Nachhaltige Chemie – Anknüpfungspunkte für den Chemieunterricht

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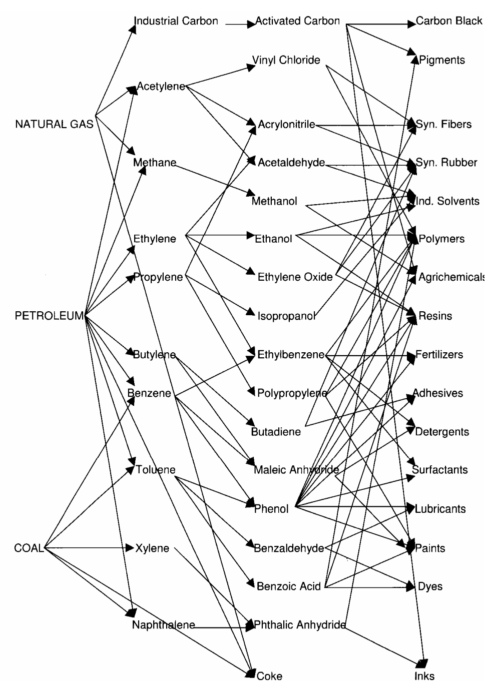
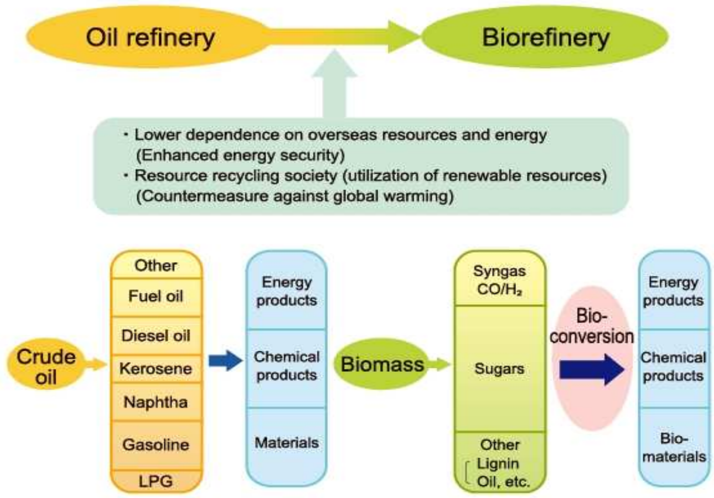
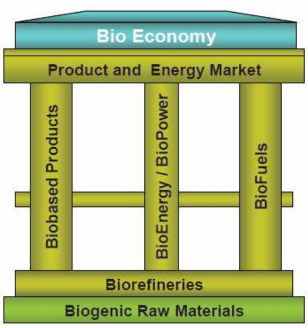






3-pillar model of a future biobased economy

In consequence, it is absolutely necessary to develop solutions in three sustainable and biobased sectors:

- Biopower/Bioenergy (electricity and heat)
- Biofuels (transportation fuels)
- Biobased Products (chemicals/materials)

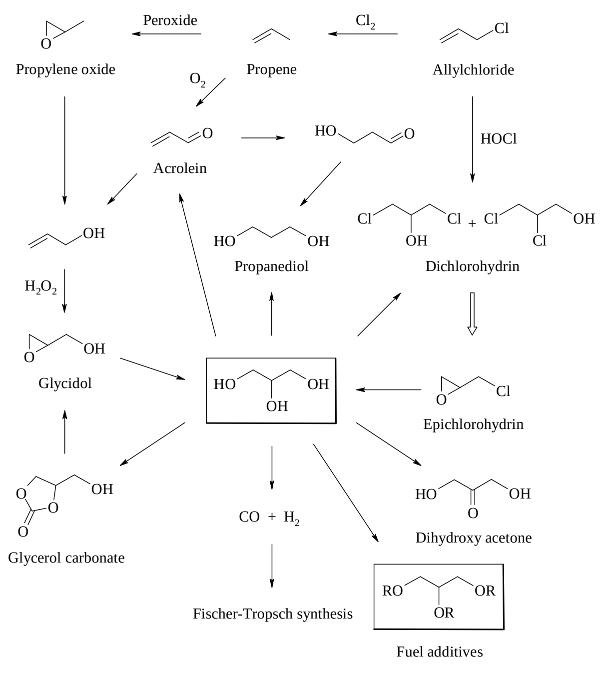
in context of a biobased economy.

A key of the development biobased industrial products and fuels are Biorefineries

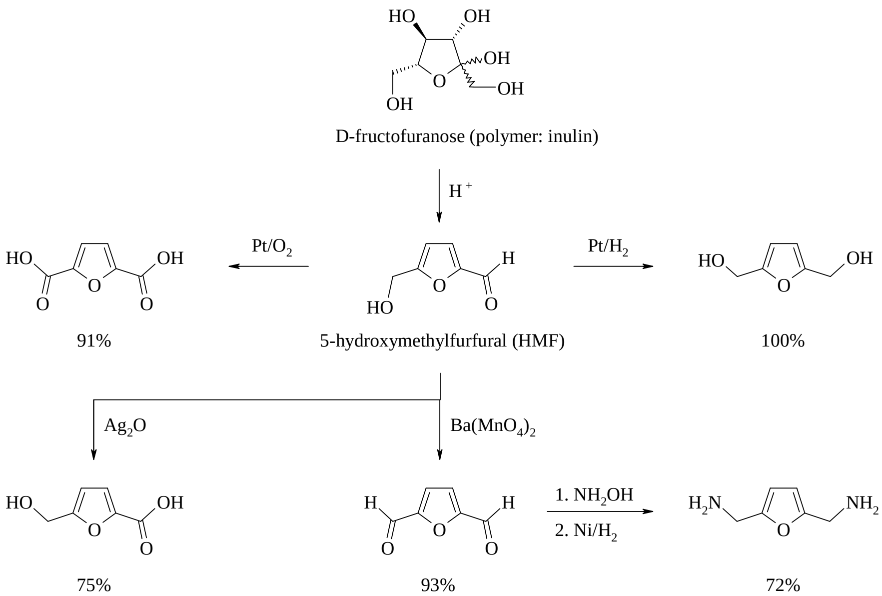
Energy: Water, wind, sun, geothermal etc.

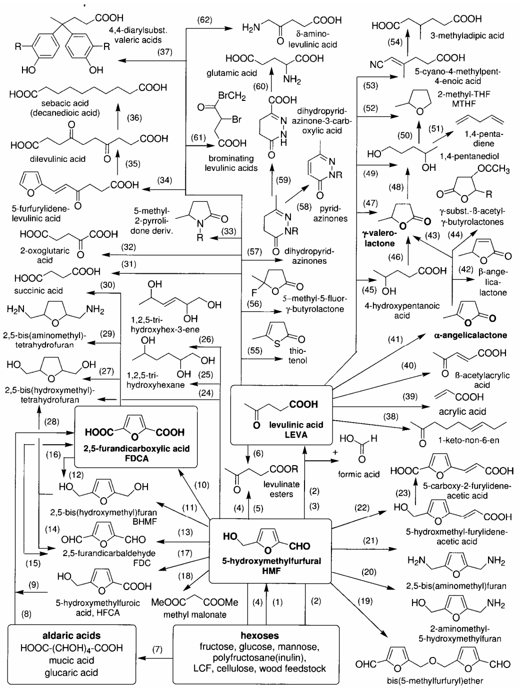
(Bio)Mass: 170 x 10^9 t of biomass is produced per year by photosynthesis (In principle any organic matter could be used, i.e. from the animal kingdom as well).

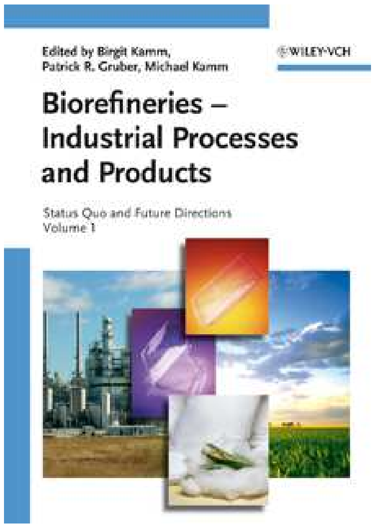
From this biomass: 75% are carbohydrates
20% lignin
5% other compounds: fats, lipids, proteins etc.



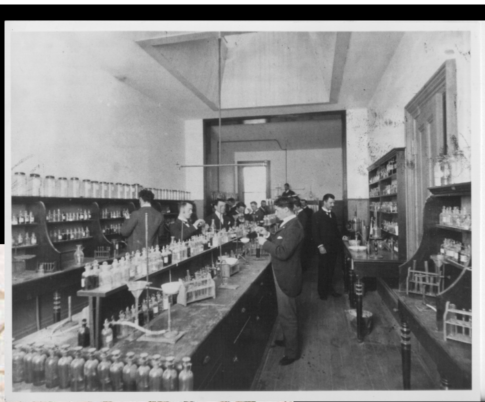
Some recent applications of carbohydrates as substrates in sustainable chemistry

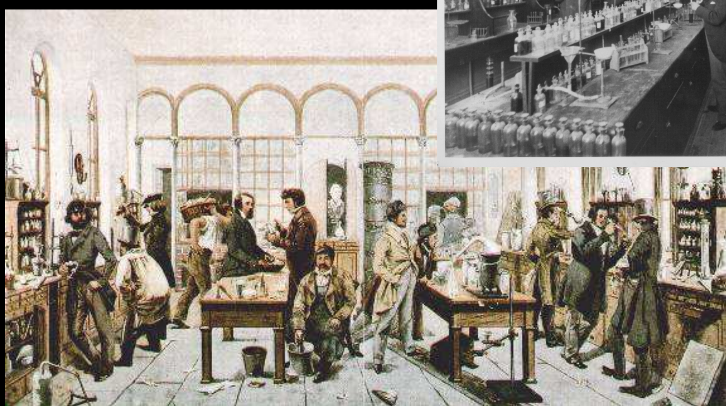






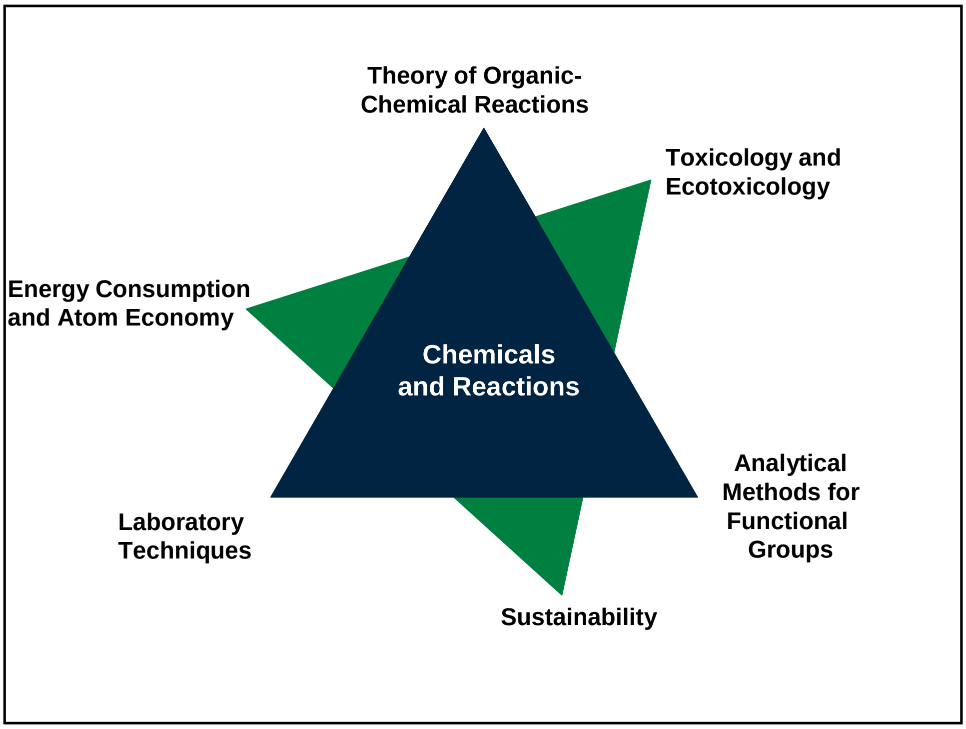
Pharmaceutical Laboratory in 1894

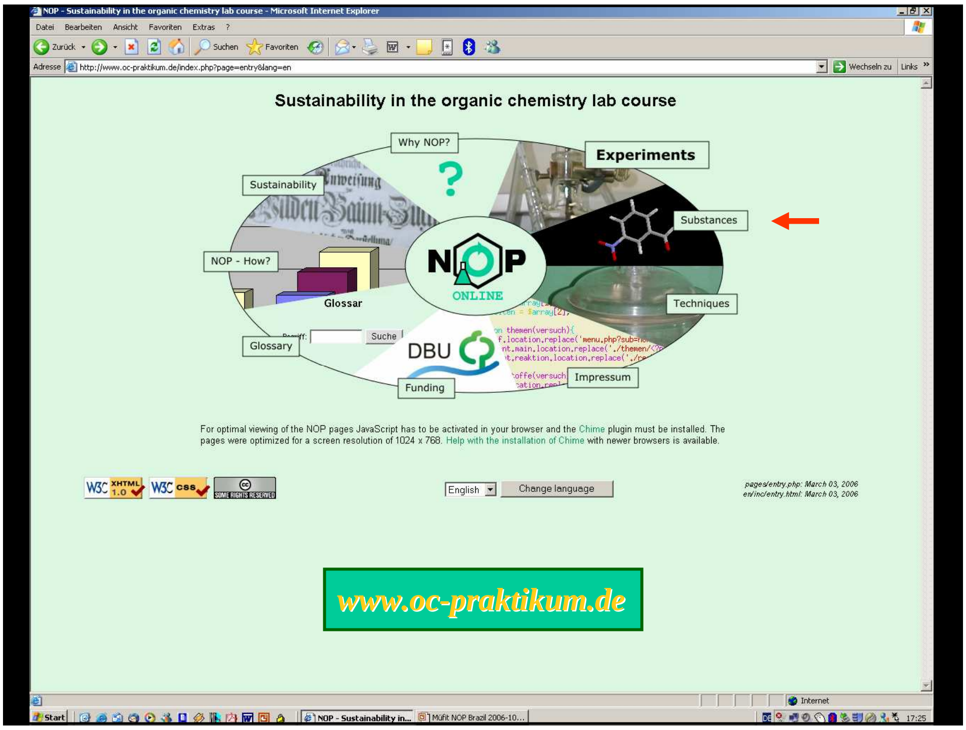




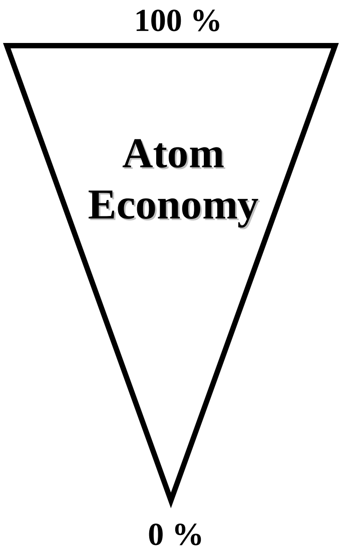
Liebig´s Analytical Laboratory at 1840


Chemical Laboratory
in Vietnam 2004
Chemical Laboratory
in Kazakhstan 2005
Chemical Laboratory
in Indonesia 2006


Theory of Organic-
Chemical Reactions
Toxicology and
Ecotoxicology
Energy Consumption
and Atom Economy
Chemicals
and Reactions
Analytical
Methods for
Functional
Groups
Laboratory
Techniques
Sustainability



The yields



Isomerization, rearrangement, addition or disproportionation

Substitution, elimination

Catalytic reactions

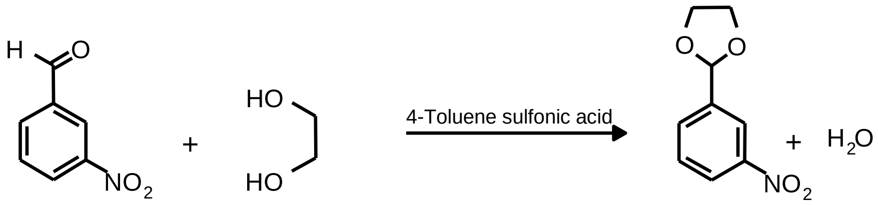
Stoichiometric reactions

no reaction, wrong reaction

B. M. Trost, *Science*, **1991**, *254*, 1471

How well does a chemical reaction work ?

