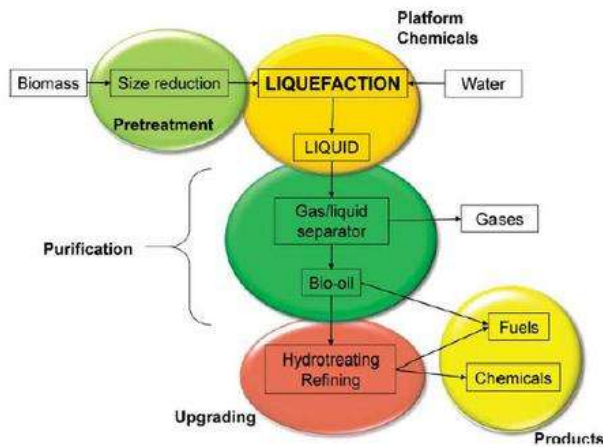
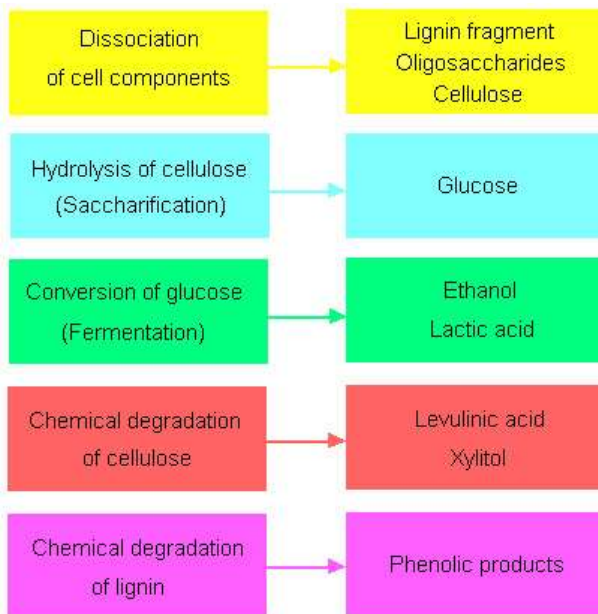
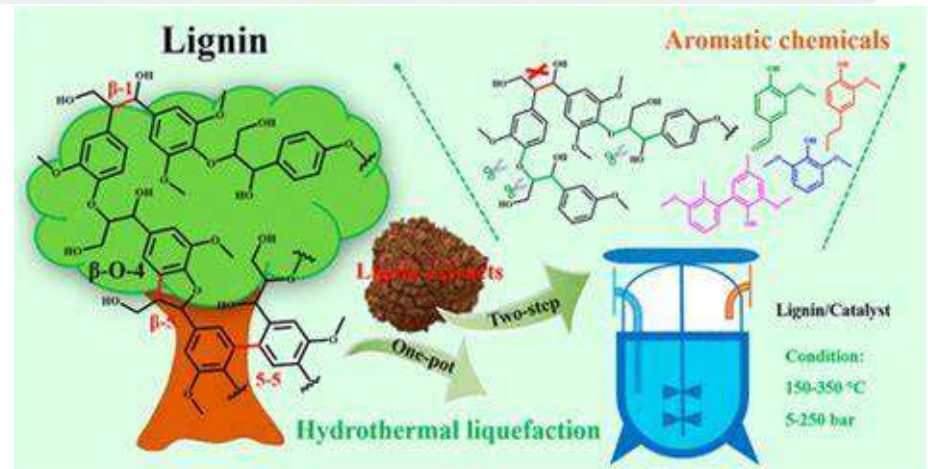


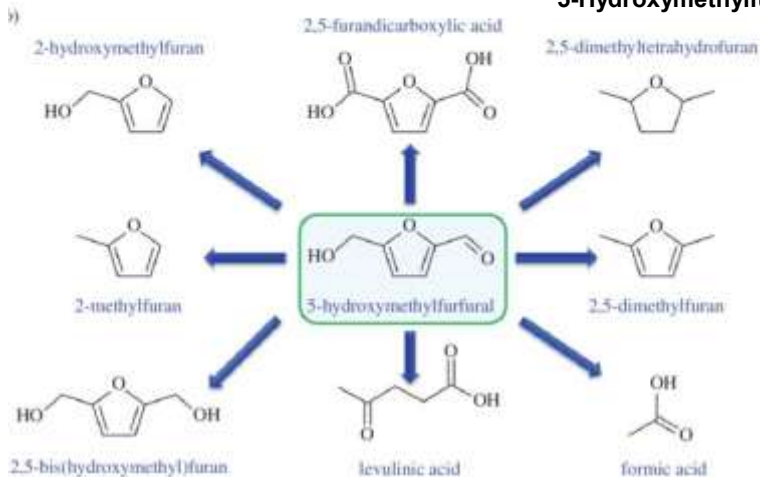
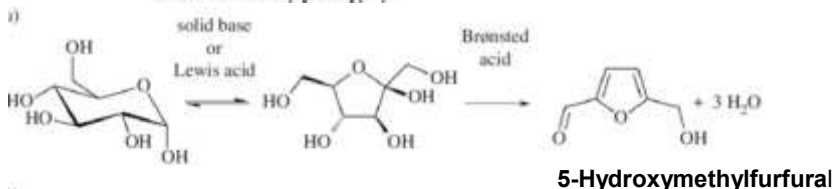
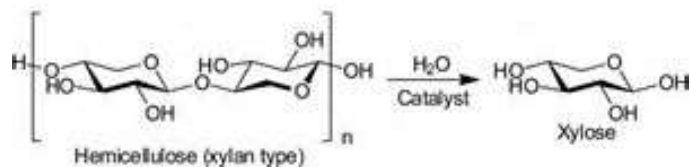
Fig. 10 Process schematic: biomass liquefaction and upgrading.



