UNIVERSITEIT GENT

FACULTY OF ENGINEERING AND ARCHITECTURE

Opportunities for Automation in the Microkinetic Assessment of Complex Reactions: from Conventional to Renewable Feeds

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http://www.lct.UGent.be

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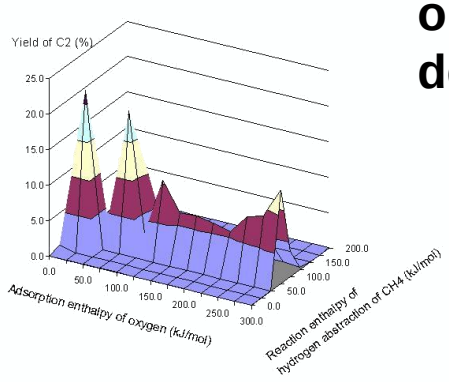
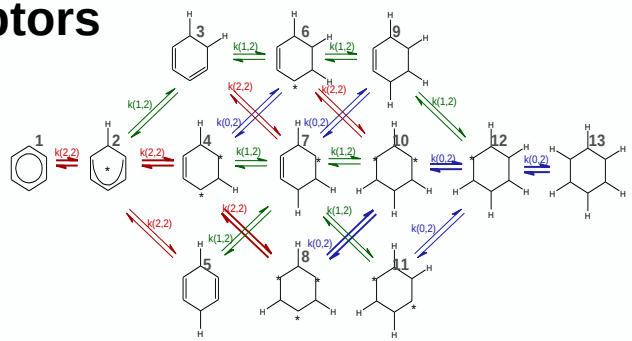
ERIC

erc

information driven catalyst & reactor design





J.W. Thybaut et al., Topics Catal. 52 (2009) 1251-1260

Single-Event MicroKinetics (SEMK)

- thermal cracking

  Sabbe et al. AIChE J. 57 (2011) 482-496

- acid catalysis
  - catalytic cracking
  - methanol to olefins

  Quintana-Solorzano et al. Chem. Eng. Sci. 62 (2007) 5033-5038

  Kumar et al. Catal. Today 215 (2013) 224-232

  Kumar et al. Ind. Eng. Chem. Res. 52 (2013) 1491-1507

- metal catalysis
  - Fischer Tropsch synthesis
  - hydrogenation

  Lozano-Blanco et al. Ind. Eng. Chem. Res. 47 (2008) 5879-5891

  J. Van Belleghem et al. Appl. Catal. A Gen. 524 (2016) 149-162

  Bera et al. ACS Catalysis 2 (2012) 1305-1318

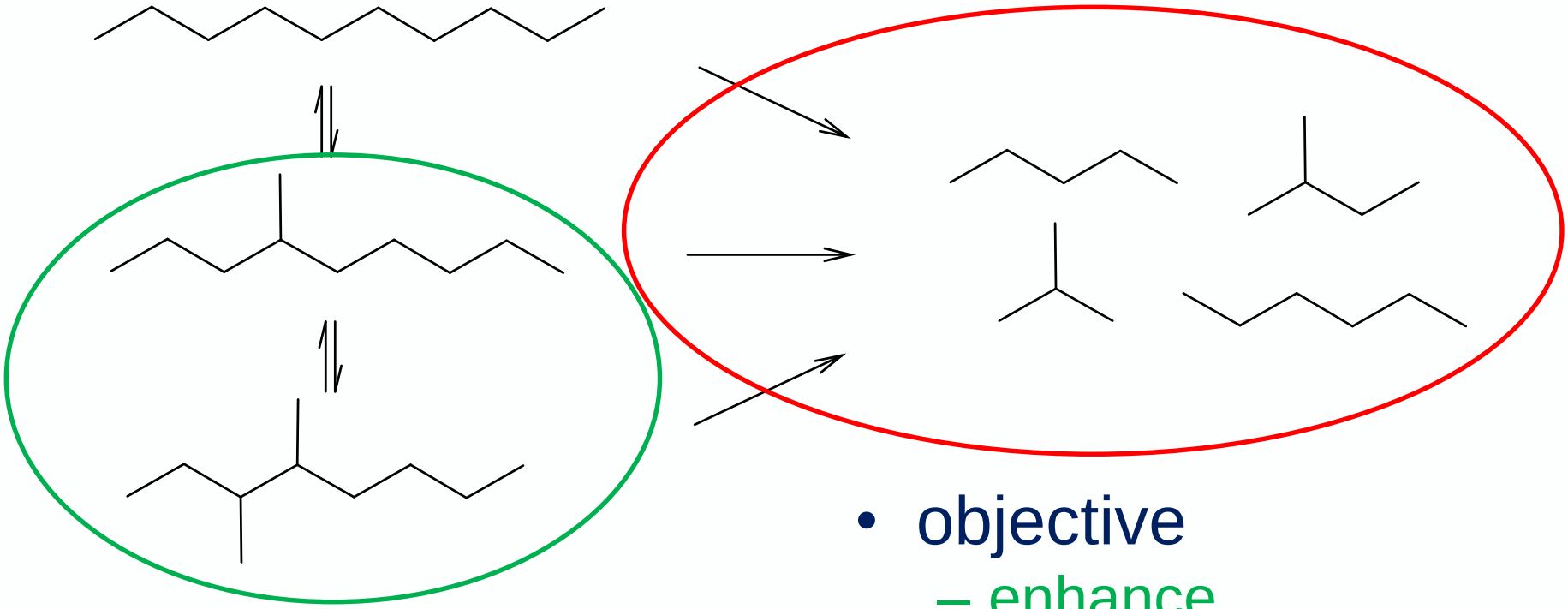
- bifunctional catalysis
  - hydrocracking
  - catalytic reforming
  - ethene oligomerization