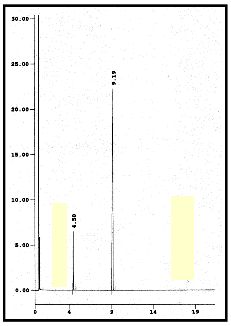
Acid catalyzed acetalization of
3-nitrobenzaldehyde with ethylene glycol to 1,3-dioxolane



$C_7H_5NO_3$	$C_2H_6O_2$	$C_7H_8O_3S \cdot H_2O$	$C_9H_9NO_4$
(151.1)	(62.1)	(190.2)	(195.2)

State-of-the-art Analyses

How clean is the reaction?
➔ Gas chromatogram of raw products

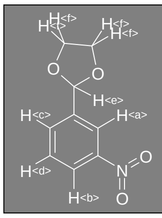


Substrate (3-Nitrobenzaldehyde)	**RT**	**4.5**	**9 %**
Product (1,3-Dioxolane)	**RT**	**9.2**	**91 %**
Other impurities in trace amounts			**< 0.1 %**

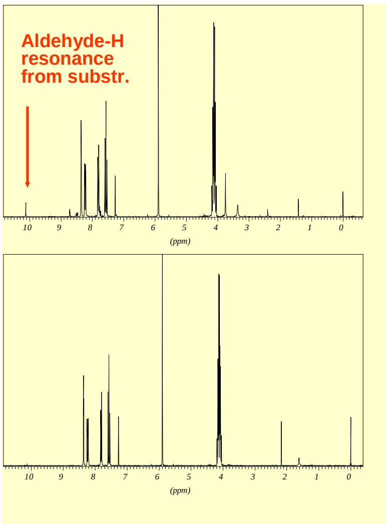
State-of-the-art Analyses

How specific is the reaction?
➔ ^{1}H-NMR spectrum of raw product

➔ ^{1}H- NMR spectrum of pure product

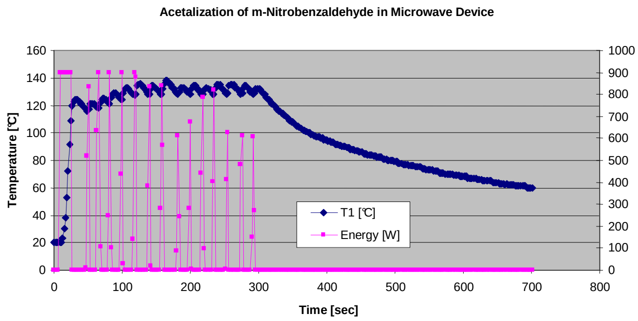


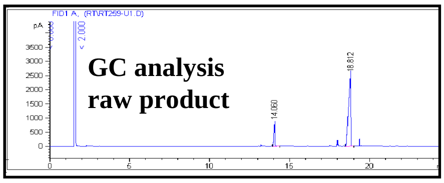
δ (ppm)	multiplicity	number H	assignment
8.37-8.35	m	1	H_a
8.25-8.20	m	1	H_b
8.83-7.79	m	1	H_c
7.60-7.54	m	1	H_d
5.90	s	1	H_e
4.18-4.05	m	4	H_f



Alternative Reaction Control

Energy Input by Microwave





After 5 min reaction time:
85 % product
15 % starting material

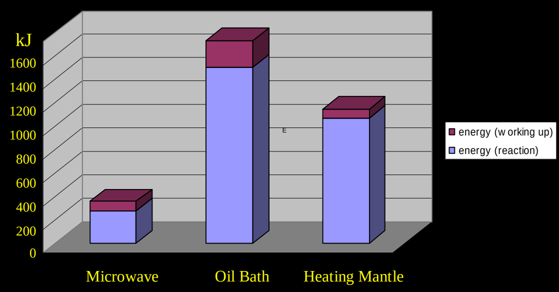
Energy Consumption

Same Reaction - Different Heating

Oil Bath Heating Mantle Microwave

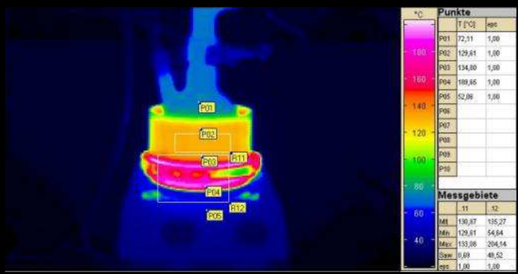
Energy Consumption

Effect of the heating method



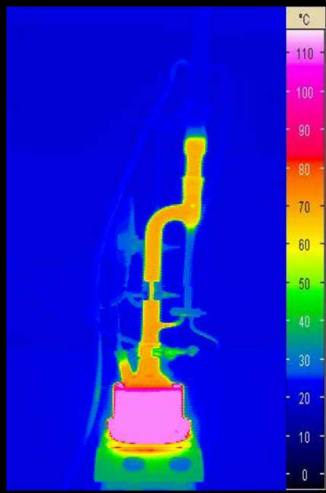
	microwave	oil bath	heating mantle	
Energy (reaction)	77	418	297	Wh
Energy (working up)	22	63	22	Wh
Energy (total)	99	481	319	Wh
Energy (reaction)	277	1505	1069	kJ
Energy (working up)	79	227	79	kJ
Energy (total)	356	1732	1148	kJ

Energy Losses



Oil Bath

Infrared photography makes energy emissions visible



Heating Mantle

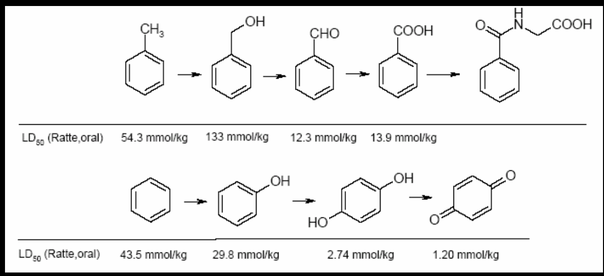
Effect factors for hazard

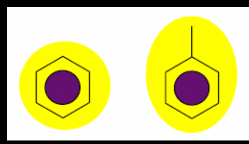
Effect factors after TRGS 440 *(GER 2001)*

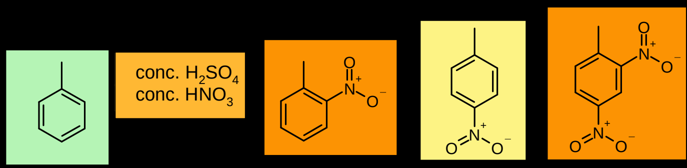
Risk phrases	Hazards	Effect factor
R45, R46, M1, M2, K1, K2	carcinogenic or mutagenic	50,000
R26, R27, R28 oder LGW < 0,1 mg/m³	highly toxic	1,000
R32, R60, R61, RE1, RE2, RF1, RF2	potential reproduction toxicity or teratogenic, formation of highly toxic gases in contact with acids	1,000
R35, R48/23, R48/24, R48/25, R42, R43	highly corrosive, high chronic toxicity, potentially sensitizing	500
R23, R24, R25, R29, R31, R34, R41, H	toxic, generation of toxic gases in contact with water or acids, cauterizing for eyes, skin absorption	100
R33, R40, K3, M3, pH < 2 oder pH > 11,5	risk of cumulative effects, potentially irreversible damages, suspected mutagenic or carcinogenic effects	100
Not tested sufficiently	= No LGW, no risk phrases	100
R48/20, R48/21, R48/22, R62, R63, RE3, RF3	chronically harmful, suspected reproduction toxicity or teratogenic effects	50
R20, R21, R22	harmful	10
R36, R37, R38, R65, R67	irritating, narcotic	5
other risk phrases or LGW > 100 mg/m³		1

LGW = Limiting values for air from TRGS 900: = either MAK value (maximum working place concentration) or TRK value (admissible requiring monitoring value) or ARW value (similar to TRK)

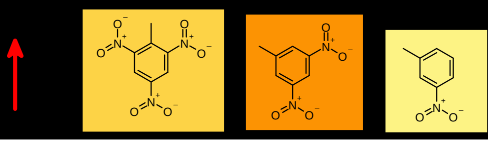
Toxic or not ?







Effect factor > 1000
Effect factor > 100 – 1000
Effect factor > 10 – 100
Effect factor 0 - 10



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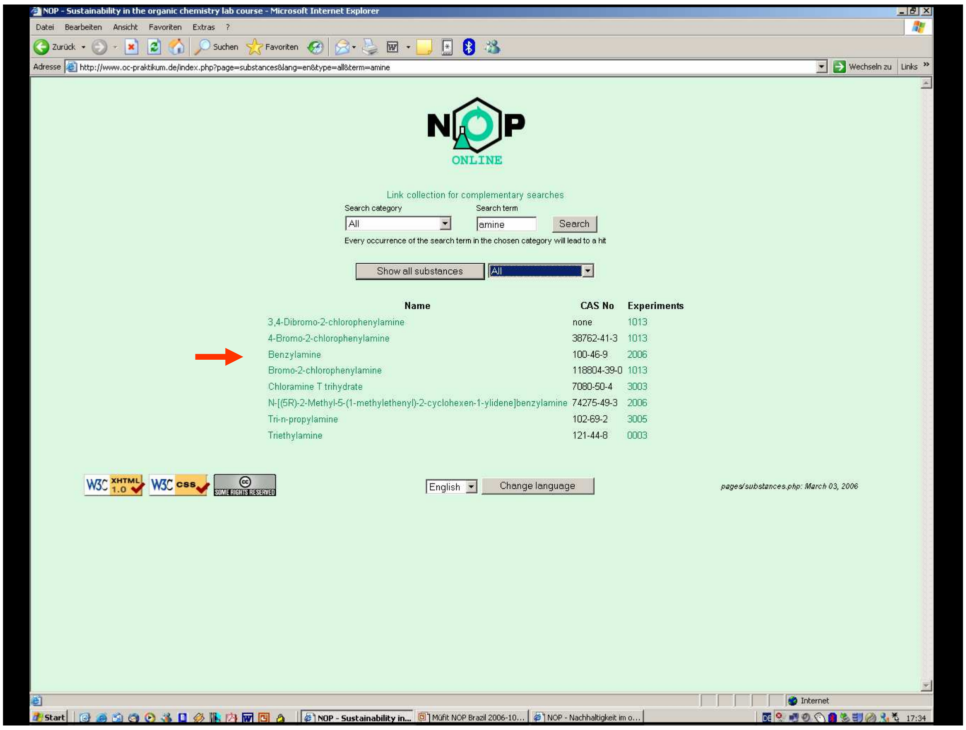
closed preset format
„complete“ supply