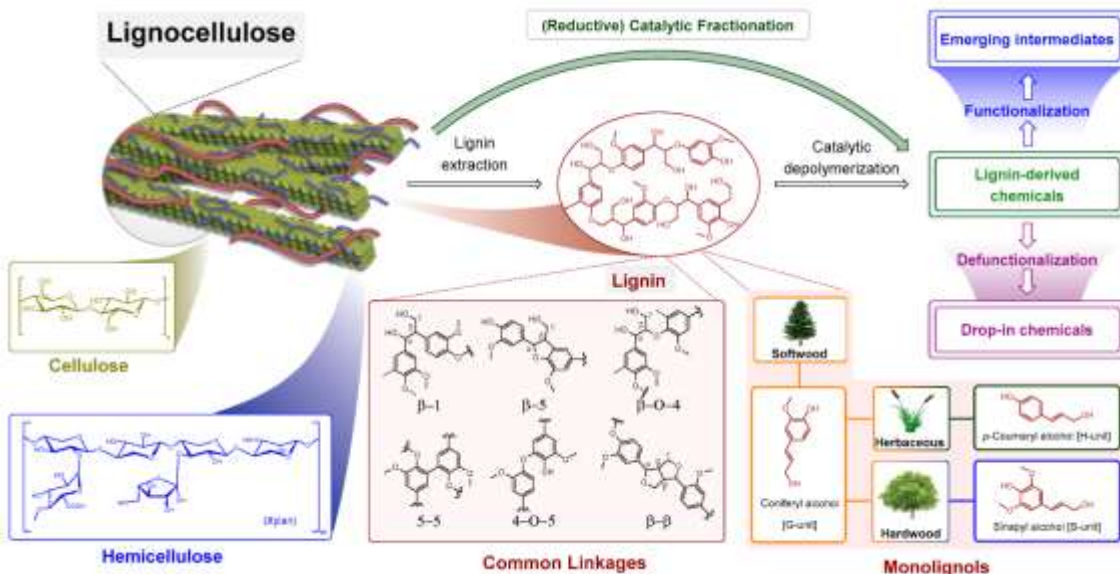
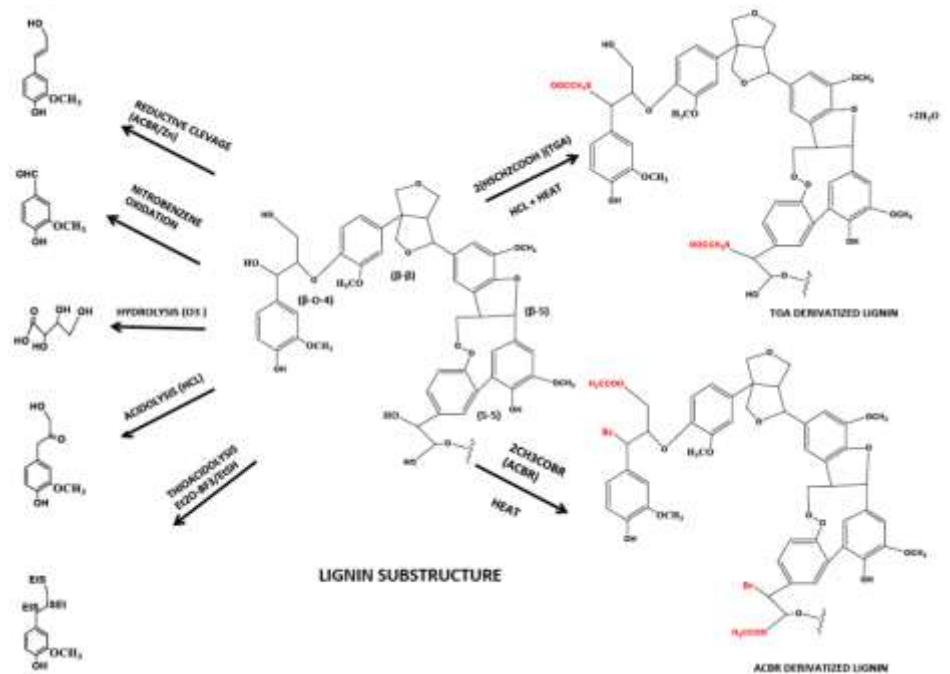
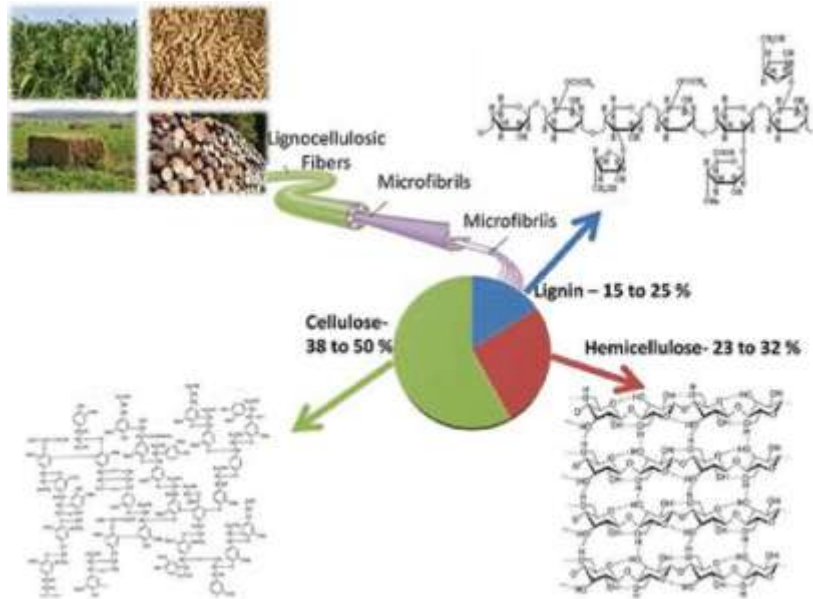
乙酰丙酸
木糖醇