  Thybaut et al. J. Catal. 202 (2001) 324-339

  Cochegrue et al. Oil Gas Sci. Technol. 66 (2011) 367-397

  Toch et al. Appl. Catal. A Gen 489 (2015) 292-304

lube oil production

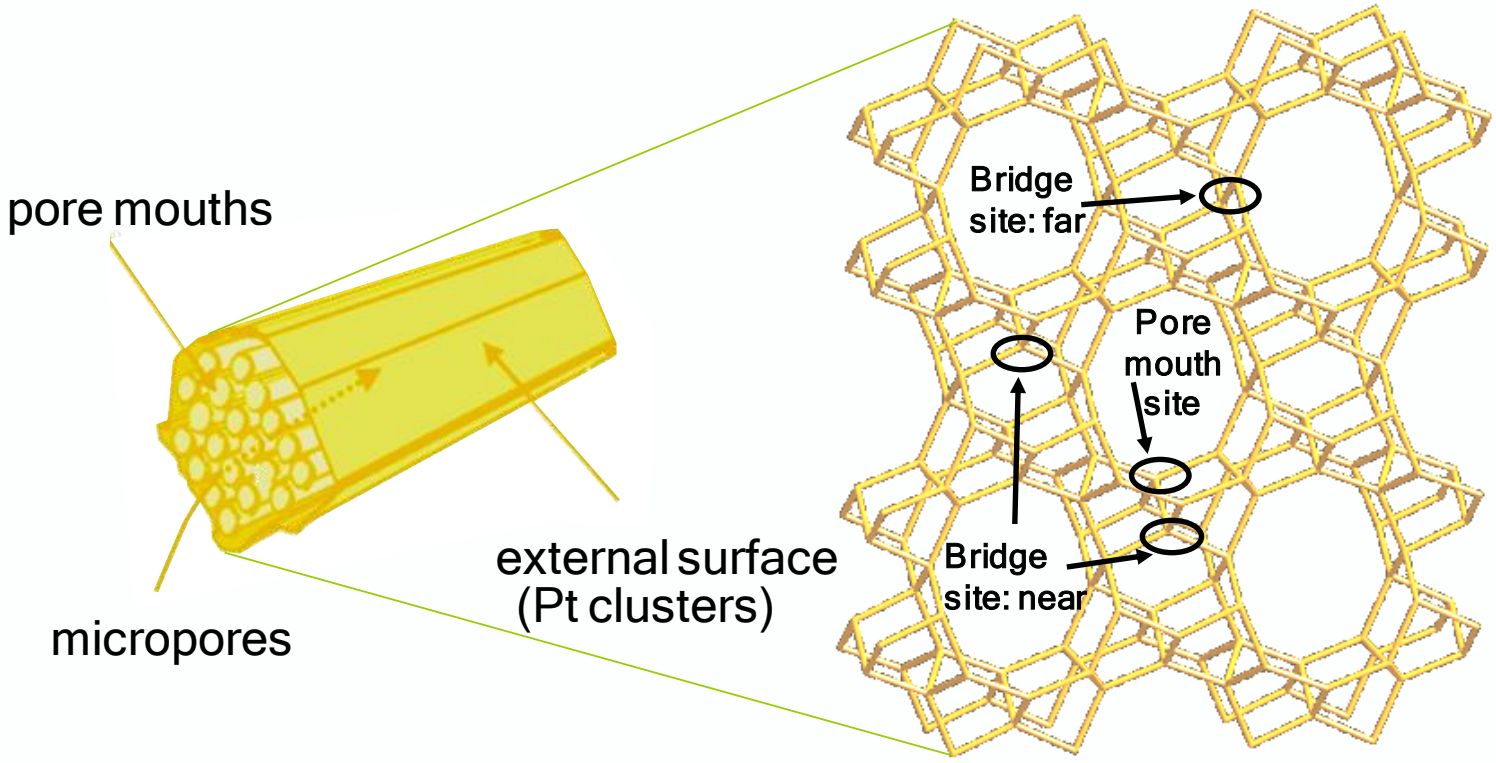


- objective
  - enhance isomerization
  - avoid product losses via cracking

- pour point reduction
- slight decrease in viscosity index

J.A. Martens et al. Angew. Chem. Intl. Ed. 34 (1995) 2528
W. Souverijns et al. J. Catal. 174 (1998) 177

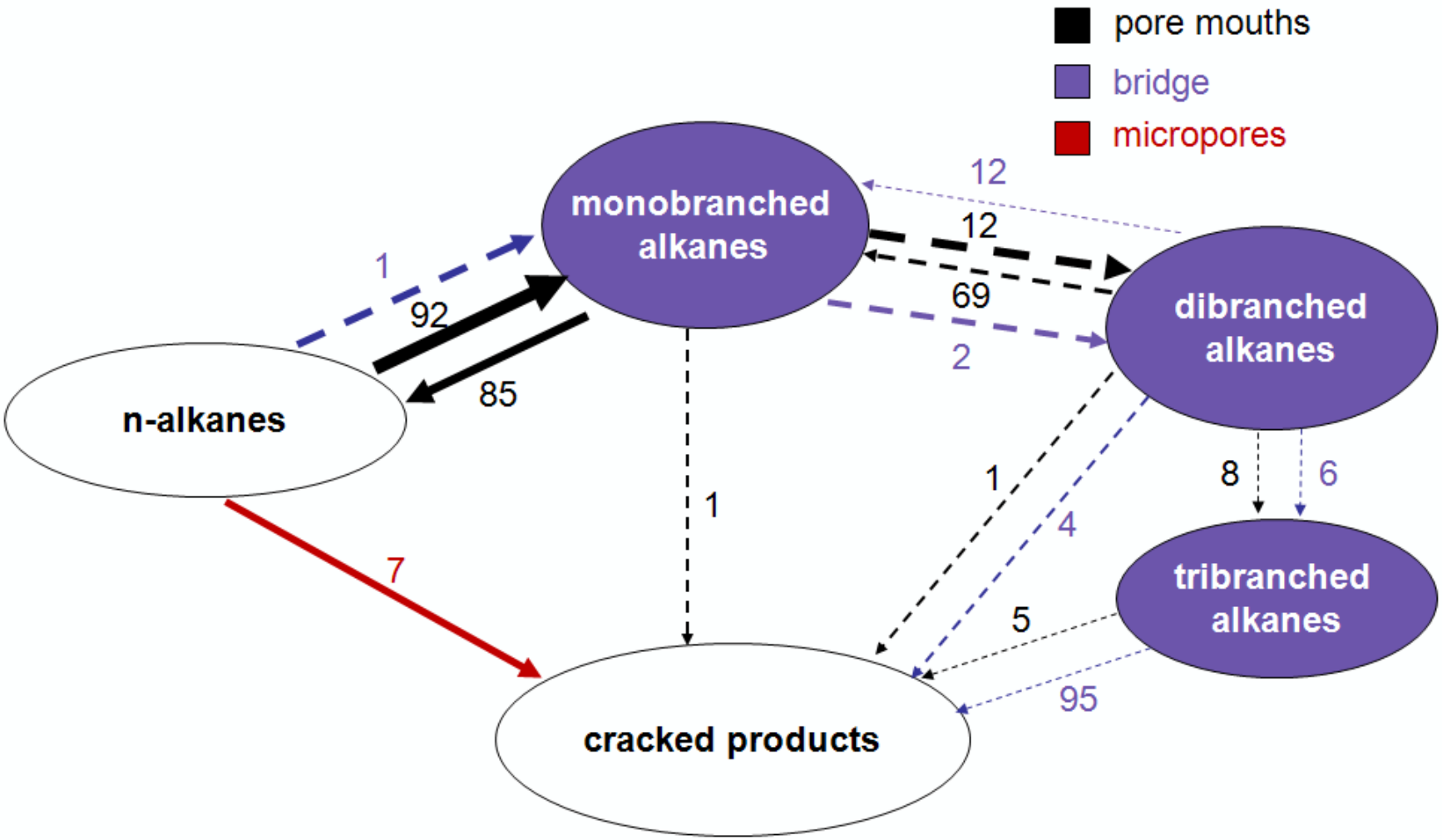
ZSM-22 as catalyst



- pore mouth sites: isomerization
- micropore sites: cracking linear alkanes
- bridge sites: aselective reactions

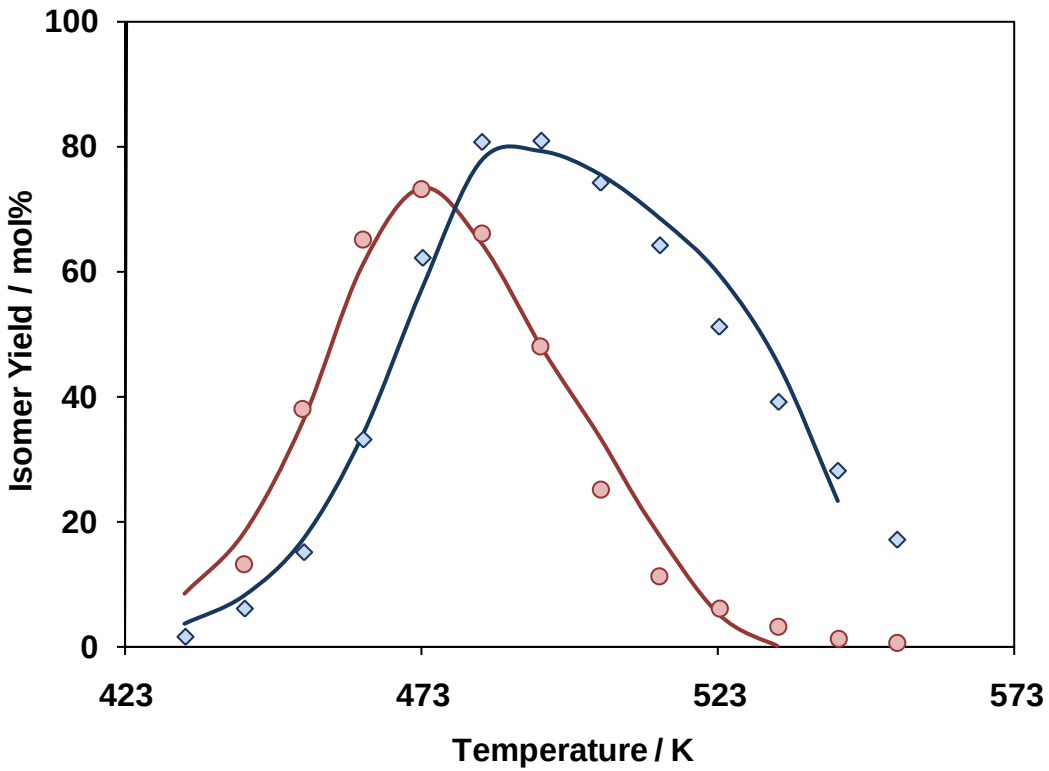
C.S.L. Narasimhan et al. J. Catal. 218 (2003) 135-147
C.S.L. Narasimhan et al. J. Catal. 220 (2003) 399-413

reaction pathway analysis



C.S.L. Narasimhan et al. J. Catal. 220 (2003) 399-413
I.R. Choudhury et al. J. Catal 290 (2012) 165-176