NOP:
flexible format for own selection
„open“ access
like Linux and Wikipedia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http://www.oc-praktikum.de/index.php?page=substances&lang=en&type=all&term=amine
NOP ONLINE
Link collection for complementary searches
Search category
All
Search term
amine
Search
Every occurrence of the search term in the chosen category will lead to a hit
Show all substances
Name
CAS No
Experiments
3,4-Dibromo-2-chlorophenylamine none 1013
4-Bromo-2-chlorophenylamine 38762-41-3 1013
Benzylamine 100-46-9 2006
Bromo-2-chlorophenylamine 118804-39-0 1013
Chloramine T trihydrate 7080-50-4 3003
N-[(5R)-2-Methyl-5-(1-methylethenyl)-2-cyclohexen-1-ylidene]benzylamine 74275-49-3 2006
Tri-n-propylamine 102-69-2 3005
Triethylamine 121-44-8 0003
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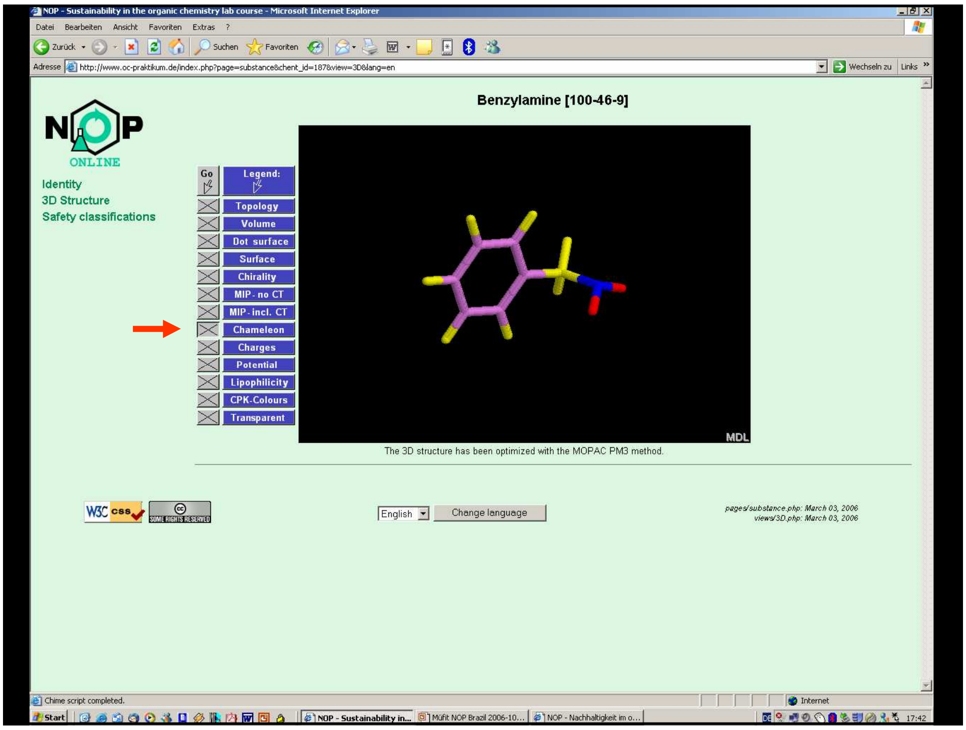
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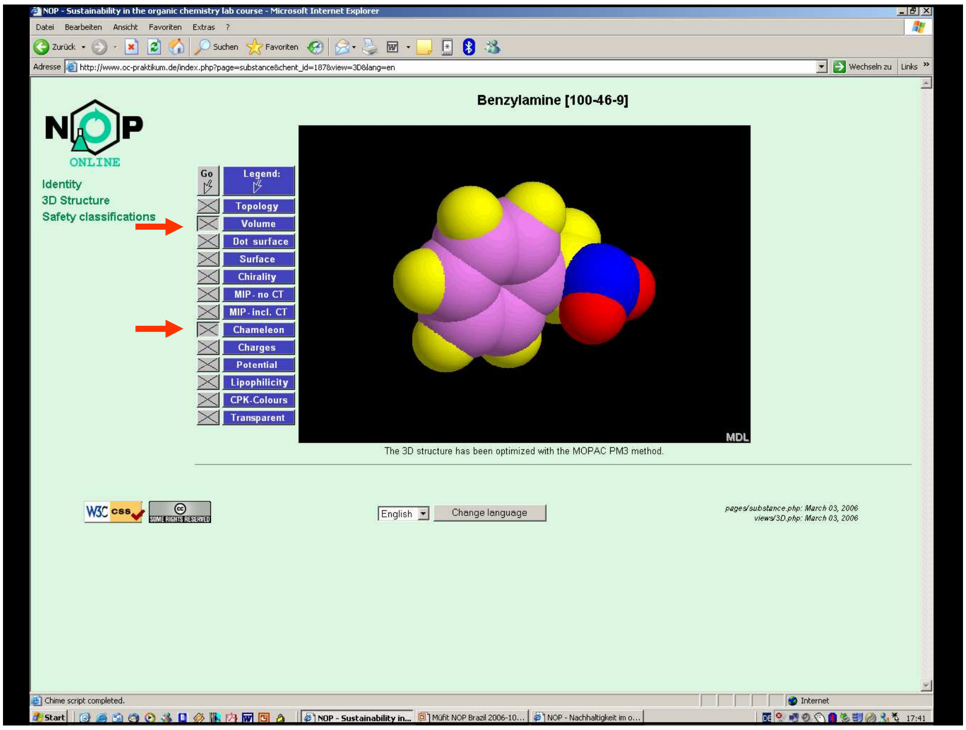
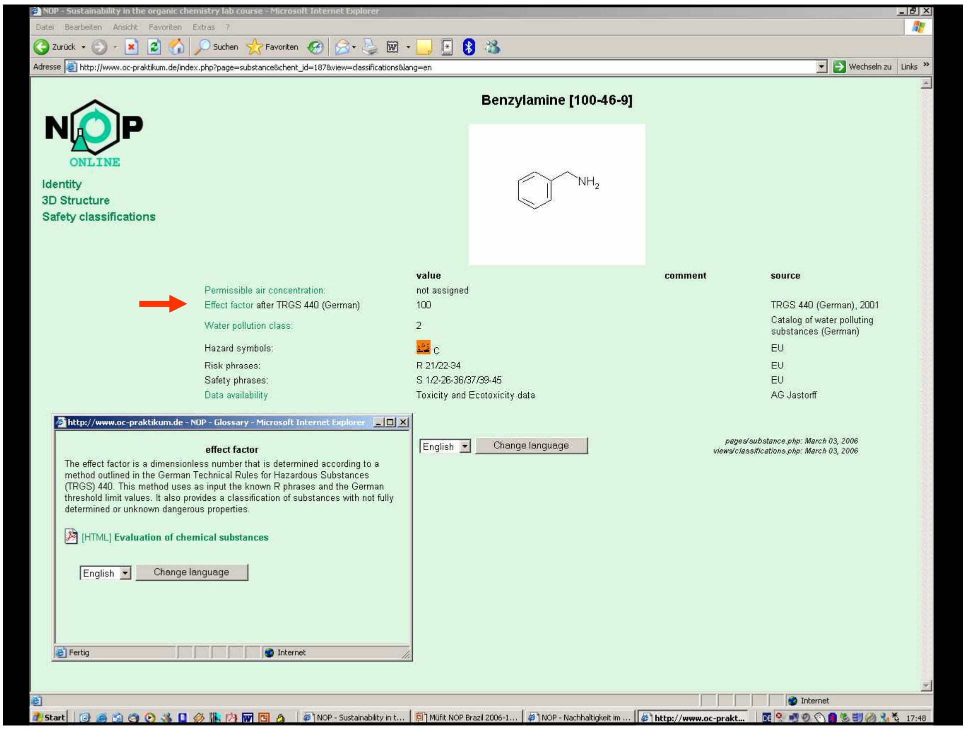
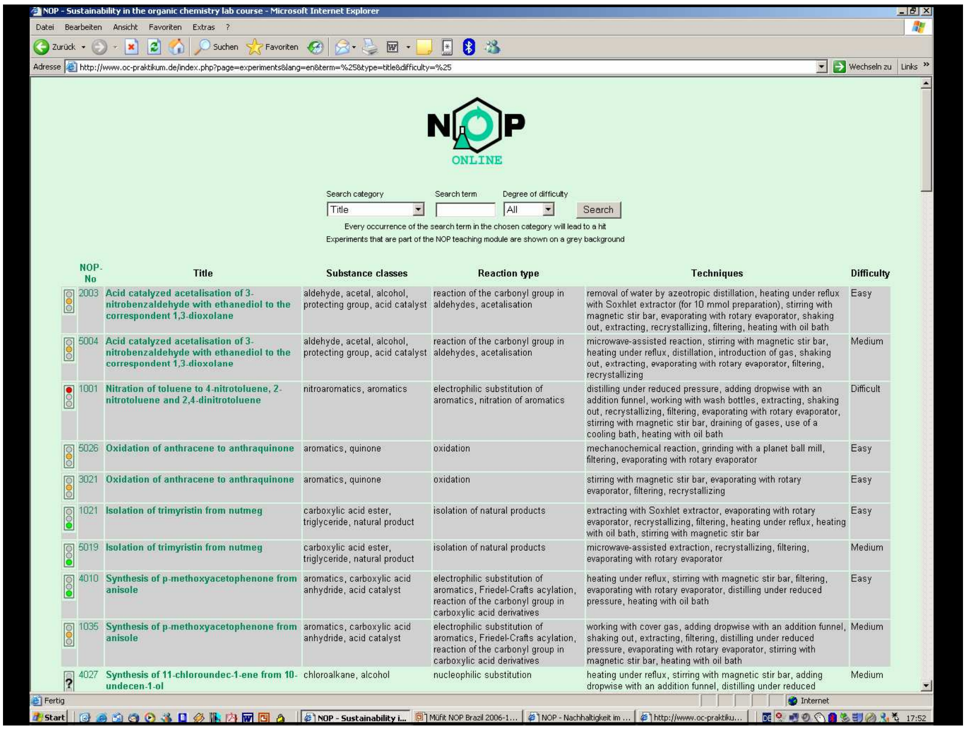
http://www.oc-praktikum.de/index.php?page=substance&chent_id=187&view=3D&lang=en
Benzylamine [100-46-9]
NOP ONLINE
Identity
3D Structure
Safety classifications
Go
Legend:
Topology
Volume
Dot surface
Surface
Chirality
MIP - no CT
MIP - incl. CT
Chameleon
Charges
Potential
Lipophilicity
CPK-Colours
Transparent
MDL
The 3D structure has been optimized with the MOPAC PM3 method.
English
Change language
pages/substance.php: March 03, 2006
views/3D.php: March 03, 2006



NOP - Sustainability in the organic chemistry lab course - Microsoft Internet Explorer
Benzylamine [100-46-9]
Identity
3D Structure
Safety classifications
Legend:
Topology
Volume
Dot surface
Surface
Chirality
MIP - no CT
MIP - incl. CT
Chameleon
Charges
Potential
Lipophilicity
CPK-Colours
Transparent
The 3D structure has been optimized with the MOPAC PM3 method.
English
Change language