The diagram illustrates the hydrolysis of cellulose. On the left, a cellulose polymer chain is shown as a repeating unit of glucose rings linked by β -1,4 glycosidic bonds, enclosed in brackets with a subscript n . The reaction arrow is labeled with H_2O above it and "Catalyst" below it. On the right, the products are individual glucose molecules, each a six-membered ring with multiple hydroxyl groups.

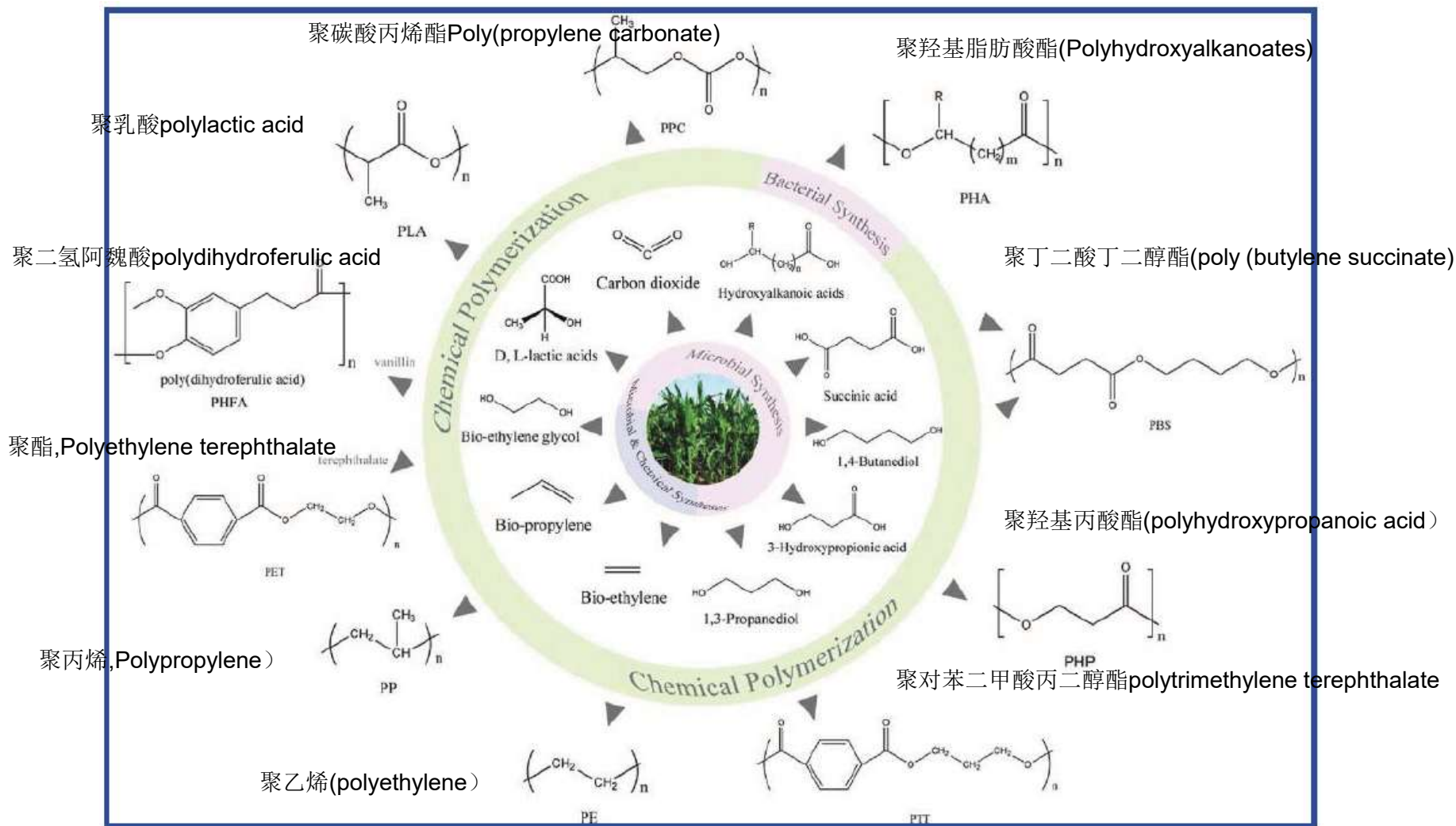
[illegible]