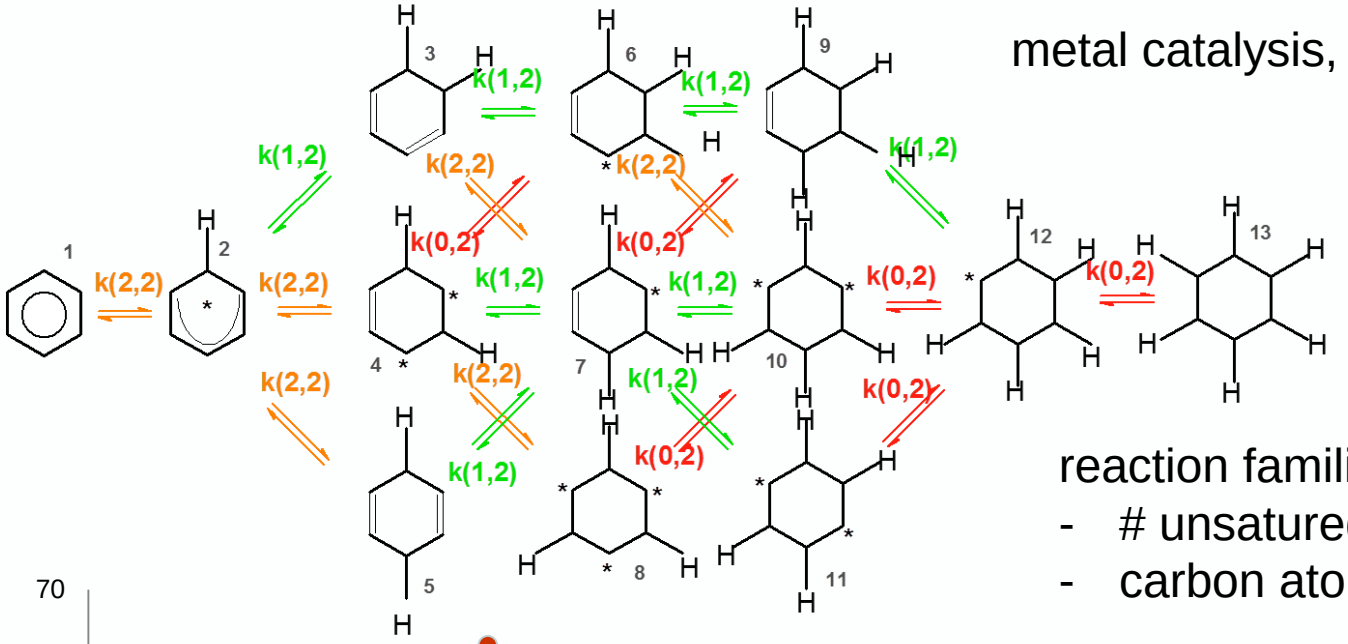
superior ZSM-22 synthesis



- original ZSM-22
  - calcination
  - “stronger” sites
  - additional micropore sites creation
- novel ZSM-22
  - dual ion exchange
  - “weaker” sites
  - comparatively less micropore sites.

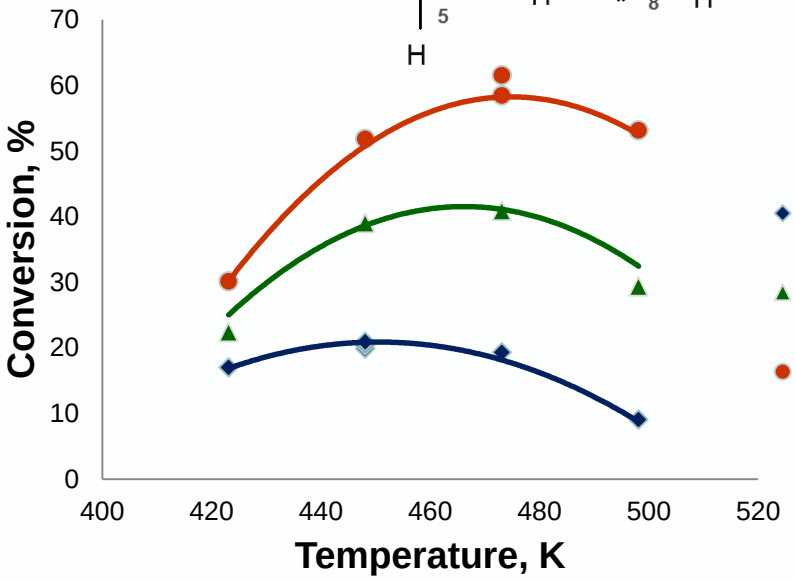
H. Kazuaki et al. Chem. Eur. J. 13 (2007) 10070-10077
US20100181229 (catalyst synthesis)
US20110042267 (lube oil dewaxing process)

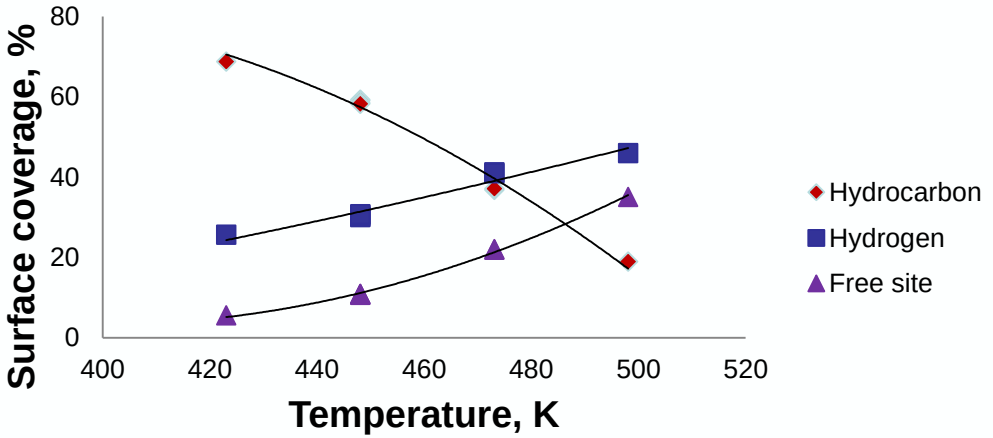
aromatic hydrogenation



metal catalysis, Pt

reaction families
- # unsatured neighbouring C atoms
- carbon atom type





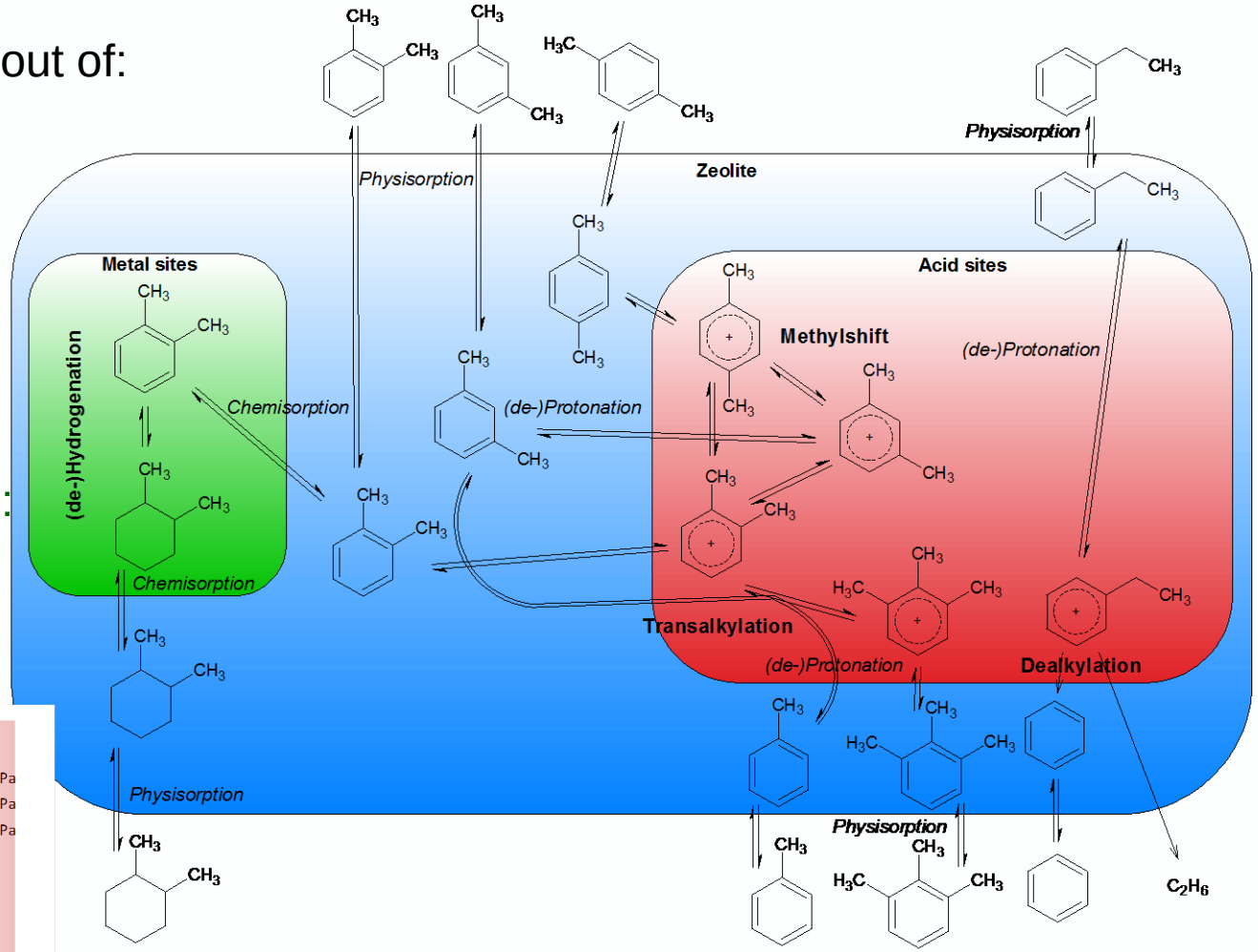
T. Bera et al. Ind. Eng. Chem. Res. 50 (2011) 12933-12945
T. Bera et al. ACS Catalysis 2 (2012) 1305-1318