NOP - Sustainability in the organic chemistry lab course - Microsoft Internet Explorer
Benzylamine [100-46-9]
Identity
3D Structure
Safety classifications
value
comment
source
Permissible air concentration: not assigned
Effect factor after TRGS 440 (German) 100 TRGS 440 (German), 2001
Water pollution class: 2 Catalog of water polluting substances (German)
Hazard symbols: C EU
Risk phrases: R 21/22-34 EU
Safety phrases: S 1/2-26-36/37/39-45 EU
Data availability Toxicity and Ecotoxicity data AG Jastorff
effect factor
The effect factor is a dimensionless number that is determined according to a method outlined in the German Technical Rules for Hazardous Substances (TRGS) 440. This method uses as input the known R phrases and the German threshold limit values. It also provides a classification of substances with not fully determined or unknown dangerous properties.
[HTML] Evaluation of chemical substances
English
Change language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ONLINE
Search category
Title
Search term
Degree of difficulty
All
Search
Every occurrence of the search term in the chosen category will lead to a hit
Experiments that are part of the NOP teaching module are shown on a grey background
NOP-No | Title | Substance classes | Reaction type | Techniques | Difficulty
2003 | Acid catalyzed acetalisation of 3-nitrobenzaldehyde with ethanediol to the correspondent 1,3-dioxolane | aldehyde, acetal, alcohol, protecting group, acid catalyst | reaction of the carbonyl group in aldehydes, acetalisation | removal of water by azeotropic distillation, heating under reflux with Soxhlet extractor (for 10 mmol preparation), stirring with magnetic stir bar, evaporating with rotary evaporator, shaking out, extracting, recrystallizing, filtering, heating with oil bath | Easy
5004 | Acid catalyzed acetalisation of 3-nitrobenzaldehyde with ethanediol to the correspondent 1,3-dioxolane | aldehyde, acetal, alcohol, protecting group, acid catalyst | reaction of the carbonyl group in aldehydes, acetalisation | microwave-assisted reaction, stirring with magnetic stir bar, heating under reflux, distillation, introduction of gas, shaking out, extracting, evaporating with rotary evaporator, filtering, recrystallizing | Medium
1001 | Nitration of toluene to 4-nitrotoluene, 2-nitrotoluene and 2,4-dinitrotoluene | nitroaromatics, aromatics | electrophilic substitution of aromatics, nitration of aromatics | distilling under reduced pressure, adding dropwise with an addition funnel, working with wash bottles, extracting, shaking out, recrystallizing, filtering, evaporating with rotary evaporator, stirring with magnetic stir bar, draining of gases, use of a cooling bath, heating with oil bath | Difficult
5026 | Oxidation of anthracene to anthraquinone | aromatics, quinone | oxidation | mechanochemical reaction, grinding with a planet ball mill, filtering, evaporating with rotary evaporator | Easy
3021 | Oxidation of anthracene to anthraquinone | aromatics, quinone | oxidation | stirring with magnetic stir bar, evaporating with rotary evaporator, filtering, recrystallizing | Easy
1021 | Isolation of trimyristin from nutmeg | carboxylic acid ester, triglyceride, natural product | isolation of natural products | extracting with Soxhlet extractor, evaporating with rotary evaporator, recrystallizing, filtering, heating under reflux, heating with oil bath, stirring with magnetic stir bar | Easy
5019 | Isolation of trimyristin from nutmeg | carboxylic acid ester, triglyceride, natural product | isolation of natural products | microwave-assisted extraction, recrystallizing, filtering, evaporating with rotary evaporator | Medium
4010 | Synthesis of p-methoxyacetophenone from anisole | aromatics, carboxylic acid anhydride, acid catalyst | electrophilic substitution of aromatics, Friedel-Crafts acylation, reaction of the carbonyl group in carboxylic acid derivatives | heating under reflux, stirring with magnetic stir bar, filtering, evaporating with rotary evaporator, distilling under reduced pressure, heating with oil bath | Easy
1035 | Synthesis of p-methoxyacetophenone from anisole | aromatics, carboxylic acid anhydride, acid catalyst | electrophilic substitution of aromatics, Friedel-Crafts acylation, reaction of the carbonyl group in carboxylic acid derivatives | working with cover gas, adding dropwise with an addition funnel, shaking out, extracting, filtering, distilling under reduced pressure, evaporating with rotary evaporator, stirring with magnetic stir bar, heating with oil bath | Medium
4027 | Synthesis of 11-chloroundec-1-ene from 10-undecen-1-ol | chloroalkane, alcohol | nucleophilic substitution | heating under reflux, stirring with magnetic stir bar, adding dropwise with an addition funnel, distilling under reduced | Medium
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Internet
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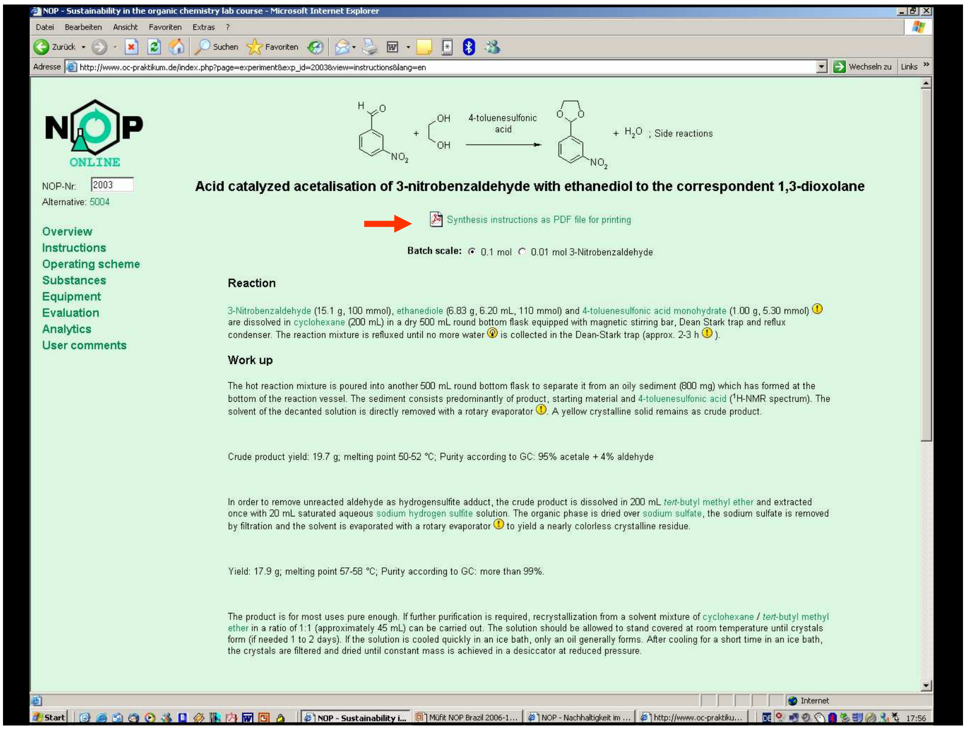
17:52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http://www.oc-praktikum.de/index.php?page=experiment&exp_id=2003&view=instructions&lang=en
ONLINE
NOP-Nr. 2003
Alternative: 5004
Overview
Instructions
Operating scheme
Substances
Equipment
Evaluation
Analytics
User comments
4-toluenesulfonic acid
+ H2O ; Side reactions
Acid catalyzed acetalisation of 3-nitrobenzaldehyde with ethanediol to the correspondent 1,3-dioxolane
Synthesis instructions as PDF file for printing
Batch scale: 0.1 mol 0.01 mol 3-Nitrobenzaldehyde
Reaction
3-Nitrobenzaldehyde (15.1 g, 100 mmol), ethanediole (6.83 g, 6.20 mL, 110 mmol) and 4-toluenesulfonic acid monohydrate (1.00 g, 5.30 mmol) are dissolved in cyclohexane (200 mL) in a dry 500 mL round bottom flask equipped with magnetic stirring bar, Dean Stark trap and reflux condenser. The reaction mixture is refluxed until no more water is collected in the Dean-Stark trap (approx. 2-3 h).
Work up
The hot reaction mixture is poured into another 500 mL round bottom flask to separate it from an oily sediment (800 mg) which has formed at the bottom of the reaction vessel. The sediment consists predominantly of product, starting material and 4-toluenesulfonic acid (1H-NMR spectrum). The solvent of the decanted solution is directly removed with a rotary evaporator . A yellow crystalline solid remains as crude product.
Crude product yield: 19.7 g; melting point 50-52 °C; Purity according to GC: 95% acetale + 4% aldehyde
In order to remove unreacted aldehyde as hydrogensulfite adduct, the crude product is dissolved in 200 mL tert-butyl methyl ether and extracted once with 20 mL saturated aqueous sodium hydrogen sulfite solution. The organic phase is dried over sodium sulfate, the sodium sulfate is removed by filtration and the solvent is evaporated with a rotary evaporator to yield a nearly colorless crystalline residue.
Yield: 17.9 g; melting point 57-58 °C; Purity according to GC: more than 99%.
The product is for most uses pure enough. If further purification is required, recrystallization from a solvent mixture of cyclohexane / tert-butyl methyl ether in a ratio of 1:1 (approximately 45 mL) can be carried out. The solution should be allowed to stand covered at room temperature until crystals form (if needed 1 to 2 days). If the solution is cooled quickly in an ice bath, only an oil generally forms. After cooling for a short time in an ice bath, the crystals are filtered and dried until constant mass is achieved in a desiccator at reduced pressure.
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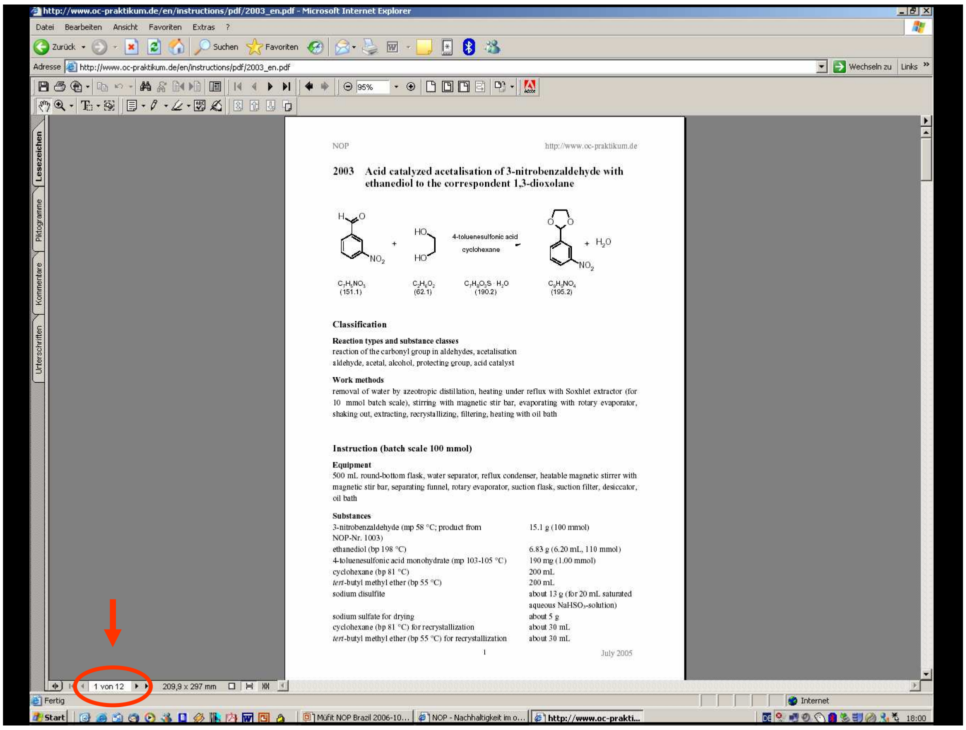
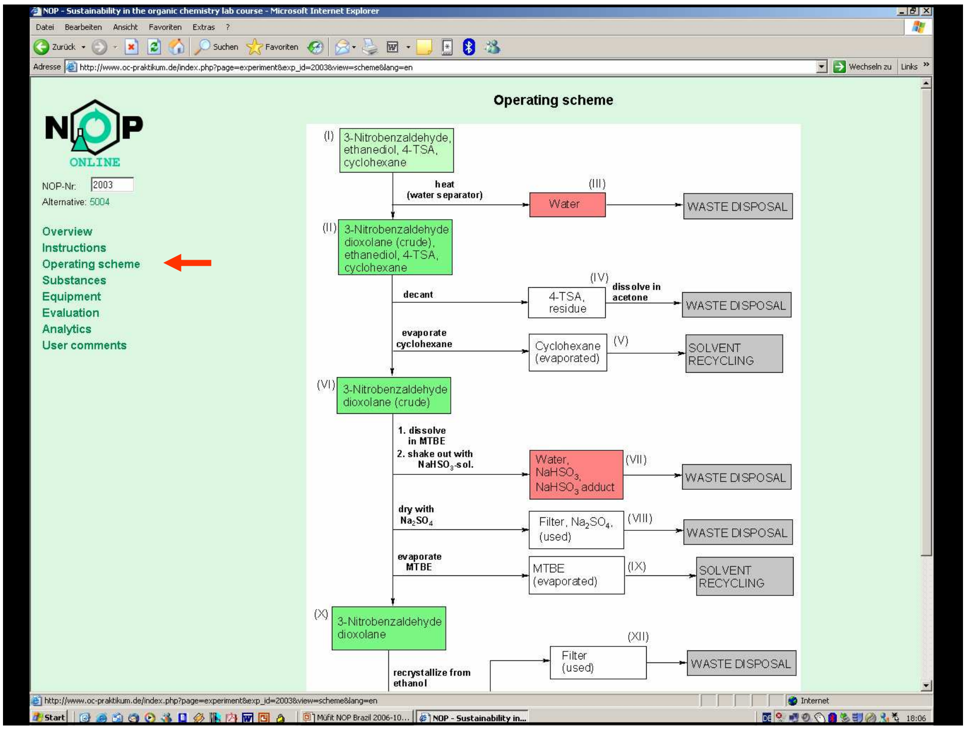
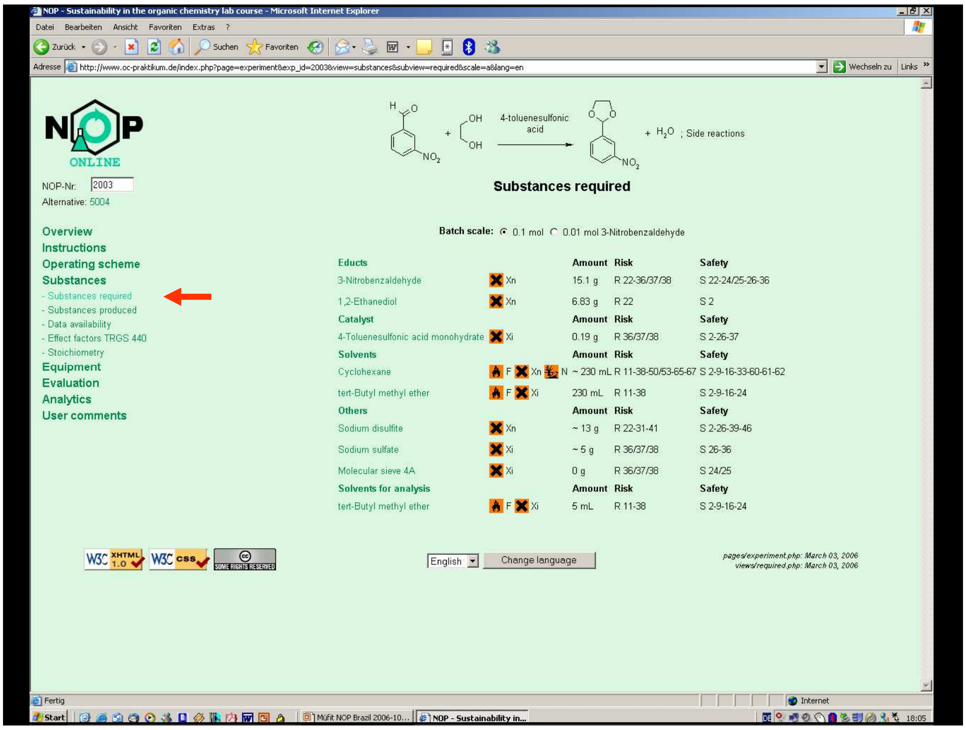
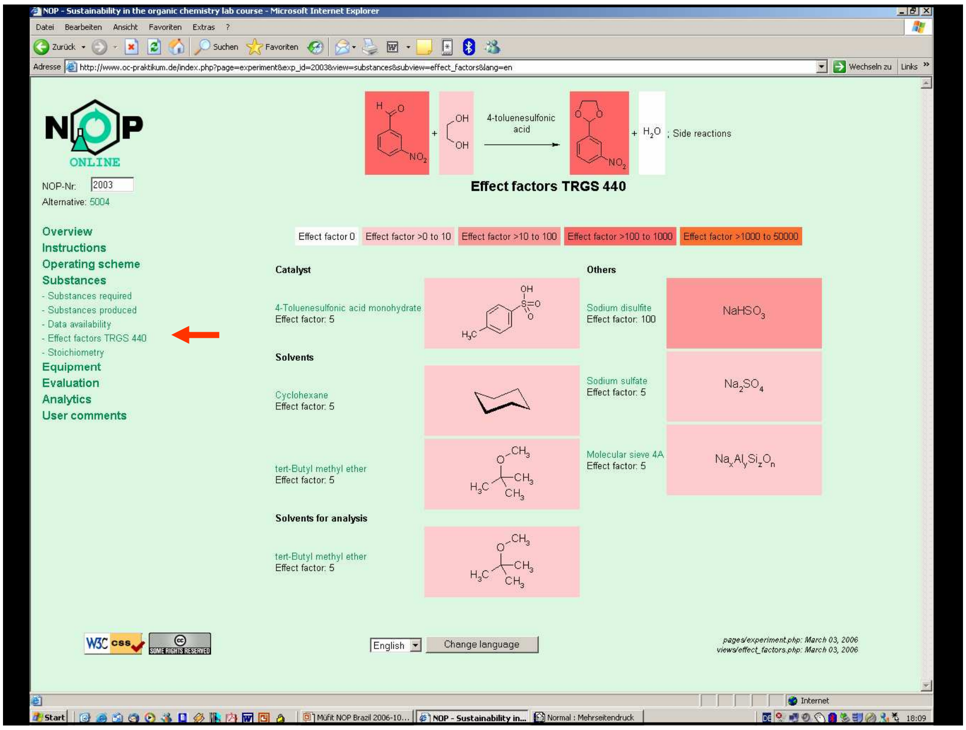
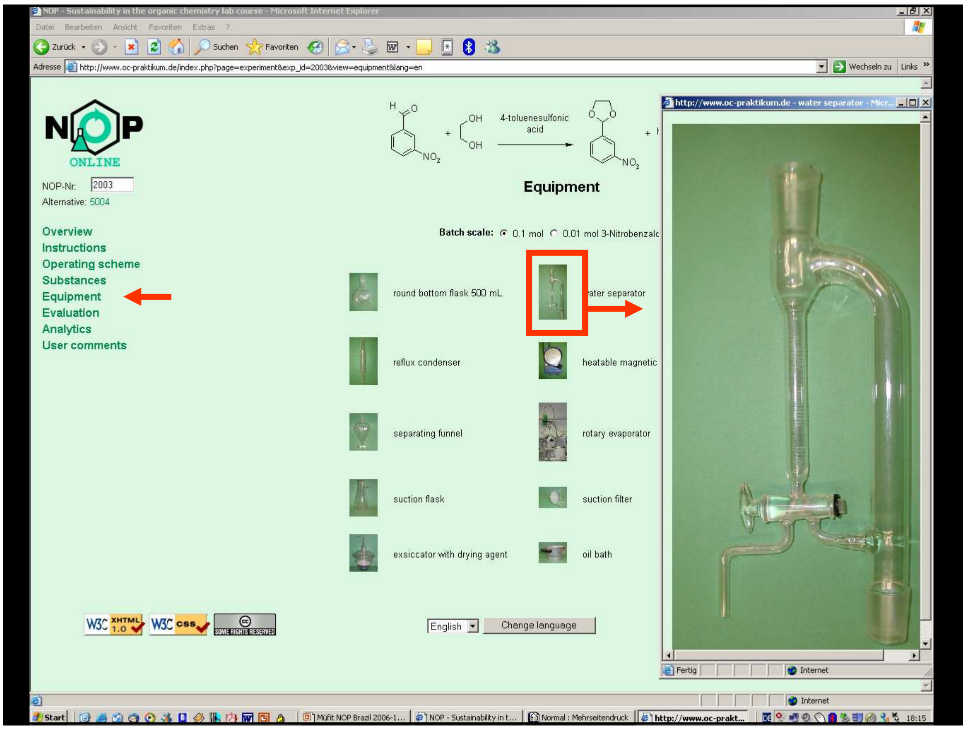
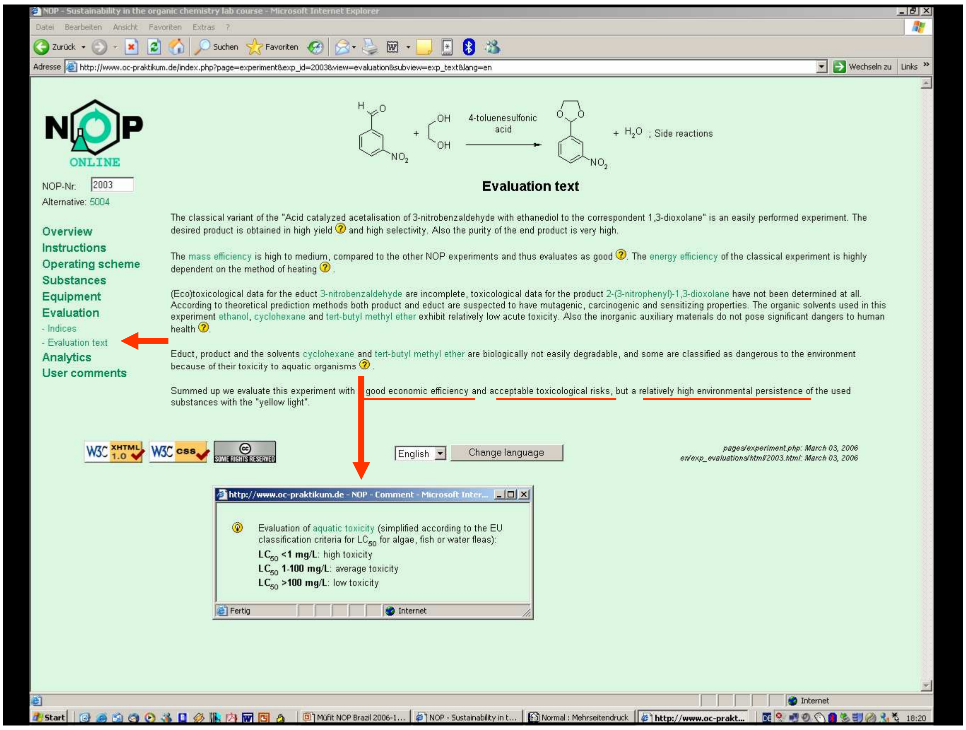

http://www.oc-praktikum.de/en/instructions/pdf/2003_en.pdf - Microsoft Internet Explorer
NOP
http://www.oc-praktikum.de
2003 Acid catalyzed acetalisation of 3-nitrobenzaldehyde with ethanediol to the correspondent 1,3-dioxolane
4-toluenesulfonic acid
cyclohexane
C7H5NO3 (151.1)
C2H6O2 (62.1)
C7H8O3S · H2O (190.2)
C9H9NO4 (195.2)
Classification
Reaction types and substance classes
reaction of the carbonyl group in aldehydes, acetalisation
aldehyde, acetal, alcohol, protecting group, acid catalyst
Work methods
removal of water by azeotropic distillation, heating under reflux with Soxhlet extractor (for 10 mmol batch scale), stirring with magnetic stir bar, evaporating with rotary evaporator, shaking out, extracting, recrystallizing, filtering, heating with oil bath
Instruction (batch scale 100 mmol)
Equipment
500 mL round-bottom flask, water separator, reflux condenser, heatable magnetic stirrer with magnetic stir bar, separating funnel, rotary evaporator, suction flask, suction filter, desiccator, oil bath
Substances
3-nitrobenzaldehyde (mp 58 °C; product from NOP-Nr. 1003) 15.1 g (100 mmol)
ethanediol (bp 198 °C) 6.83 g (6.20 mL, 110 mmol)
4-toluenesulfonic acid monohydrate (mp 103-105 °C) 190 mg (1.00 mmol)
cyclohexane (bp 81 °C) 200 mL
tert-butyl methyl ether (bp 55 °C) 200 mL
sodium disulfite about 13 g (for 20 mL saturated aqueous NaHSO3-solution)
sodium sulfate for drying about 5 g
cyclohexane (bp 81 °C) for recrystallization about 30 mL
tert-butyl methyl ether (bp 55 °C) for recrystallization about 30 mL
1
July 2005
1 von 12
209,9 x 297 mm