Phenolic products from lignin



<div>Lignin</div> <div>Treatment Methods and Products</div>				
Pyrolysis	Hydrogenolysis	Oxidation	Gasification	Combustion
Thermal Treatment No Oxygen With or Without Catalyst	Thermal Treatment With Hydrogen	Thermal Treatment With Oxygen	Heat Solid Lignin Breakdown	With Oxygen
Solid Char	Liquid Monomeric Phenols	Aldehydes (Vanillin, syringaldehyde)	Biogas H ₂ , CO, CO ₂ , CH ₄	Heat
Pyrolysis Oil		Solid Char		Gases
Gases (CO, CO ₂)		Gases		Solid Char
<div>Biochemicals</div> <div>Biofuels</div> <div>Bioelectricity</div>				

Biopolymers derived from biological sources



Biotechnological and Chemical Conversions for the Production of Bio-Based Monomers

Table 3. Biotechnological and Chemical Conversions for the Production of Bio-Based Monomers

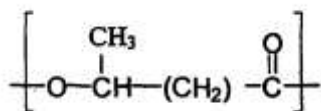
琥珀酸放线杆菌

Bio-Plastics	Bio-based monomers	Production routes	Refs
PHA	Hydroxyalkanoates	Glucose or Fatty acids $\xrightarrow{\text{Bacterial fermentation}}$ Hydroxyalkanoyl-CoA $\xrightarrow{\text{In vivo transformation}}$ Hydroxyalkanoates	5, 55, 56
PLA	D, L-lactic acids	Glucose $\xrightarrow{\text{Fermentation of lactic acid bacteria}}$ D-lactic acids or L-lactic acids	23
PBS	Succinic acid, 1,4-butanediol	Glucose $\xrightarrow{\text{Fermentation of } Actinobacillus\ succinogenes, Anaerobiospirillum\ succiniciproducens\ \text{or}\ Mannheimia\ succiniproducens}$ Succinic acid Succinic acid $\xrightarrow{\text{Hydrogenation under the catalysis of activated carbon-supported Ru and Pd catalysts}}$ 1,4-Butanediol	25
PPC	Carbon dioxide	Bio-respiration or chemical oxidation	6
PTT	1,3-Propanediol	Glycerol $\xrightarrow{\text{Fermentation of } Klebsiella\ pneumoniae, Enterobacter\ agglomerans\ \text{or}\ Citrobacter\ freundii}$ 1,3-Propanediol	36
PE	Bio-ethylene	Glucose $\xrightarrow{\text{Yeast fermentation}}$ Ethanol $\xrightarrow{\text{Dehydration under the catalysis of activated clay, phosphoric acid or activated alumina}}$ Ethylene	40
PP	Bio-isobutanol	Glucose $\xrightarrow{\text{Fermentation of recombinant } E. coli}$ isobutanol $\xrightarrow{\text{Dehydration}}$ butylenes $\xrightarrow{\text{Isomerization}}$ 2-butylene $\xrightarrow{\text{Metathesis with ethylene}}$ Propylene	42-45
PET	Bio-ethylene glycol	Glucose $\xrightarrow{\text{Yeast fermentation}}$ Ethanol $\xrightarrow{\text{Dehydration under the catalysis of activated clay, phosphoric acid or activated alumina}}$ Ethylene Ethylene $\xrightarrow{\text{Direct oxidation of ethylene followed by thermal hydrolysis}}$ Ethylene glycol	47, 49