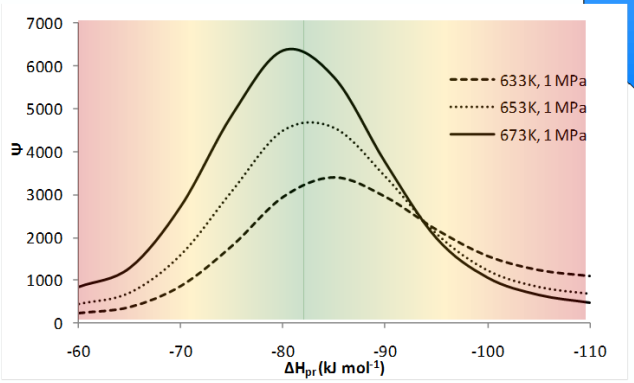
xylene isomerization: SEMK catalyst design

Xylene isomerization on a bifunctional Pt/H-ZSM-5 catalyst

Reaction network consists out of:

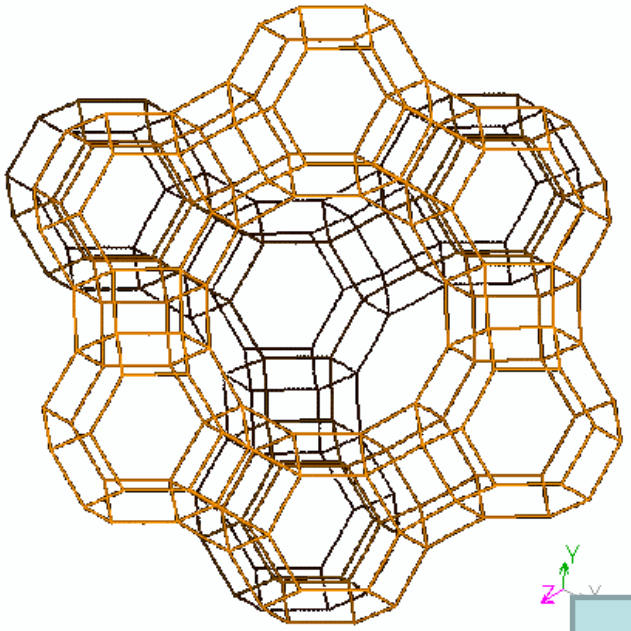
- acid catalyzed reactions:
  - (de-)protonation,
  - alkyl shift (MS),
  - dealkylation, (DA)
  - transalkylation (TA)
- metal catalyzed reactions:
  - Hydrogenation (HYD)
- physisorption