NOP - Sustainability in the organic chemistry lab course - Microsoft Internet Explorer
http://www.oc-praktikum.de/index.php?page=experiment&exp_id=2003&view=scheme&lang=en
Operating scheme
NOP ONLINE
NOP-Nr. 2003
Alternative: 5004
Overview
Instructions
Operating scheme
Substances
Equipment
Evaluation
Analytics
User comments
(I) 3-Nitrobenzaldehyde, ethanediol, 4-TSA, cyclohexane
heat (water separator)
(III) Water
WASTE DISPOSAL
(II) 3-Nitrobenzaldehyde dioxolane (crude), ethanediol, 4-TSA, cyclohexane
decant
(IV) 4-TSA, residue
dissolve in acetone
WASTE DISPOSAL
evaporate cyclohexane
Cyclohexane (evaporated)
(V)
SOLVENT RECYCLING
(VI) 3-Nitrobenzaldehyde dioxolane (crude)
1. dissolve in MTBE
2. shake out with NaHSO3-sol.
Water, NaHSO3, NaHSO3 adduct
(VII)
WASTE DISPOSAL
dry with Na2SO4
Filter, Na2SO4, (used)
(VIII)
WASTE DISPOSAL
evaporate MTBE
MTBE (evaporated)
(IX)
SOLVENT RECYCLING
(X) 3-Nitrobenzaldehyde dioxolane
recrystallize from ethanol
Filter (used)
(XII)
WASTE DISPOSAL


NOP - Sustainability in the organic chemistry lab course - Microsoft Internet Explorer
NOP ONLINE
NOP-Nr: 2003
Alternative: 5004
4-toluenesulfonic acid
+ H2O ; Side reactions
Substances required
Overview
Instructions
Operating scheme
Substances
- Substances required
- Substances produced
- Data availability
- Effect factors TRGS 440
- Stoichiometry
Equipment
Evaluation
Analytics
User comments
Batch scale: 0.1 mol 0.01 mol 3-Nitrobenzaldehyde
Educts Amount Risk Safety
3-Nitrobenzaldehyde Xn 15.1 g R 22-36/37/38 S 22-24/25-26-36
1,2-Ethanediol Xn 6.83 g R 22 S 2
Catalyst Amount Risk Safety
4-Toluenesulfonic acid monohydrate Xi 0.19 g R 36/37/38 S 2-26-37
Solvents Amount Risk Safety
Cyclohexane F Xn N ~ 230 mL R 11-38-50/53-65-67 S 2-9-16-33-60-61-62
tert-Butyl methyl ether F Xi 230 mL R 11-38 S 2-9-16-24
Others Amount Risk Safety
Sodium disulfite Xn ~ 13 g R 22-31-41 S 2-26-39-46
Sodium sulfate Xi ~ 5 g R 36/37/38 S 26-36
Molecular sieve 4A Xi 0 g R 36/37/38 S 24/25
Solvents for analysis Amount Risk Safety
tert-Butyl methyl ether F Xi 5 mL R 11-38 S 2-9-16-24
English Change language
pages/experiment.php: March 03, 2006
views/required.php: March 03, 2006

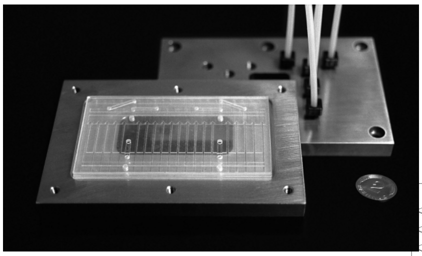

NOP - Sustainability in the organic chemistry lab course - Microsoft Internet Explorer
NOP ONLINE
NOP-Nr: 2003
Alternative: 5004
4-toluenesulfonic acid
+ H2O ; Side reactions
Effect factors TRGS 440
Overview
Instructions
Operating scheme
Substances
- Substances required
- Substances produced
- Data availability
- Effect factors TRGS 440
- Stoichiometry
Equipment
Evaluation
Analytics
User comments
Effect factor 0 Effect factor >0 to 10 Effect factor >10 to 100 Effect factor >100 to 1000 Effect factor >1000 to 50000
Catalyst
4-Toluenesulfonic acid monohydrate
Effect factor: 5
Solvents
Cyclohexane
Effect factor: 5
tert-Butyl methyl ether
Effect factor: 5
Solvents for analysis
tert-Butyl methyl ether
Effect factor: 5
Others
Sodium disulfite
Effect factor: 100
NaHSO3
Sodium sulfate
Effect factor: 5
Na2SO4
Molecular sieve 4A
Effect factor: 5
NaxAlySizOn
English Change language
pages/experiment.php: March 03, 2006
views/effect_factors.php: March 03, 2006

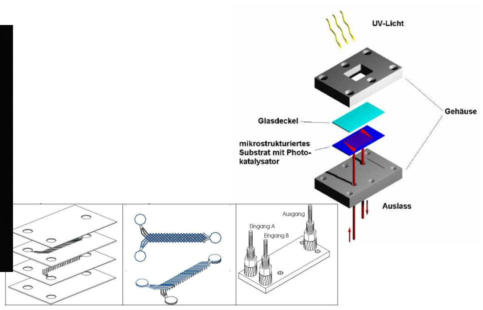

NOP ONLINE
NOP-Nr. 2003
Alternative: 5004
Overview
Instructions
Operating scheme
Substances
Equipment
Evaluation
Analytics
User comments
4-toluenesulfonic acid
Equipment
Batch scale: 0.1 mol 0.01 mol 3-Nitrobenzaldehyde
round bottom flask 500 mL
water separator
reflux condenser
heatable magnetic
separating funnel
rotary evaporator
suction flask
suction filter
exsiccator with drying agent
oil bath
English
Change language
http://www.oc-praktikum.de - water separator

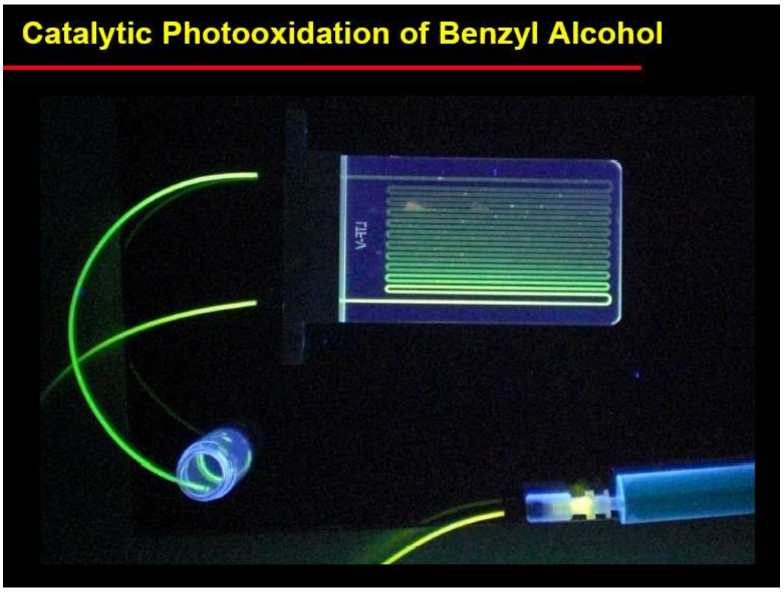

NOP ONLINE
NOP-Nr. 2003
Alternative: 5004
Overview
Instructions
Operating scheme
Substances
Equipment
Evaluation
- Indices
- Evaluation text
Analytics
User comments
4-toluenesulfonic acid
+ H2O ; Side reactions
Evaluation text
The classical variant of the "Acid catalyzed acetalisation of 3-nitrobenzaldehyde with ethanediol to the correspondent 1,3-dioxolane" is an easily performed experiment. The desired product is obtained in high yield and high selectivity. Also the purity of the end product is very high.
The mass efficiency is high to medium, compared to the other NOP experiments and thus evaluates as good. The energy efficiency of the classical experiment is highly dependent on the method of heating.
(Eco)toxicological data for the educt 3-nitrobenzaldehyde are incomplete, toxicological data for the product 2-(3-nitrophenyl)-1,3-dioxolane have not been determined at all. According to theoretical prediction methods both product and educt are suspected to have mutagenic, carcinogenic and sensitizing properties. The organic solvents used in this experiment ethanol, cyclohexane and tert-butyl methyl ether exhibit relatively low acute toxicity. Also the inorganic auxiliary materials do not pose significant dangers to human health.
Educt, product and the solvents cyclohexane and tert-butyl methyl ether are biologically not easily degradable, and some are classified as dangerous to the environment because of their toxicity to aquatic organisms.
Summed up we evaluate this experiment with good economic efficiency and acceptable toxicological risks, but a relatively high environmental persistence of the used substances with the "yellow light".
English
Change language
pages/experiment.php: March 03, 2006
en/exp_evaluations/html/2003.html: March 03, 2006
http://www.oc-praktikum.de - NOP - Comment - Microsoft Inter...
Evaluation of aquatic toxicity (simplified according to the EU classification criteria for LC50 for algae, fish or water fleas):
LC50 <1 mg/L: high toxicity
LC50 1-100 mg/L: average toxicity
LC50 >100 mg/L: low toxicity

The next steps:

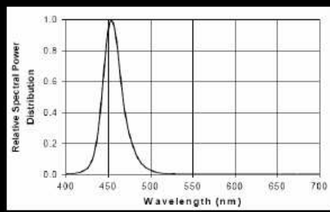
New Contents: micro process organic synthesis







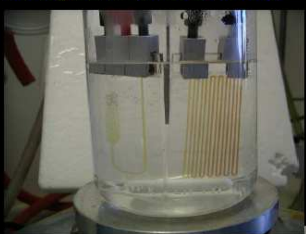
Catalytic Photooxidation of Benzyl Alcohol

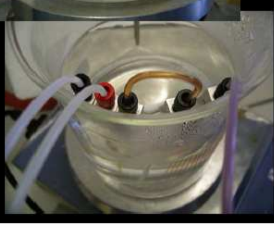


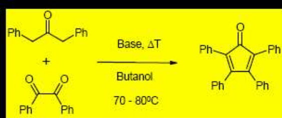
Synthesis of Tetracyclone

DBU
Deutsche Bundesstiftung Umwelt

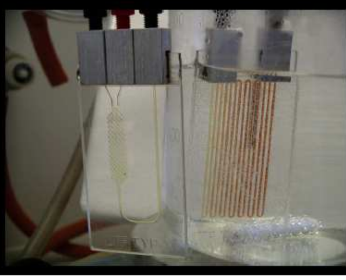
Mixing and reaction at +80ºC:

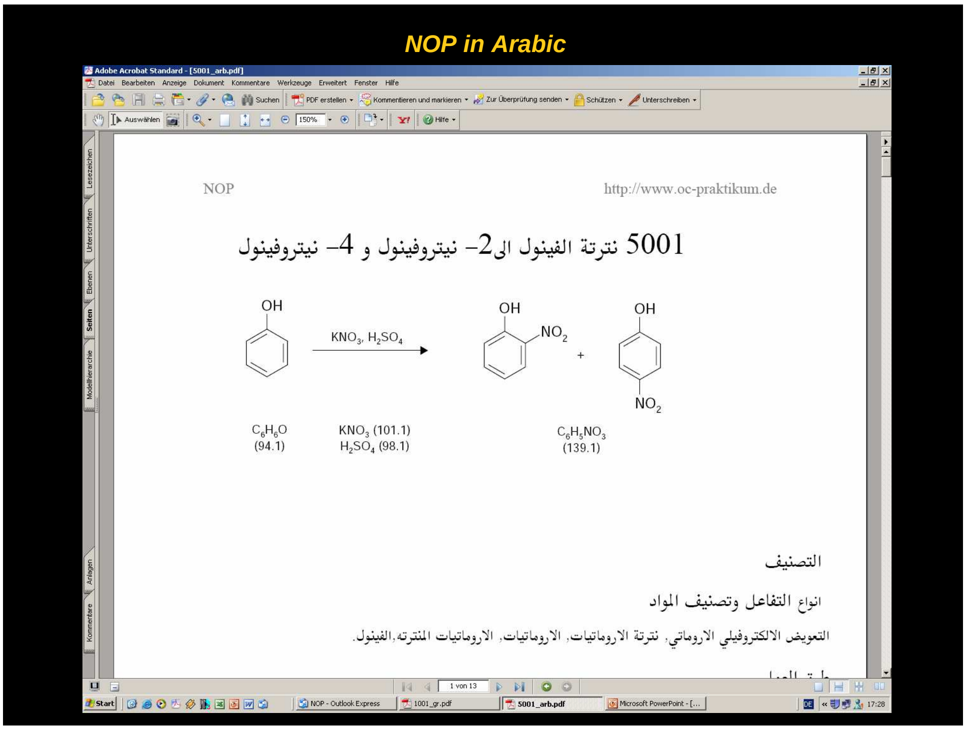


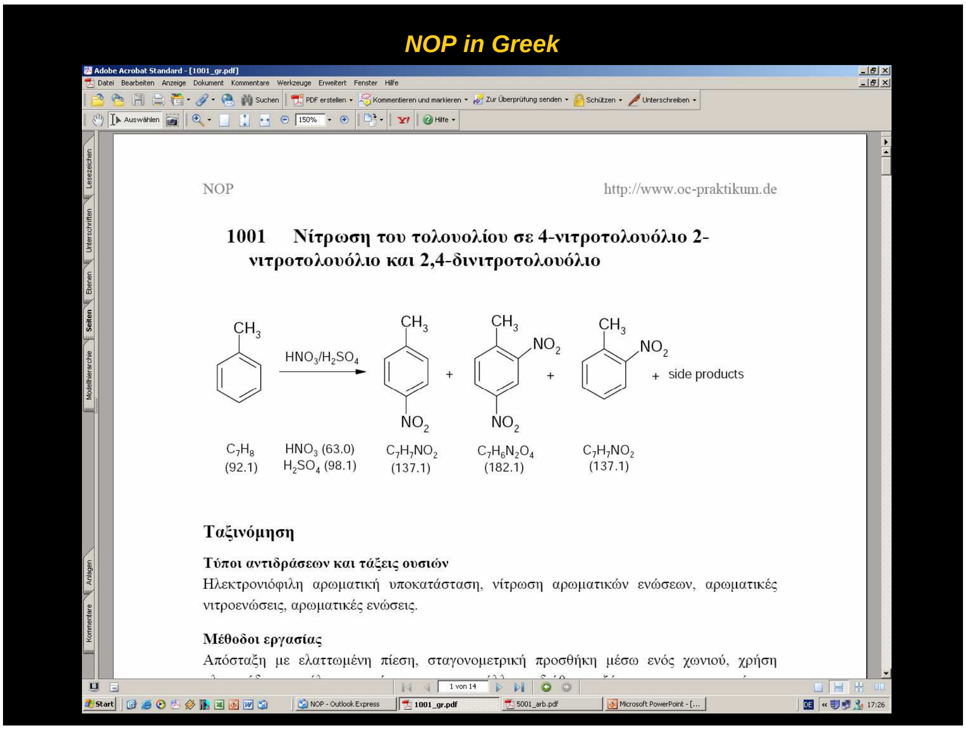




Mixing and reaction at + 90ºC:




NOP in Arabic
NOP
http://www.oc-praktikum.de
5001 نترتة الفينول الى2– نيتروفينول و 4– نيتروفينول
OH
KNO3, H2SO4
OH
NO2
+
OH
NO2
C6H6O
(94.1)
KNO3 (101.1)
H2SO4 (98.1)
C6H5NO3
(139.1)
التصنيف
انواع التفاعل وتصنيف المواد
التعويض الالكتروفيلي الاروماتي, نترتة الاروماتيات, الاروماتيات, الاروماتيات المنترتة,الفينول.