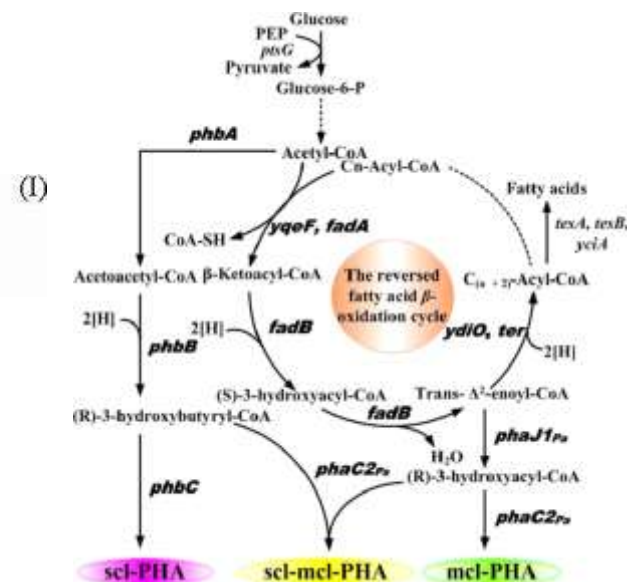
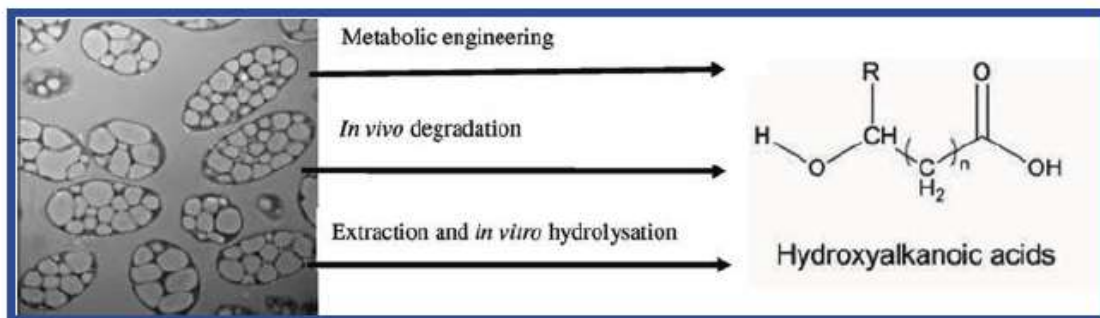
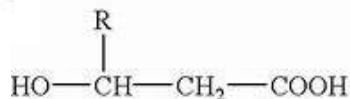
克雷伯菌