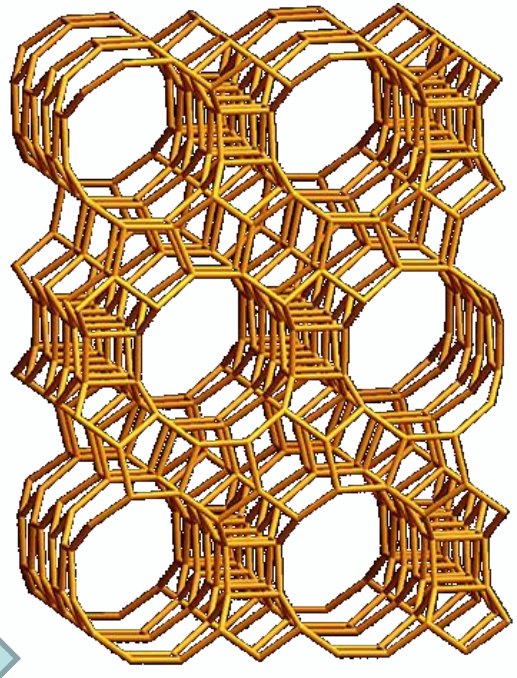




K. Toch et al. Appl. Catal. A-Gen 425 (2012) 130-144

long alkane hydrocracking over BETA



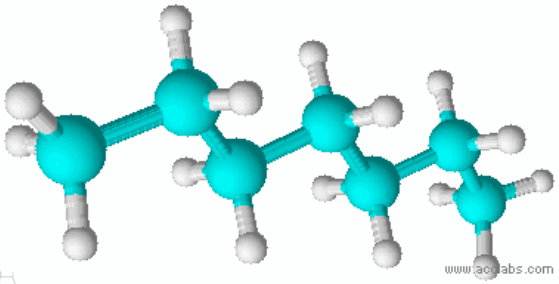


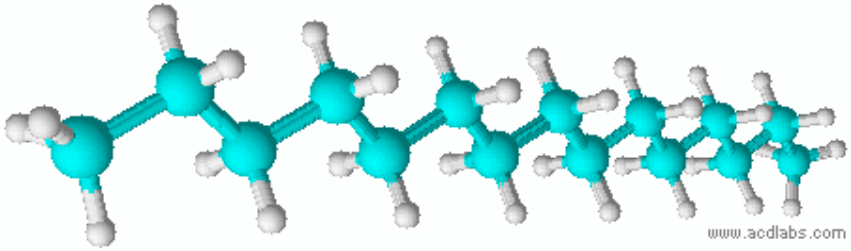
shape selectivity

size entropy effects

USY n-octane

BETA n-hexadecane

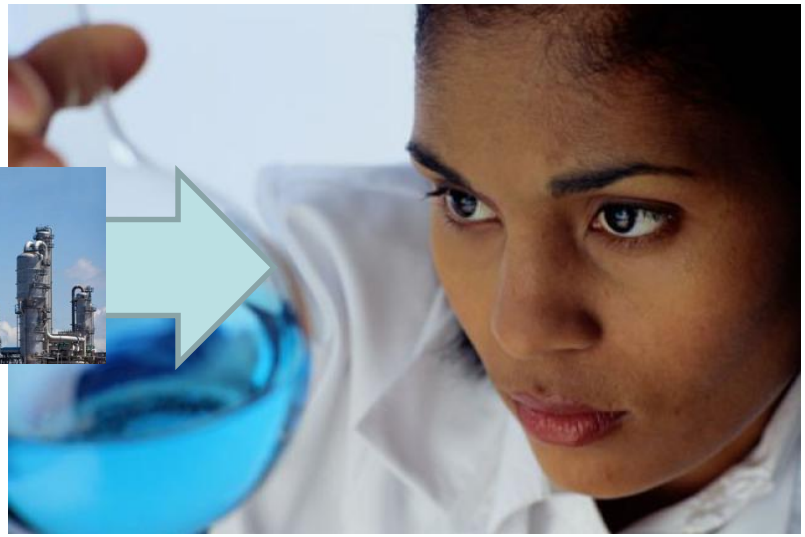


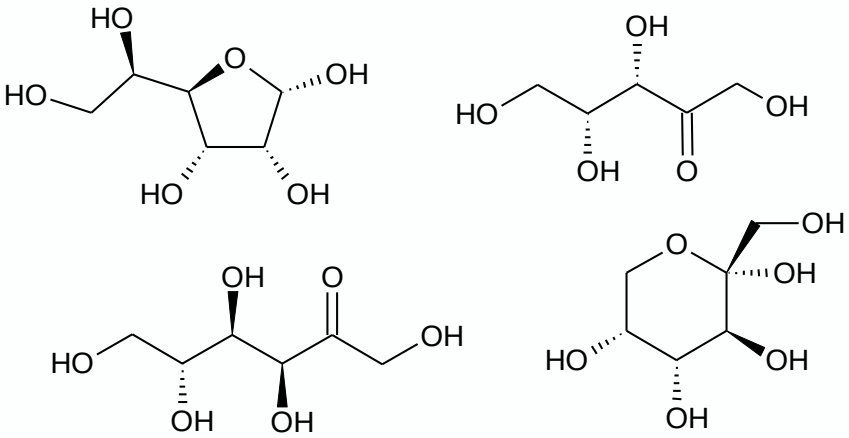


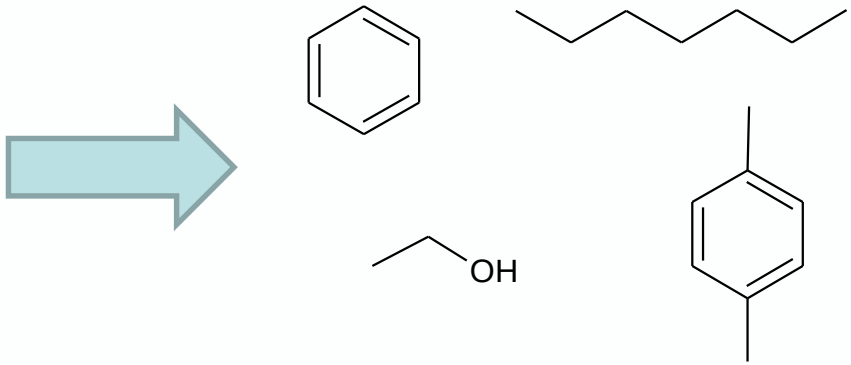
INSTITUTO DE TECNOLOGÍA QUÍMICA

B. Vandegehuchte et al. Appl. Catal. A-Gen 441-442 (2012) 10-20

renewable feed conversion







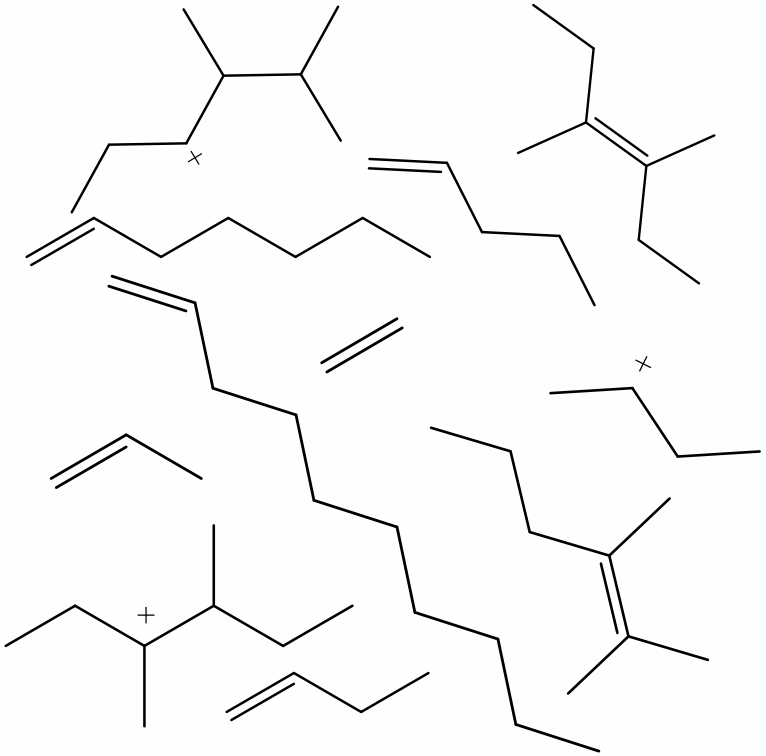
complex mixtures → model compounds

outline

- introduction
- kinetics assessment automation
  - opportunities
  - Fischer Tropsch synthesis
  - network generation algorithm
- renewable feeds
  - challenges and strategy
  - glycerol hydrogenolysis
- conclusions

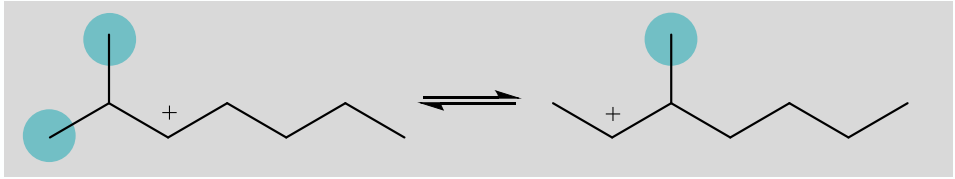
opportunities for automation

complex mixture



energy - enthalpy

entropy



reaction families

- reaction types
  - (de)protonation
  - pcp-branching
  - β-scission
  - alkylation
- intermediate stability
  - carbon atom type
  - nearest neighbour effects

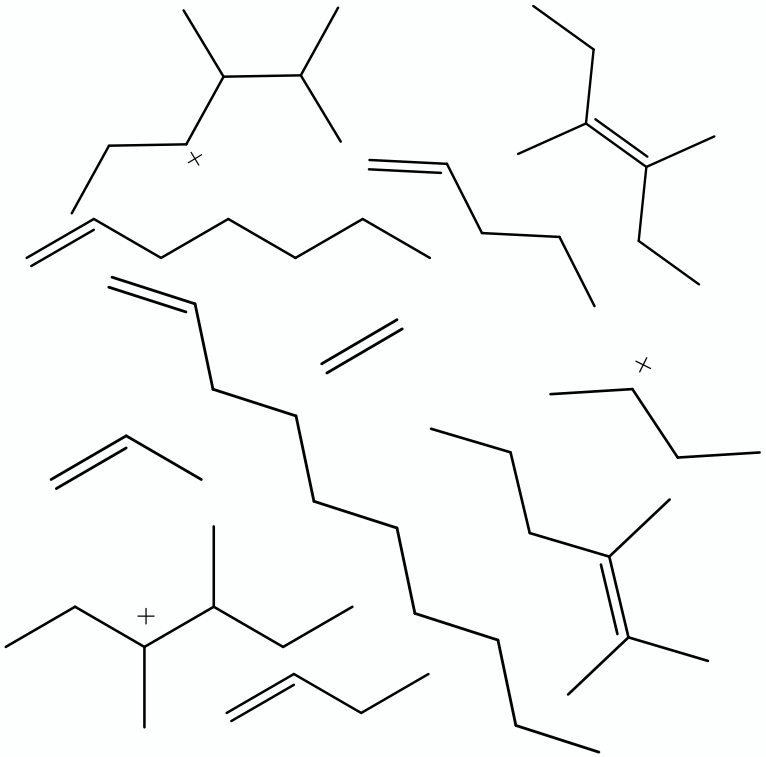
$$k = \frac{\sigma^{reactant}_{global}}{\sigma^{\#}_{global}} \frac{k_b T}{h} \exp\left(\frac{\Delta \tilde{S}^{0,\#}}{R}\right) \exp\left(-\frac{\Delta H^{0,\#}}{RT}\right)$$

n_e $\tilde{k}$

J.W. Thybaut and G.B. Marin, J. Catal. 308 (2013) 352-362

opportunities for automation

complex mixture



ethene oligomerization on Ni on acid support

number of alkenes	1220
number of carbenium ions	972
number of elementary steps	
metal-ion oligomerization	5
protonation	1985
deprotonation	1985
pcp-branching	1096
1,2 alkyl shift	668
alkylation	330
β-scission	330