NOP in Greek
NOP
http://www.oc-praktikum.de
1001 Νίτρωση του τολουολίου σε 4-νιτροτολουόλιο 2-νιτροτολουόλιο και 2,4-δινιτροτολουόλιο
CH3
HNO3/H2SO4
CH3
NO2
+
CH3
NO2
NO2
+
CH3
NO2
+ side products
C7H8
(92.1)
HNO3 (63.0)
H2SO4 (98.1)
C7H7NO2
(137.1)
C7H6N2O4
(182.1)
C7H7NO2
(137.1)
Ταξινόμηση
Τύποι αντιδράσεων και τάξεις ουσιών
Ηλεκτρονιόφιλη αρωματική υποκατάσταση, νίτρωση αρωματικών ενώσεων, αρωματικές νιτροενώσεις, αρωματικές ενώσεις.
Μέθοδοι εργασίας
Απόσταξη με ελαττωμένη πίεση, σταγονομετρική προσθήκη μέσω ενός χωνιού, χρήση

Participants in this project

Optimization of experimental conditions:
Prof. Lenoir/Prof. Parlar, Munich University of Technology
Prof. Metzger, University of Oldenburg
Prof. Hopf, Braunschweig University of Technology
Prof. König, University of Regensburg

Analyses of toxic by-products / collection of safety data:
Prof. Bahadir, Braunschweig University of Technology

Assessment of the reactions:
Prof. Jastorff, University of Bremen
Prof. Kreisel, University of Jena

Alternative reaction control:
Prof. Ondruschka, University of Jena

Italian Edition:
Prof. Pierro Tundo, University of Venedig; INCA

Project granting

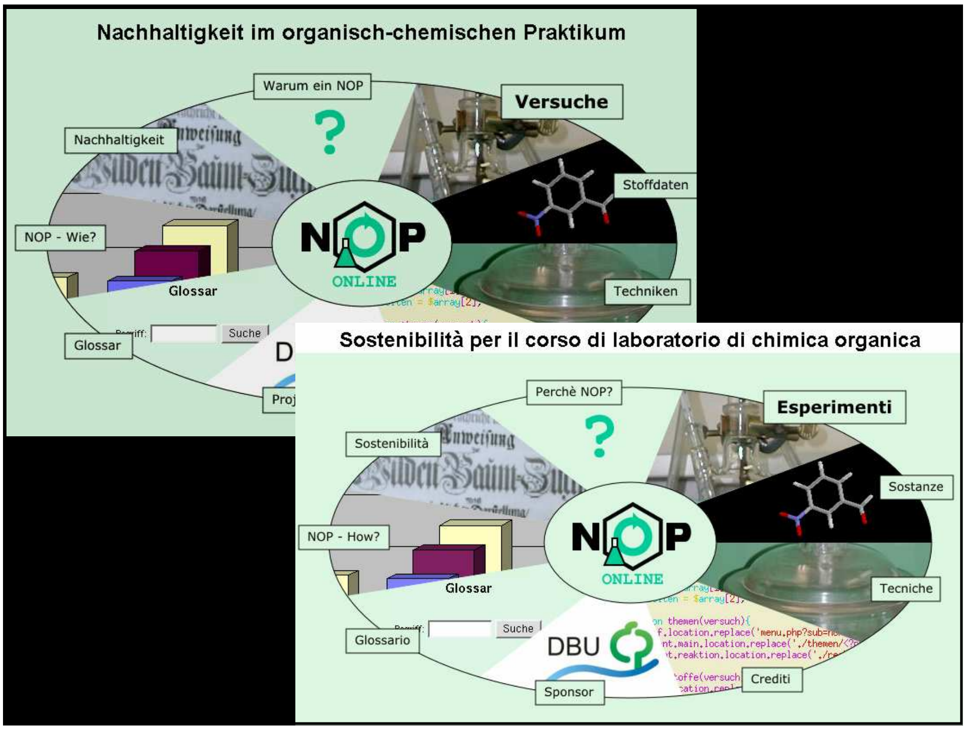
Development of the database for

NOP – *Organic Chemistry Lab Course*

was granted by:

Deutsche Bundesstiftung Umwelt
(German Environmental Foundation)

UMWELT STIFTUNG



Factor of Env. Acceptability after Sheldon

$$E = \frac{\text{kg Waste + By-products}}{\text{kg Target Product}}$$

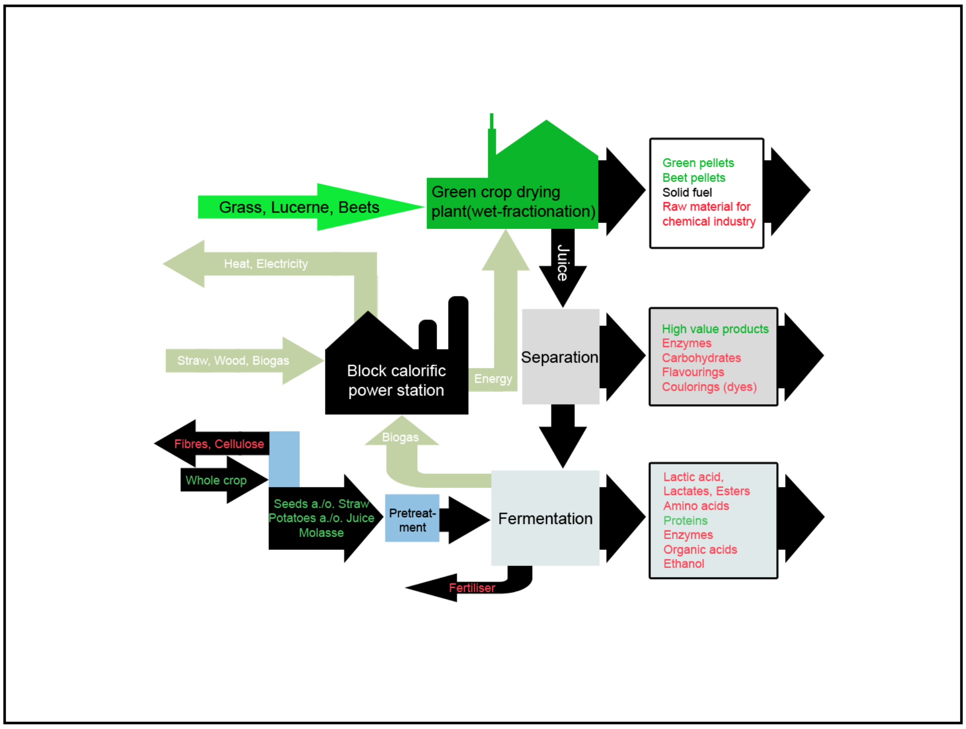
E = Environmental acceptability

	Production Volume [Tons per Year]	E (Sheldon) -Faktor
Petroleum Refining	10^6 - 10^8	0.1
Bulk Chemicals	10^4 - 10^6	< 1.5
Fine Chemicals	10^2 - 10^4	5 - 50
Pharmaceuticals	10^1 - 10^4	25 - >100

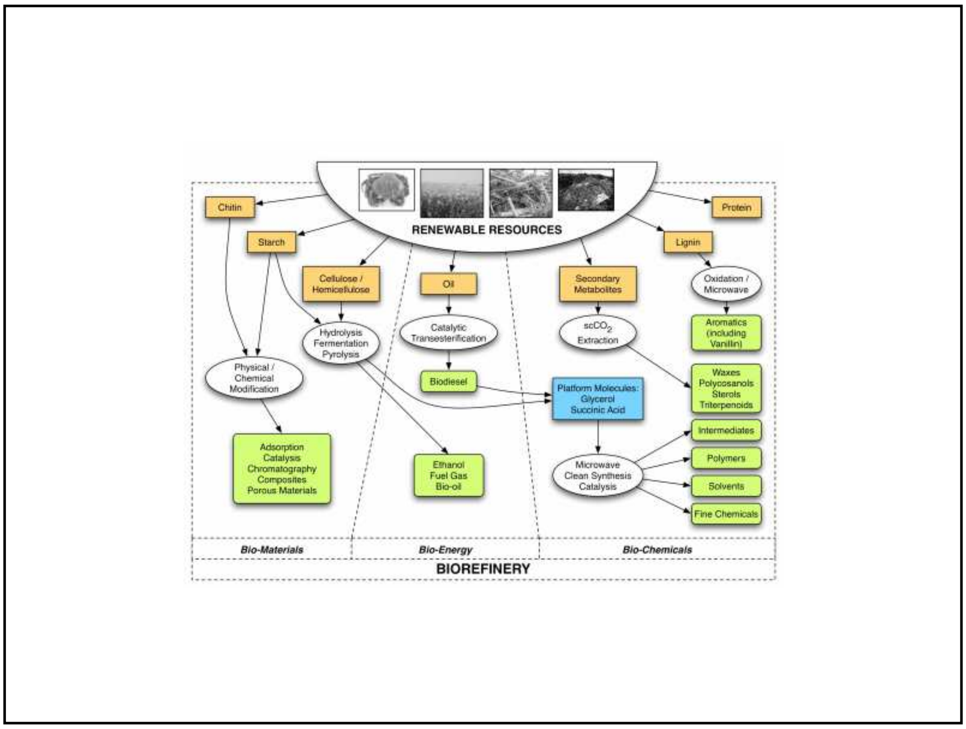
↑ Better Optimized

↓ higher Complexity, more Steps

Sheldon, *Chem. Tech.* **1994**, *24*, 38.



Grass, Lucerne, Beets
Green crop drying plant(wet-fractionation)
Green pellets
Beet pellets
Solid fuel
Raw material for chemical industry
Juice
Heat, Electricity
Straw, Wood, Biogas
Block calorific power station
Energy
Separation
High value products
Enzymes
Carbohydrates
Flavourings
Coulorings (dyes)
Fibres, Cellulose
Whole crop
Biogas
Seeds a./o. Straw
Potatoes a./o. Juice
Molasse
Pretreat-ment
Fermentation
Lactic acid,
Lactates, Esters
Amino acids
Proteins
Enzymes
Organic acids
Ethanol
Fertiliser



RENEWABLE RESOURCES
Chitin
Protein
Starch
Lignin
Cellulose / Hemicellulose
Oil
Secondary Metabolites
Oxidation / Microwave
Hydrolysis Fermentation Pyrolysis
Catalytic Transesterification
scCO2 Extraction
Aromatics (including Vanillin)
Physical / Chemical Modification
Biodiesel
Platform Molecules: Glycerol Succinic Acid
Waxes Polycosanols Sterols Triterpenoids
Intermediates
Adsorption Catalysis Chromatography Composites Porous Materials
Ethanol Fuel Gas Bio-oil
Microwave Clean Synthesis Catalysis
Polymers
Solvents
Fine Chemicals
Bio-Materials
Bio-Energy
Bio-Chemicals
BIOREFINERY

Life-cycle analysis of CH_3-$(CH_2)_{10-16}$-CH_2-$OSO_3^-Na^+$

⟶ 70% less use of fossil resources

⟶ 50% less emission to the atmosphere

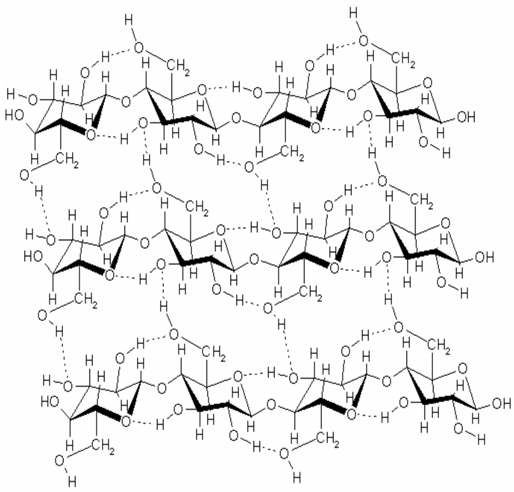
⟶ 15% less waste

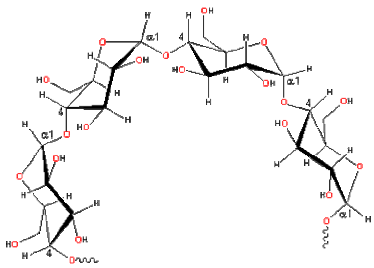
⟶ 50% more emissions to water

Improvement in natural oil composition by plant breeding (“tailor-made fatty acids”)

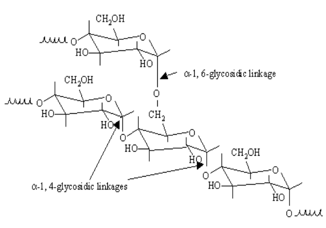
Soybean:

Method of changing composition	Fatty acid				
	16:0	18:0	18.1	18:2	18:3
Natural composition	11	4	23	54	8
mutagenesis	10.5	4.6	23.2	59.6	2.0
mutagenesis	3.7	3.7	24.1	58.9	8.9
mutagenesis	17.3	2.9	16.8	54.5	8.3
mutagenesis	8.4	28.1	19.8	35.5	6.6
gene technology	6.6	3.8	84.9	0.6	1.9





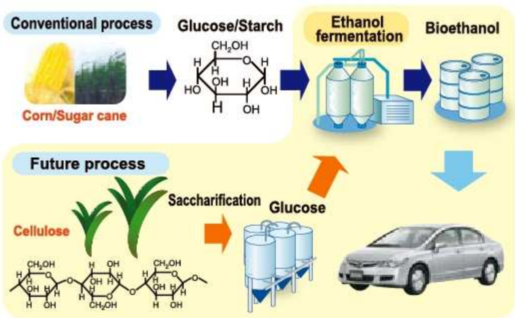
Starch: Amylose

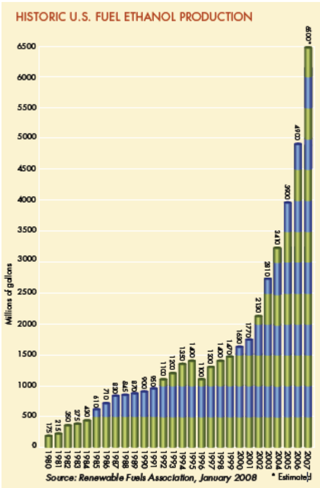


Starch: Amylopectin

Concentration (%) of starch in different foods

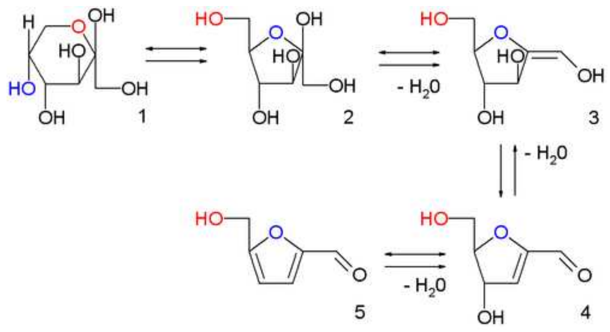
	maize (corn)	potato	wheat	rice
moisture	16	75	11	14
starch	62	19	60	77
proteins	8	2	13	7
minerals (ash)	1.2	1.2	1.7	0.5