Microbial production of hydroxyalkanoic acids and PHA

PHA: polyhydroxyalkanoates 聚羟基脂肪酸酯



3-hydroxyalkanoic acid

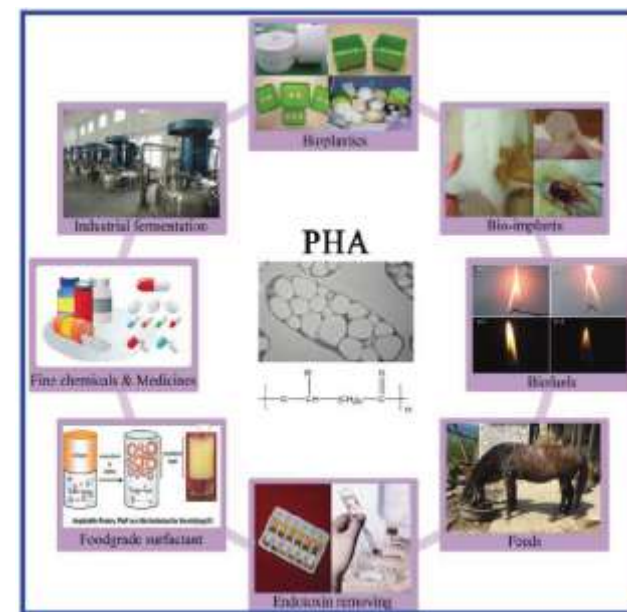


真氧产碱杆菌

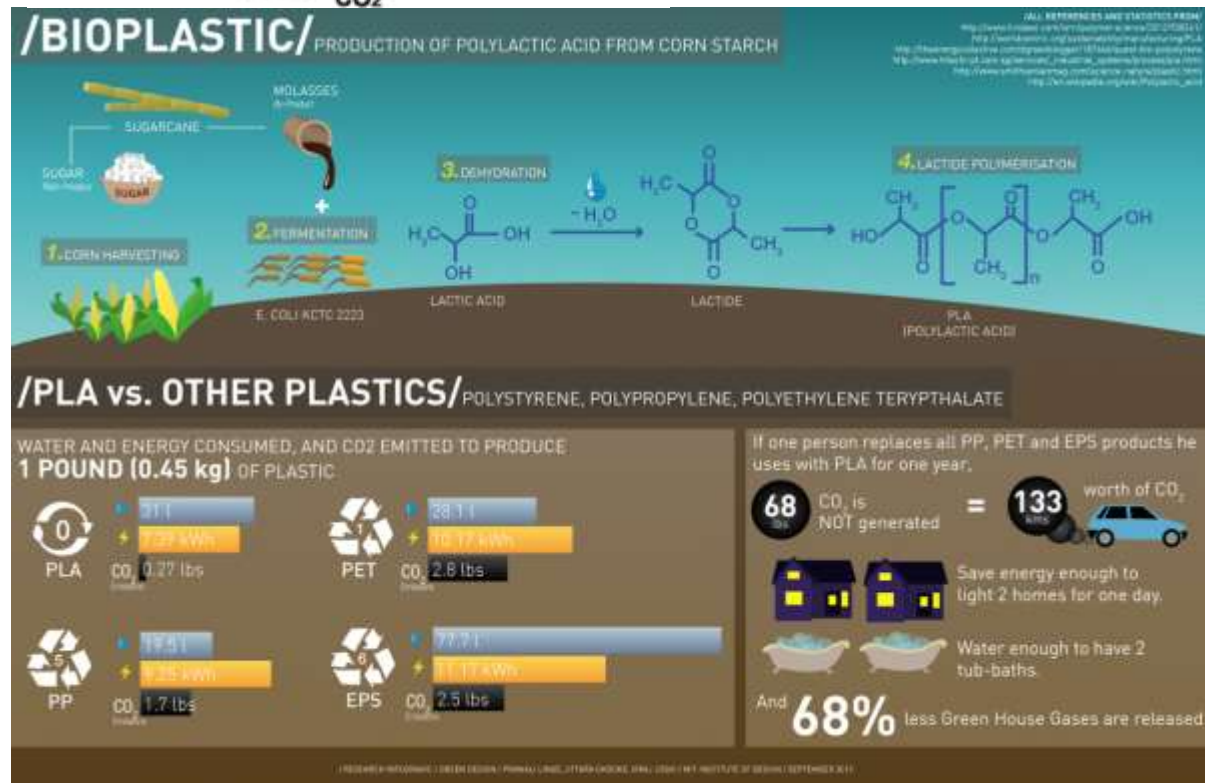
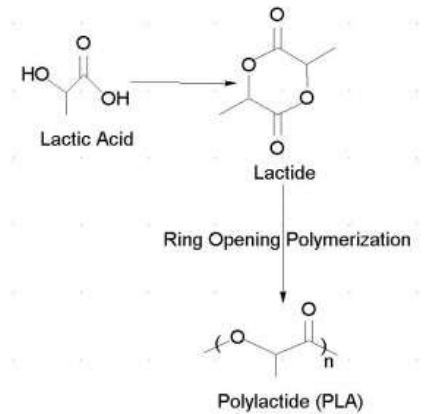
嗜水气单胞菌

恶臭假单胞菌

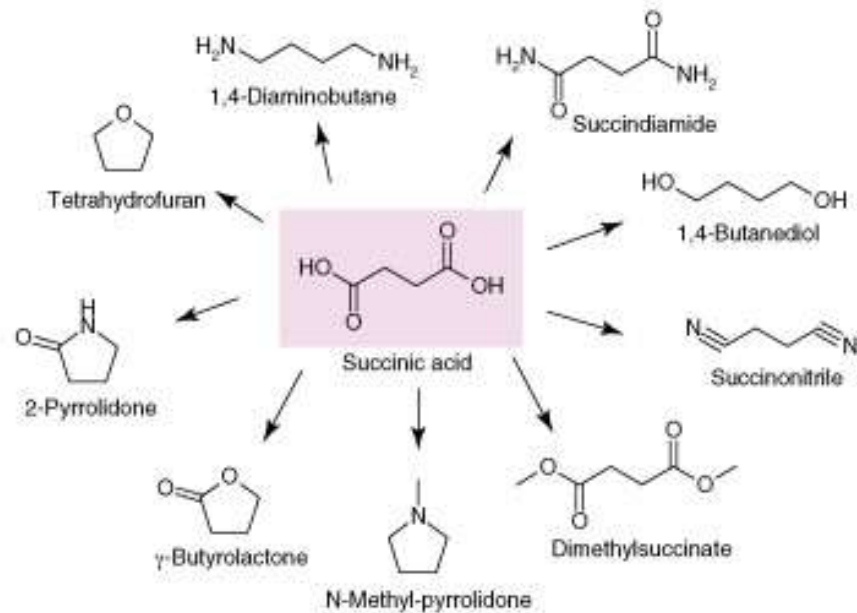
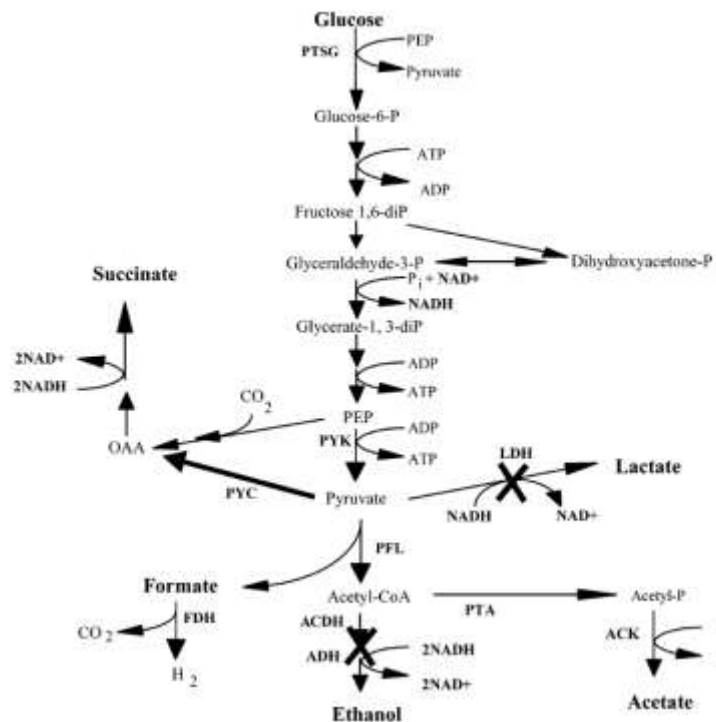
Microorganisms	PHA synthesized	PHA chemical structure
<i>Ralstonia eutropha</i>	PHB [poly(3-hydroxybutyrate)]	$\left[\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{C}(=\text{O}) \right]_n$
	PHBV [poly(3-hydroxybutyrate-co-3-hydroxyvalerate)]	$\left[\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{C}(=\text{O})-\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{C}(=\text{O}) \right]_n$
	P3HB4HB [poly(3-hydroxybutyrate-co-4-hydroxybutyrate)]	$\left[\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O}) \right]_n$
<i>Aeromonas hydrophila</i>	PHBHHx [poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)]	$\left[\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O}) \right]_n$
<i>Pseudomonas putida</i>	PHOHHx [poly(3-hydroxyoctanoate-co-3-hydroxyhexanoate)]	$\left[\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O}) \right]_n$