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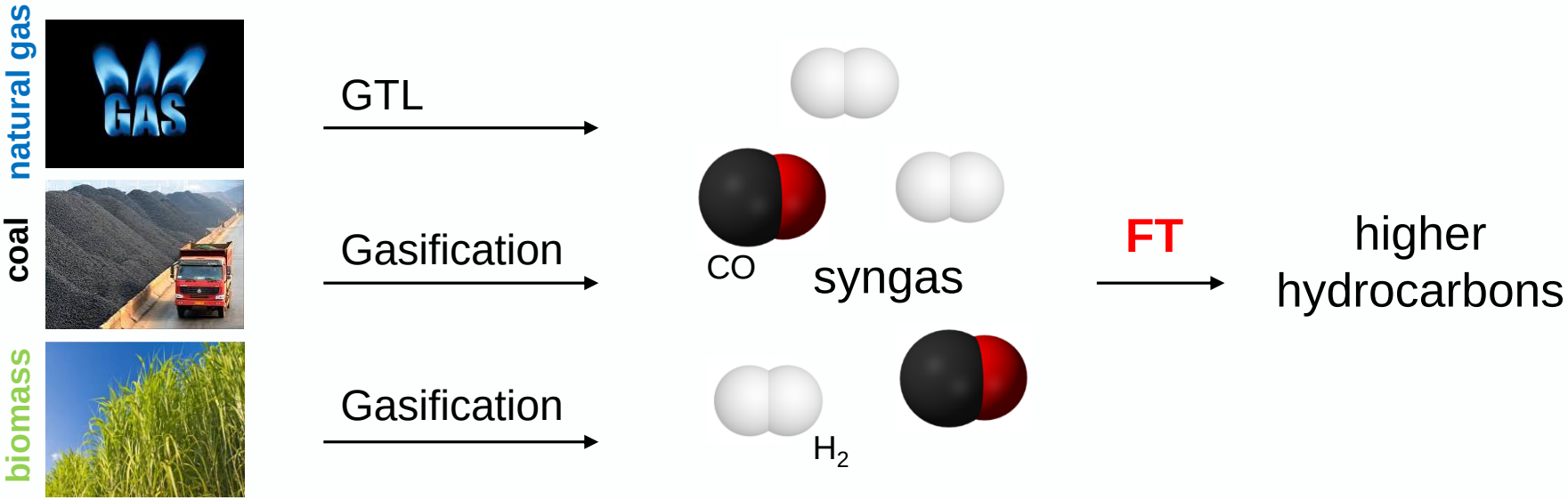
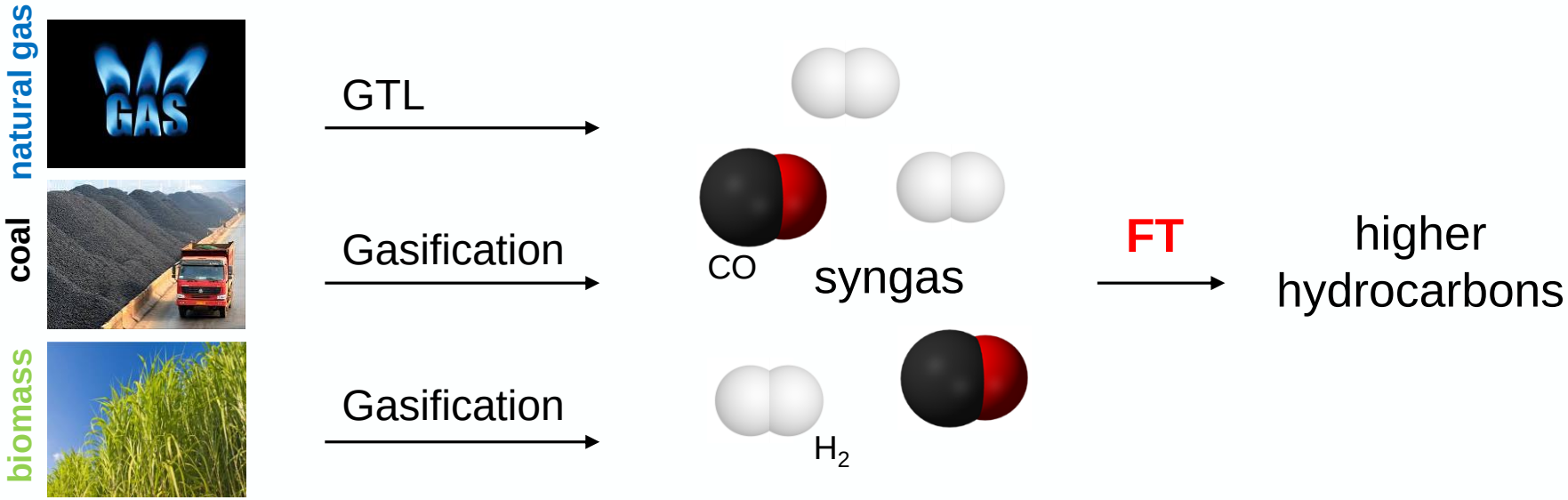
example: Fischer-Tropsch synthesis



reaction families based on carbene insertion mechanism

1. **initiation**: dissociation of hydrogen and CO formation of CH_x groups on the surface
2. **chain growth**: CH_2 group insertion into adsorbed alkyl species
3. **termination**: hydrogenation or recombination of surface species to paraffins and desorption of olefins

example: Fischer-Tropsch synthesis



reaction families based on carbene insertion mechanism

1. **initiation**
2. **chain growth**
3. **termination**

reaction families

hydrogen adsorption	carbon hydrogenation
hydrogen desorption	carbene insertion
CO adsorption	carbene deinsertion
CO desorption	olefin desorption
CO dissociation	olefin adsorption
oxygen hydrogenation	β- Hydrogen elimination

Fischer Tropsch reaction network

reaction families

- hydrogen adsorption
- hydrogen desorption
- CO adsorption
- CO desorption
- CO dissociation
- oxygen hydrogenation
- carbon hydrogenation
- carbene insertion
- carbene deinsertion
- olefin desorption
- olefin adsorption
- β- Hydrogen elimination

user input

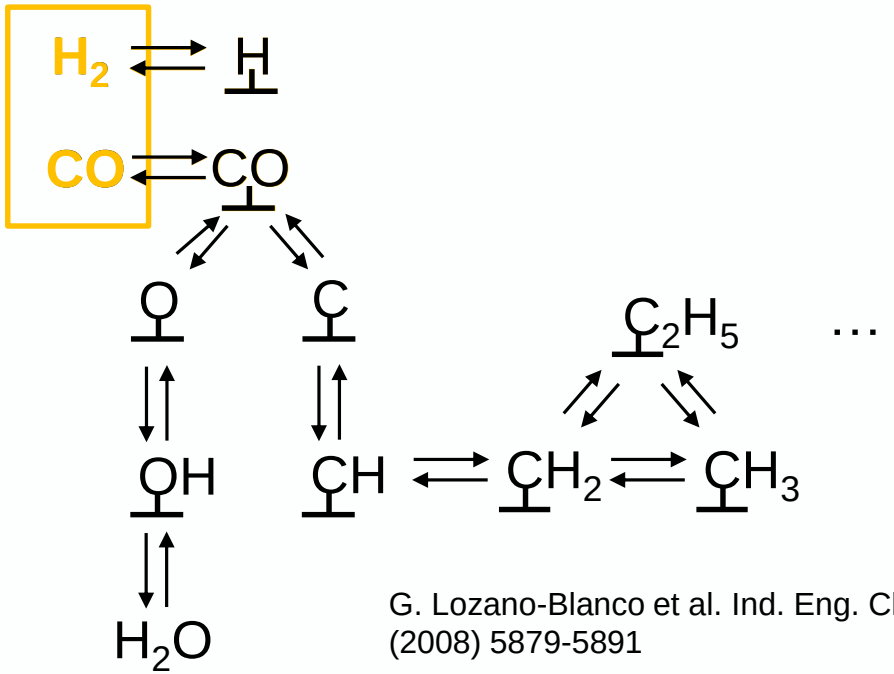
iterate over species

check each reaction family

execute reaction family recipe

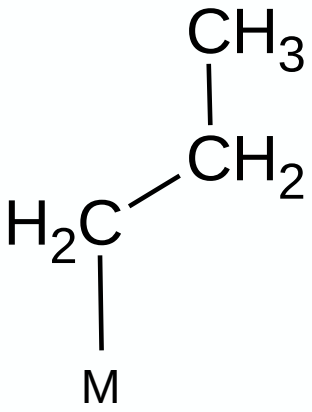
add products and reactions to network

are termination criteria met?



G. Lozano-Blanco et al. Ind. Eng. Chem. Res. 47 (2008) 5879-5891

species representation



Standarized label

$$\begin{bmatrix} 1 & 2 & 2 & 1 \\ 1 & 2 & 3 & 3 \end{bmatrix}$$

Boolean matrix

$$\begin{bmatrix} M & 0 & 1 & 0 & 0 \\ C & 1 & 0 & 1 & 0 \\ C & 0 & 1 & 0 & 1 \\ C & 0 & 0 & 1 & 0 \end{bmatrix}$$

Used to store the species

Are interconverted at runtime

Used to generate the reactions

G. Lozano-Blanco et al. Ind. Eng. Chem. Res. 47 (2008) 5879-5891

kinetic model parameters

for each reaction family:

$$k = \frac{\sigma_{gl,r}}{\sigma_{gl,\ddagger}} \frac{k_B T}{h} exp\left(\frac{\Delta \tilde{S}^{0,\ddagger}}{R}\right) exp\left(\frac{\Delta H^{0,\ddagger}}{RT}\right)$$

determined by the reaction network generation code

constant for a reaction family (chain length independent)

$\Delta \tilde{S}^{0,\ddagger}$ single-event activation entropy

Calculated based on changes in translational degrees of freedom

$\Delta H^{0,\ddagger}$ activation enthalpy

obtained by regression to experimental data

$$n_{parameters} = n_{reaction\ families}$$

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thermodynamic model parameters