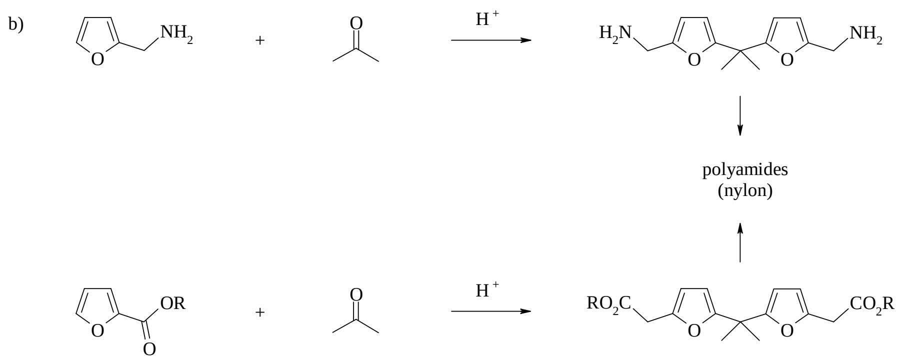


Composition (%) of various lignocellulose-based materials

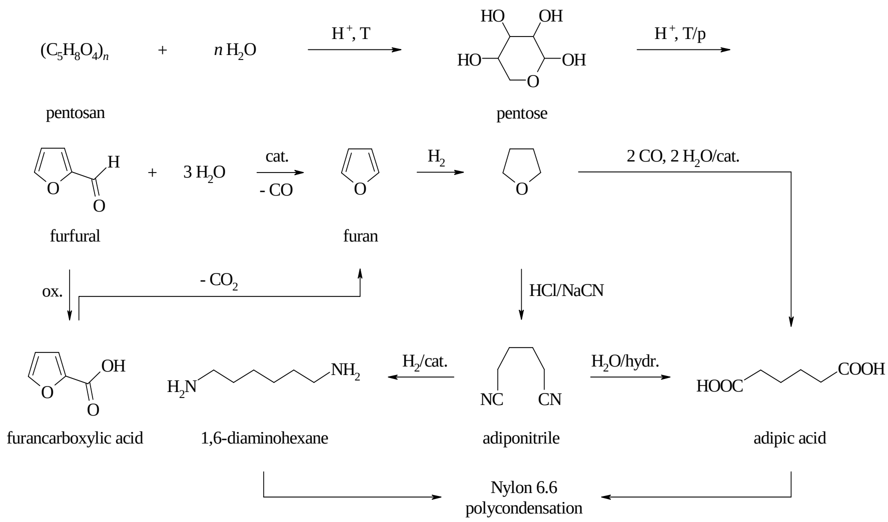
.	cellulose	hemicellulose	lignin .
hard wood	30-45	20-30	20-25
cereal straw	38-40	20-30	6-20



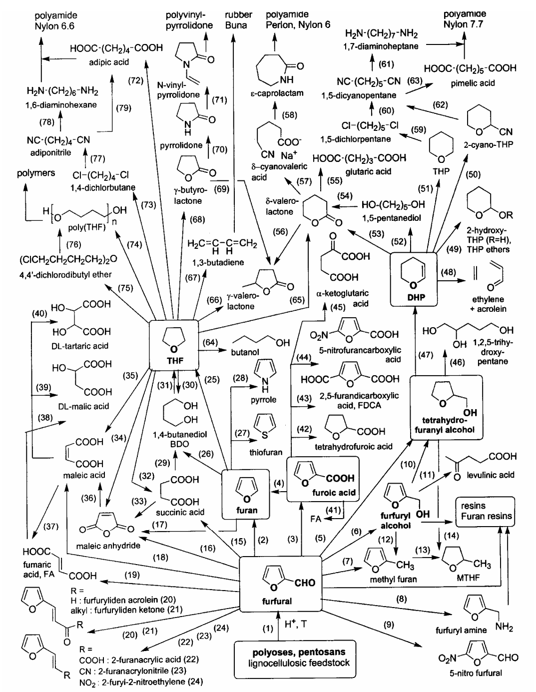
HO
OH
H
HO
OH
1
HO
OH
HO
OH
OH
2
- H2O
HO
HO
OH
OH
3
- H2O
HO
5
- H2O
HO
OH
4



b)
NH2
O
+
O
H+
H2N
O
O
NH2
polyamides
(nylon)
OR
O
O
+
O
H+
RO2C
O
O
CO2R



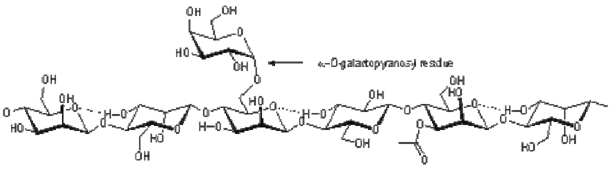
(C5H8O4)n + n H2O
H+, T
HO OH
HO OH
O
H+, T/p
pentosan
pentose
H
O
O
+ 3 H2O
cat.
- CO
O
H2
O
2 CO, 2 H2O/cat.
furfural
furan
ox.
- CO2
HCl/NaCN
OH
O
O
H2N
NH2
H2/cat.
NC CN
H2O/hydr.
HOOC
COOH
furancarboxylic acid
1,6-diaminohexane
adiponitrile
adipic acid
Nylon 6.6
polycondensation

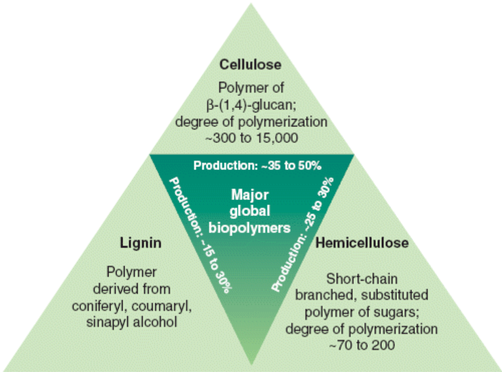


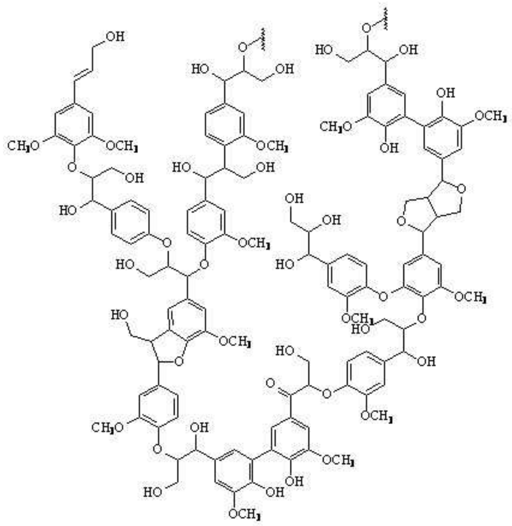
polyamide
Nylon 6.6
HOOC-(CH2)4-COOH
adipic acid
H2N-(CH2)6-NH2
1,6-diaminohexane
NC-(CH2)4-CN
adiponitrile
Cl-(CH2)4-Cl
1,4-dichlorbutane
polymers
poly(THF)
(ClCH2CH2CH2CH2)2O
4,4'-dichlorodibutyl ether
polyvinyl-
pyrrolidone
N-vinyl-
pyrrolidone
pyrrolidone
γ-butyro-
lactone
rubber
Buna
1,3-butadiene
polyamide
Perlon, Nylon 6
ε-caprolactam
δ-cyanovaleric
acid
δ-valero-
lactone
γ-valero-
lactone
H2N-(CH2)7-NH2
1,7-diaminoheptane
polyamide
Nylon 7.7
NC-(CH2)5-CN
1,5-dicyanopentane
HOOC-(CH2)5-COOH
pimelic acid
Cl-(CH2)5-Cl
1,5-dichlorpentane
2-cyano-THP
HOOC-(CH2)3-COOH
glutaric acid
THP
HO-(CH2)5-OH
1,5-pentanediol
2-hydroxy-
THP (R=H),
THP ethers
α-ketoglutaric
acid
DHP
ethylene
+ acrolein
DL-tartaric acid
DL-malic acid
THF
butanol
5-nitrofurancarboxylic
acid
1,2,5-trihy-
droxy-
pentane
pyrrole
2,5-furandicarboxylic
acid, FDCA
thiofuran
tetrahydrofuroic acid
tetrahydro-
furanyl alcohol
1,4-butanediol
BDO
maleic acid
succinic acid
furan
furoic acid
levulinic acid
maleic anhydride
furfuryl
alcohol
resins
Furan resins
fumaric
acid, FA
methyl furan
MTHF
furfural
R =
H : furfuryliden acrolein (20)
alkyl : furfuryliden ketone (21)
R =
COOH : 2-furanacrylic acid (22)
CN : 2-furanacrylonitrile (23)
NO2 : 2-furyl-2-nitroethylene (24)
polyoses, pentosans
lignocellulosic feedstock
furfuryl amine
5-nitro furfural

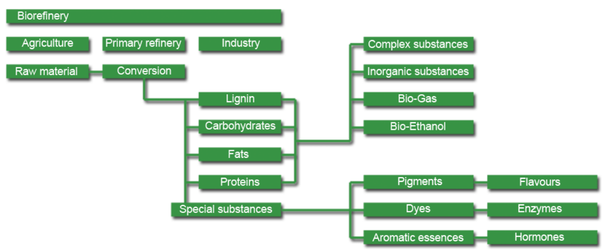
Structure of hemicellulose (pseudocellulose, polyose):

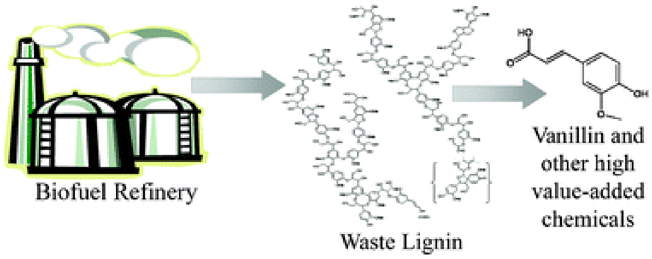
Typical building blocks: glucose, arabinose, mannose, galactose etc.



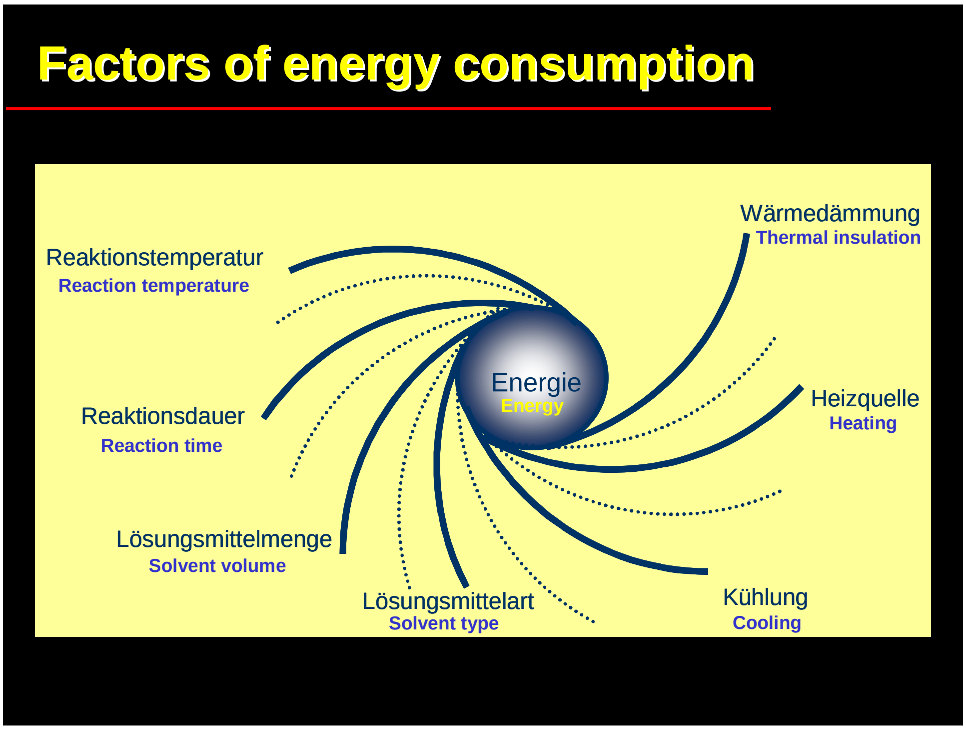


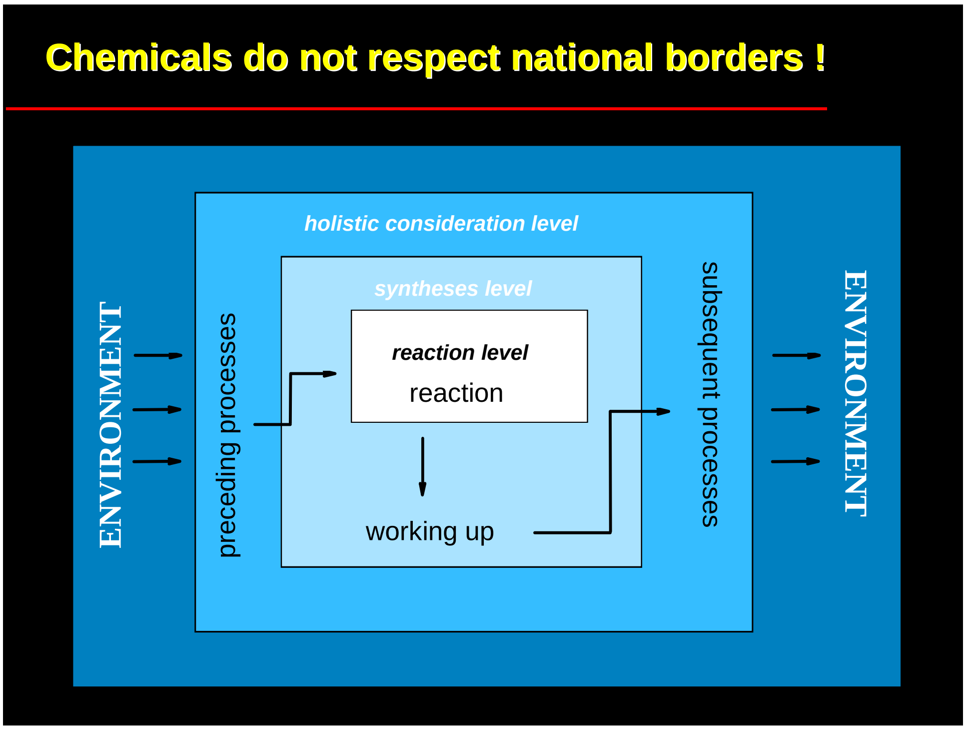


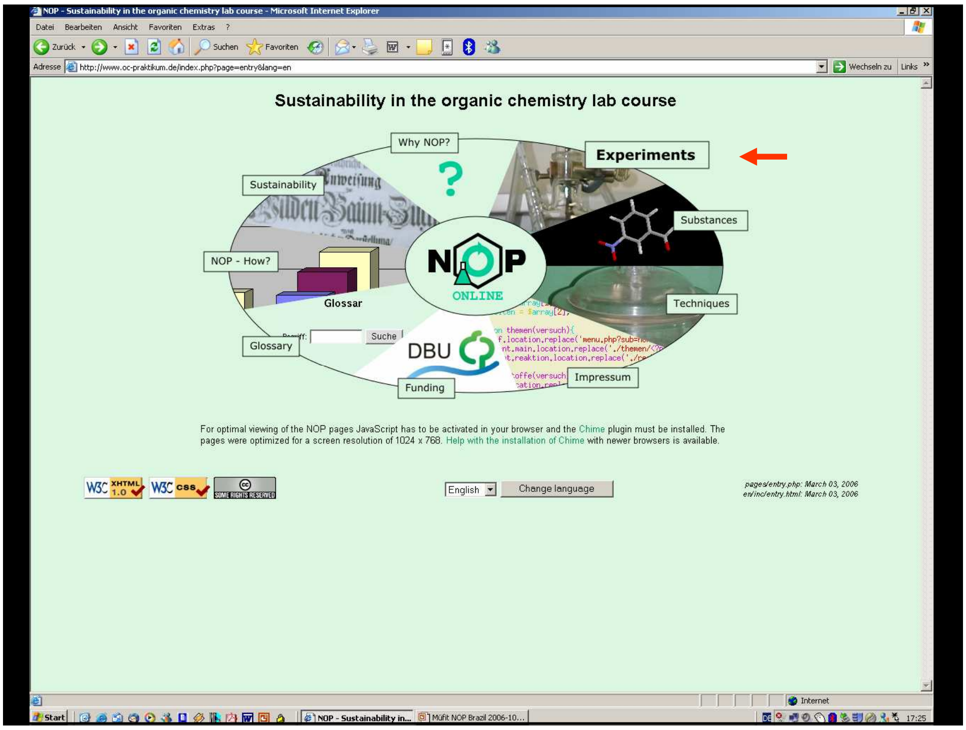

Biorefinery
Agriculture
Primary refinery
Industry
Raw material
Conversion
Lignin
Carbohydrates
Fats
Proteins
Special substances
Complex substances
Inorganic substances
Bio-Gas
Bio-Ethanol
Pigments
Flavours
Dyes
Enzymes
Aromatic essences
Hormones