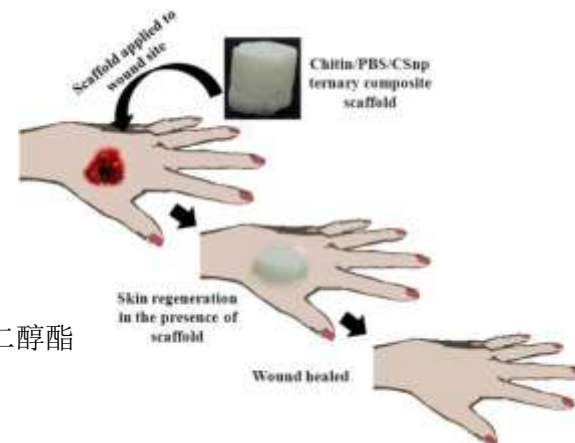
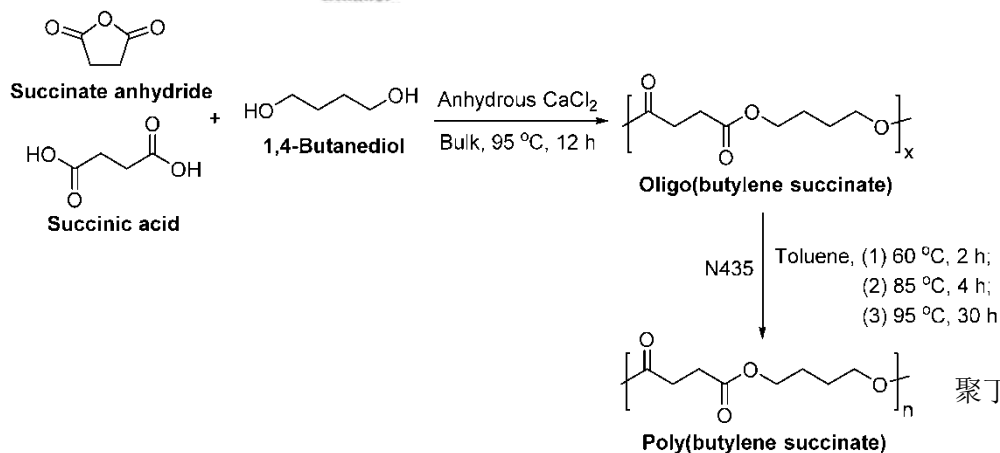
Lactic acid: is produced naturally in response to demanding physical activities that stress the muscles and cause an increased need for energy. In this way, it's a response that naturally makes you want to slow down and rest when your muscles are stressed and you're exerting lots of energy.