Thermodynamic consistency of the overall Fischer Tropsch reaction is guaranteed by using the principle of microscopic reversibility:

$$E_a^{rev} = E_a^{for} - \Delta H_{R,surf}^0 \rightarrow \Delta H_{R,surf}^0 = \Delta H_{R,gas}^0 + \sum_{i=1}^{react} \nu_i \Delta H_{chem,i}^0 - \sum_{i=1}^{prod} \nu_i \Delta H_{chem,i}^0$$

$$\tilde{A}^{rev} = \frac{\tilde{A}^{for}}{exp\left(\frac{\Delta \tilde{S}_R^0}{R}\right)}$$

$$\Delta H_{chem,i}^0 = f(Q_C, Q_O, Q_H) \text{ by UBI-QEP}$$

parameters in the model and are determined by regression

$$\Delta H_{R,gas}^0 = \sum_{i=1}^{prod} \nu_i \Delta_f h_i^0 - \sum_{i=1}^{react} \nu_i \Delta_f h_i^0$$

are taken from existing databases

$$\rightarrow n_{parameters} = \frac{1}{2} n_{reaction\ families} + 3$$

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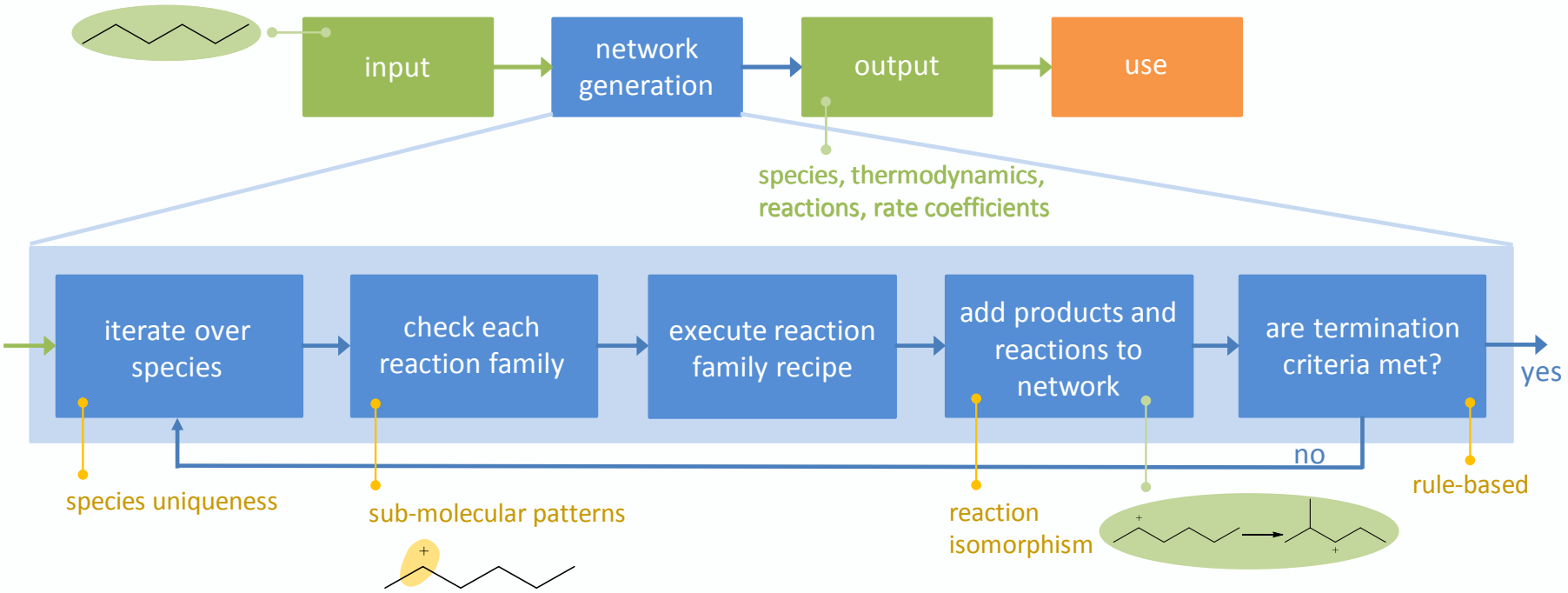
network generation algorithm



ReNGeP – Reaction Network Generation Program

↳ reaction family concept, nearest neighbour effects

outline

- introduction
- kinetics assessment automation
  - opportunities
  - Fischer Tropsch synthesis
  - network generation algorithm
- renewable feeds
  - challenges and strategy
  - glycerol hydrogenolysis
- conclusions

challenges renewable feedstocks

new **challenges** for network generation and kinetic model construction?

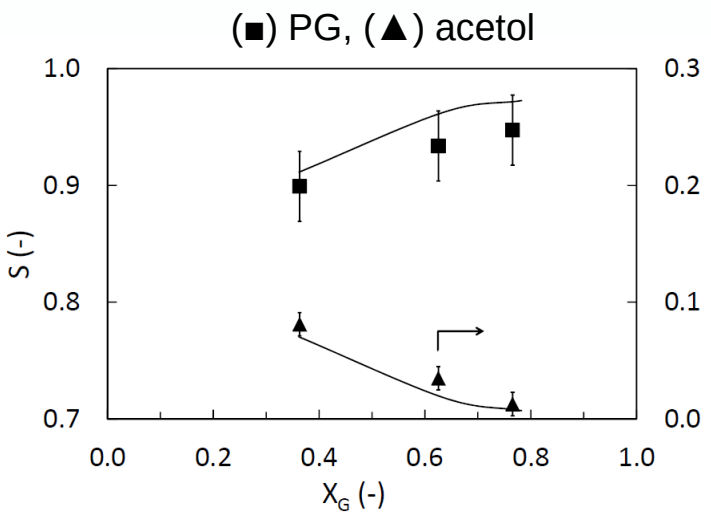
- accounting for heteroatoms
- new functions → new reaction families, next nearest neighbour effects,…
- smarter (adaptive) network size control

corresponding **strategy**

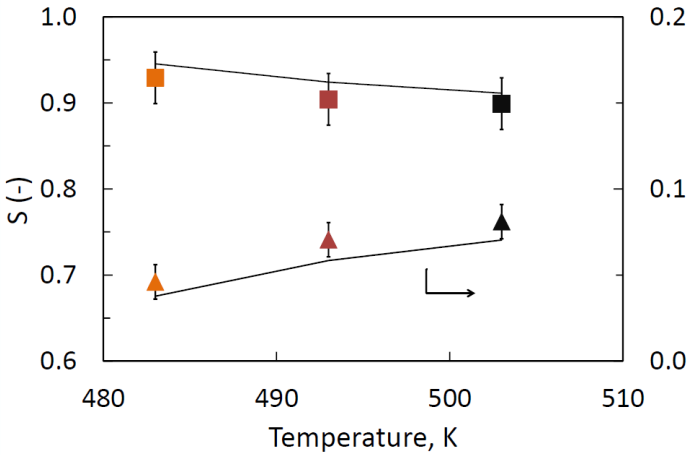
- assessment of simple reaction network: glycerol hydrogenolysis
- extension towards more complex ones: hydrodeoxygenation

R. Van de Vijver et al. Current Opinion Chem. Eng. 13 (2016) 142-149

glycerol hydrogenolysis kinetics

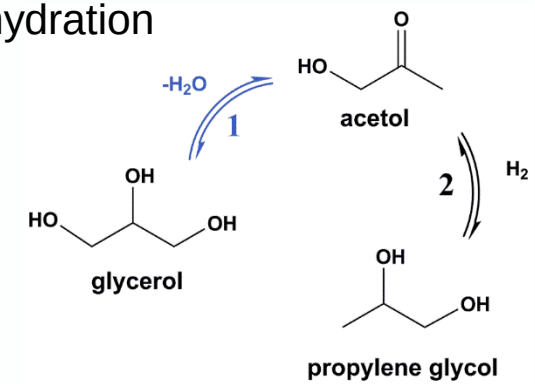


p: 7.0 MPa, F_{H2}/F_{gly}: 5, T: 503 K

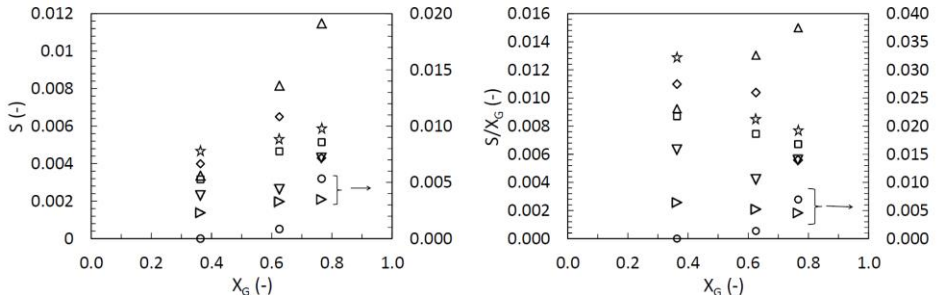


p: 7.5 MPa, F_{H2}/F_{gly}: 5, X ~ 0.35

- acetol is a primary product (from glycerol dehydration)
- acetol hydrogenation is faster than glycerol dehydration



- higher activation energy for dehydration step



(◇) 1,3-propanediol; (▷) ethylene glycol; (□) propionic acid; (★) ethanol; (△) methanol; (▽) 1-propanol; (○) 2-propanol.