Biofuel Refinery
Waste Lignin
Vanillin and
other high
value-added
chemicals


ADVANCES IN BIOCHEMICAL
ENGINEERING/BIOTECHNOLOGY
105
Series Editor T. Scheper
Volume Editors R. Ulber · D. Sell
White
Biotechnology
Springer


Factors of energy consumption
Reaktionstemperatur
Reaction temperature
Wärmedämmung
Thermal insulation
Energie
Energy
Reaktionsdauer
Reaction time
Heizquelle
Heating
Lösungsmittelmenge
Solvent volume
Lösungsmittelart
Solvent type
Kühlung
Cooling


Chemicals do not respect national borders !
holistic consideration level
syntheses level
reaction level
reaction
working up
preceding processes
subsequent processes
ENVIRONMENT
ENVIRONMENT



Prof. Dr. H. Hopf
Institute of Organic Chemistry
Technical University Braunschweig
Hagenring 30
D-38106 Braunschweig

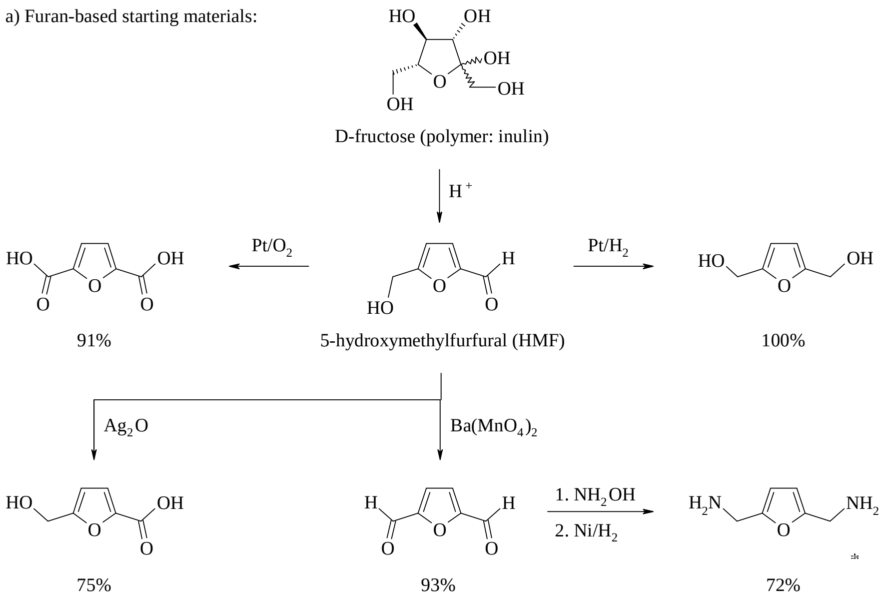
Germany

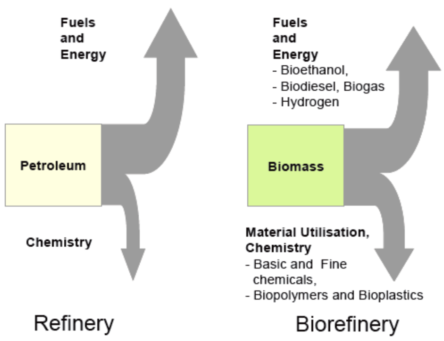
The use of renewable organic compounds in industrial organic chemistry – en route to a sustainable chemistry

h.hopf@tu-bs.de

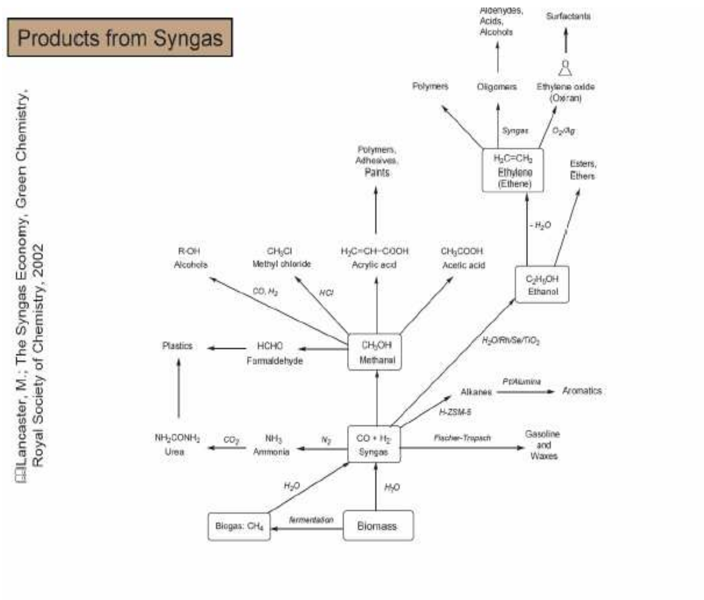
Some recent applications of carbohydrates as substrats in sustainable chemistry

a) Furan-based starting materials:



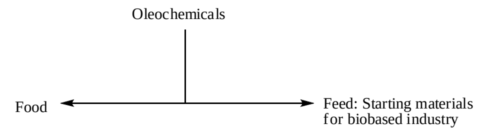


Biobased industrial products can only compete with petro-chemically based products if the raw materials are optimally exploited and a variety of value-creating chains are developed and established.
→ development of substance-converting basic product systems and multi product systems, especially biorefineries.

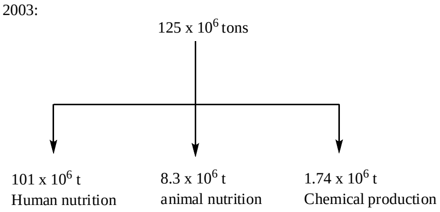


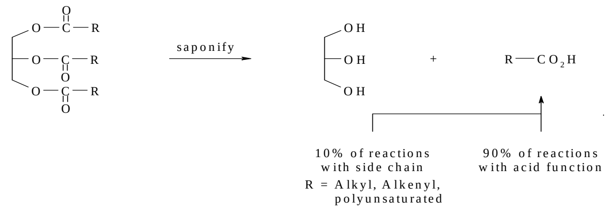
Starting materials	Products: Wanted	Products: unwanted
Plant	pharmaceuticals	plant material, inactive products
Animal	food	bones
Mineral	(precious) metal	top layer, ashes
Petroleum	gasoline	tar, asphalt
Coal	coke, gas	coal tar

Industrial applications of Oleochemicals

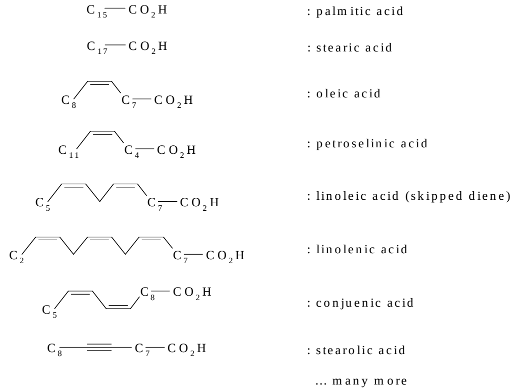


Production in 2003:





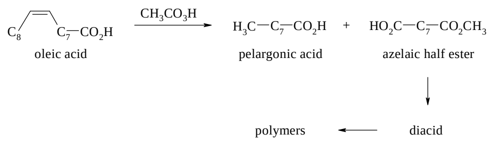
Typical saturated and unsaturated fatty acids:



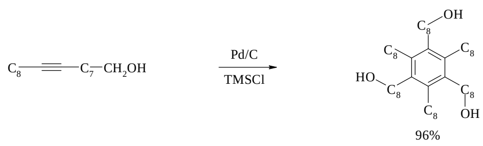
... many more

Reaction of unsaturated fatty acids

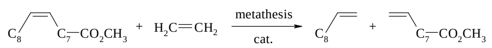
1) Oxidative cleavage:



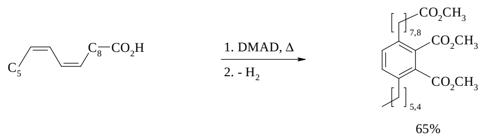
2) Catalytic trimerization:



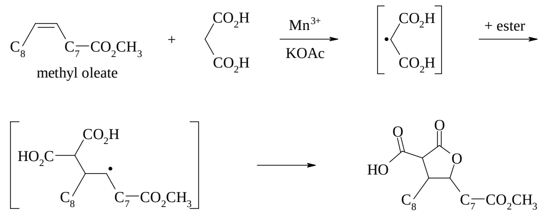
3) Olefin metathesis:



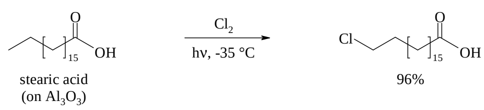
4) Diels-Alder additions:

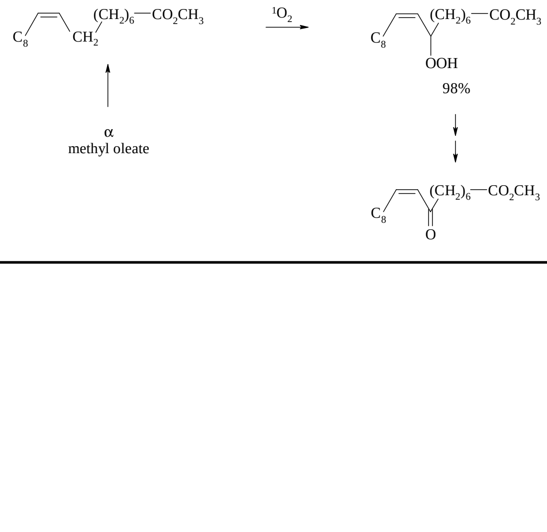


5) Radical additions:



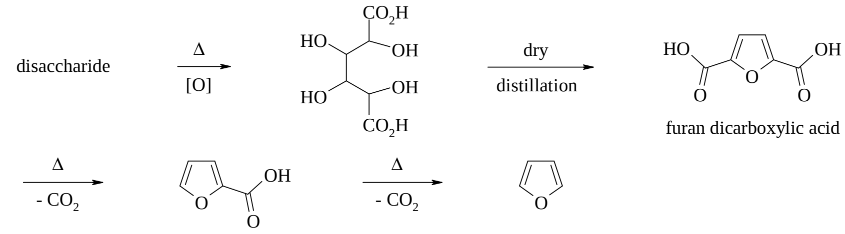
6) Functionalization of saturated chain:



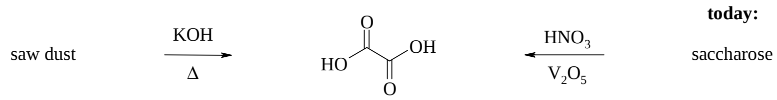


Classical uses of lignocellulose chemistry

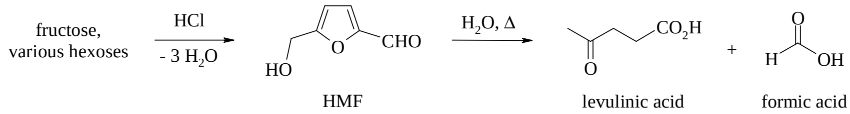
1) Dry distillation of disaccharides:



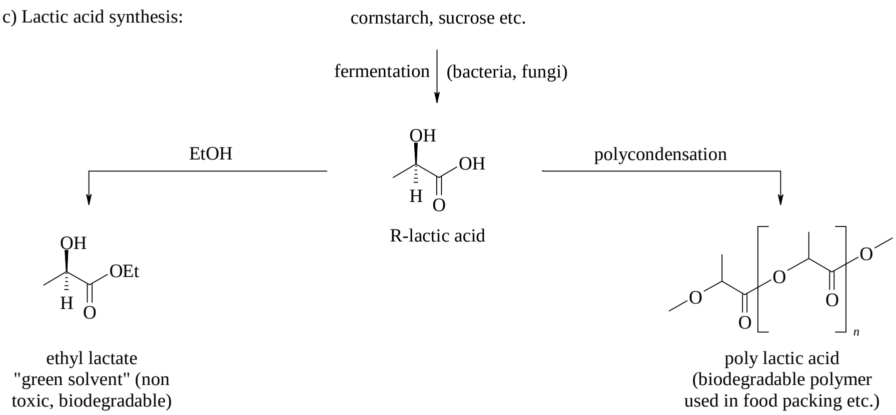
2) Oxalic acid production (Gay Lussac):



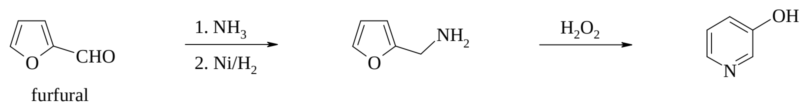
3) Levulinic acid (1840):



c) Lactic acid synthesis:



d) Pyridines from furfural:



Carbohydrates [$C_n(H_2O)_n$]

Food

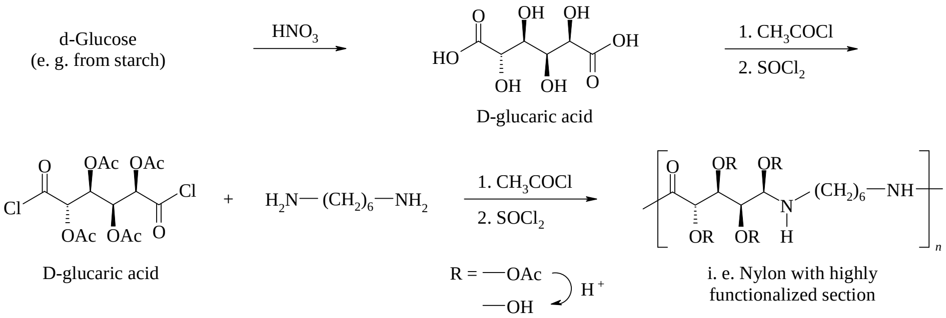
Industries:
Textiles (cotton),
Paper (cellulose),
Coatings (cellulose & starch derivatives).

Main advantages:

→ Available in large amounts (sucrose: 1.4 x 10^8 t/a)

→ Inexpensive (sucrose: 0.20 €/Kg)

e) New polyamide polymers:



Classical uses of lignocellulose chemistry

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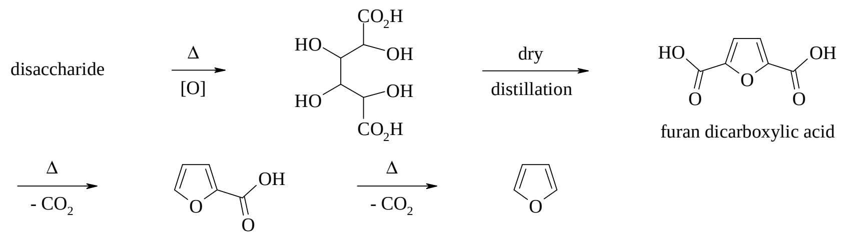

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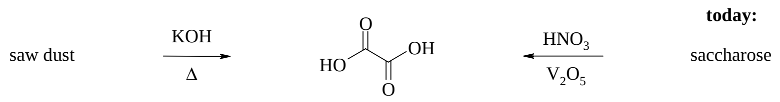

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