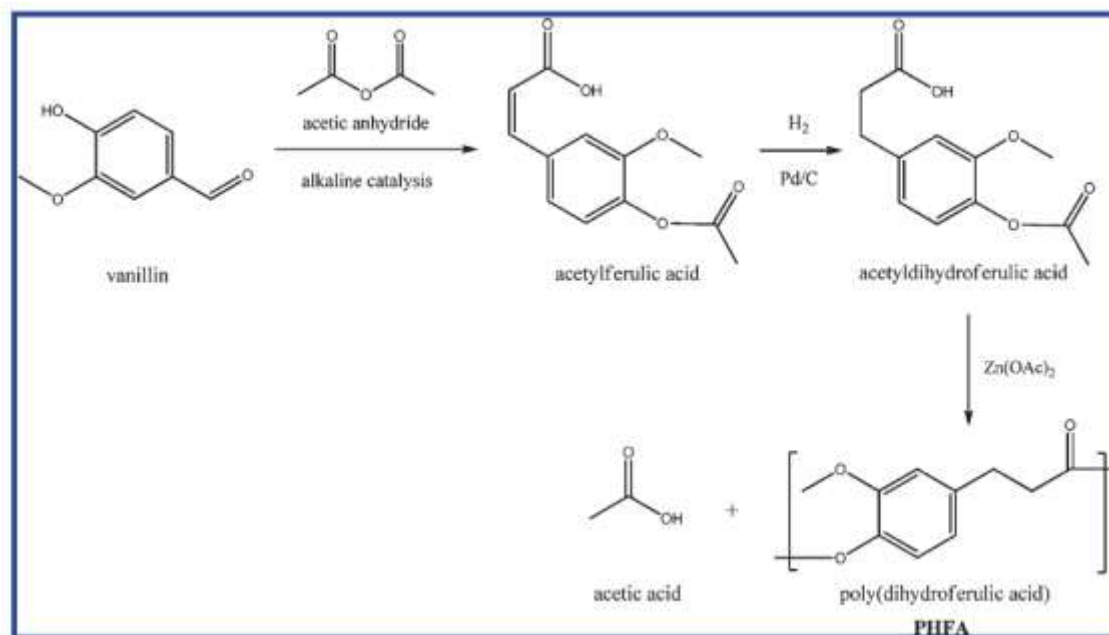
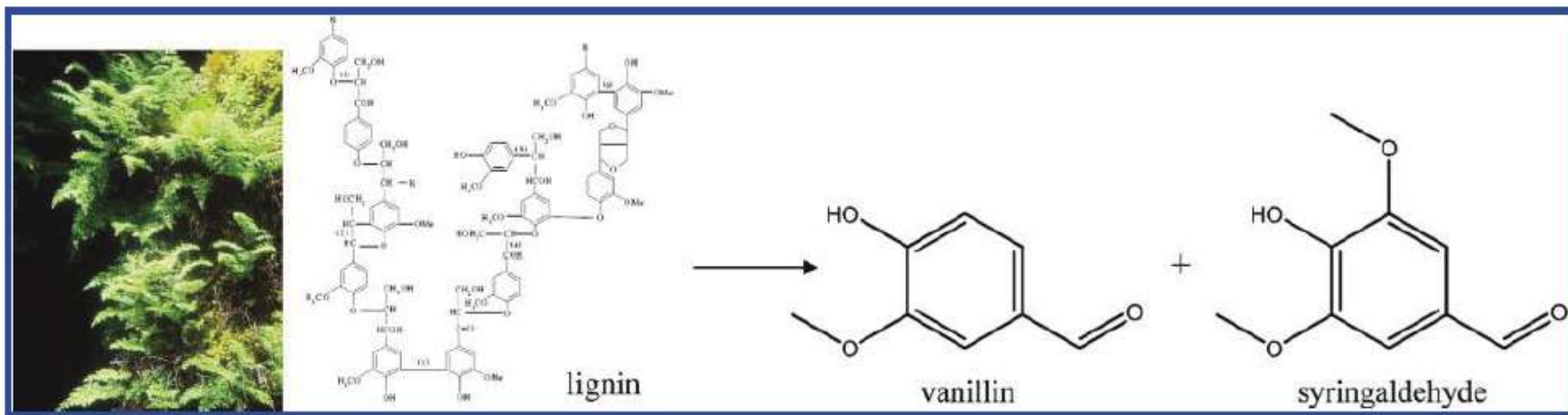
Succinic acid



TRENDS in Biotechnology



Vanillin from lignin extraction



聚二氢阿魏酸

Thank You!

Presentation

- **Oct. 22:** 李羽辰 李玲琦 袁智涵
- **Oct. 29:** 张翔俣 陈爽 罗曼文
- **Nov. 05 :** 任皓然 陈怡达 凌宇涵
- **Nov. 12:** 黄淳奕 戴嘉玲 仲昕杰
- **Nov. 19:** 董润泽 陆佳文 薛 磊
- **Nov. 26:** 郭潘缘 方徐易 孔锦垚
- **Dec. 03:** 陈子田 王子衿 朱许源
- **Dec. 10:** 张昊 周智然 胡金妍
- **Dec. 17:** 周帅 徐永强

Home work of today

What is methanol economy? Why does its implementation and development contribute to a sustainable carbon cycle?