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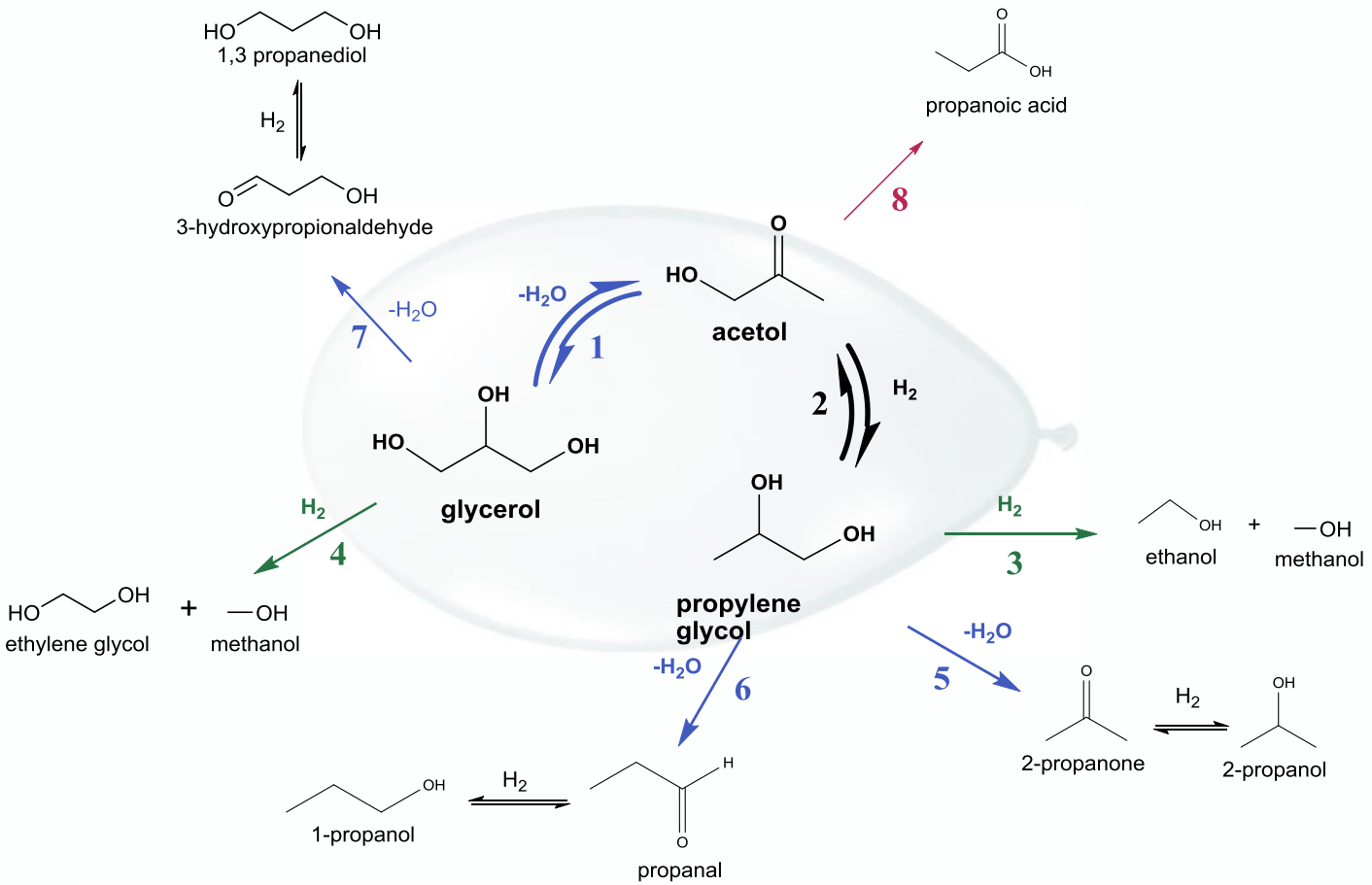
reaction network



reaction families

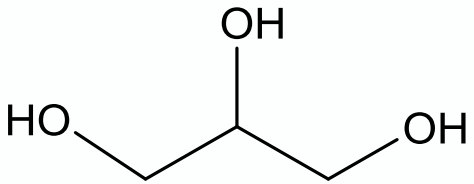
dehydration

hydrogenation

C-C bond scission

isomerization

graph representation

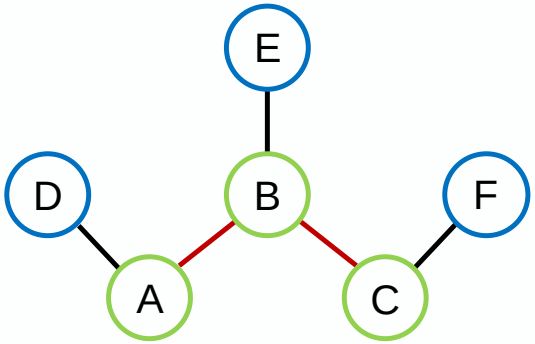


boolean matrix

$$\begin{bmatrix} C & 0 & 1 & 0 & 1 & 0 & 0 \\ C & 1 & 0 & 1 & 0 & 1 & 0 \\ C & 0 & 1 & 0 & 0 & 0 & 1 \\ O & 1 & 0 & 0 & 0 & 0 & 0 \\ O & 0 & 1 & 0 & 0 & 0 & 0 \\ O & 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix}$$

graph theory
object-oriented programming

graph

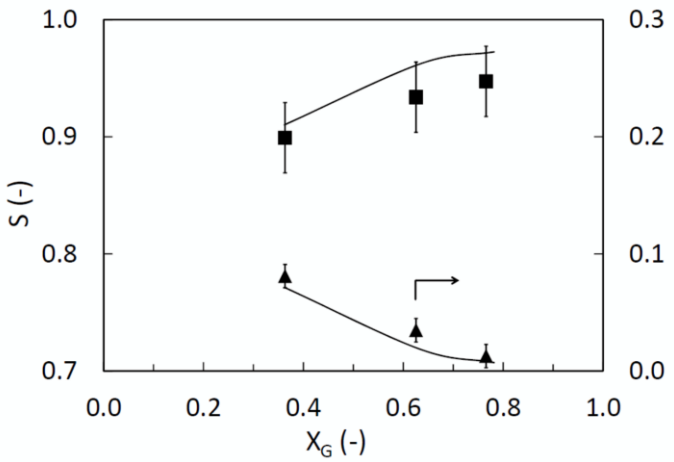


- ✓ simplicity
- x covers small range of
  - possible elements
  - possible structures

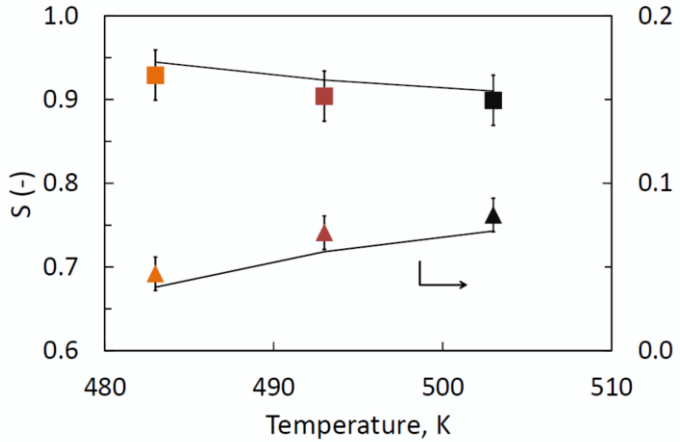
- ✓ more complex, flexible data structures
- ✓ application graph-theoretic algorithms chemoinformatics
  - e.g. calculation symmetry numbers

kinetics assesment and model performance

(■) PG, (▲) acetol



p: 7.0 MPa, F_{H2}/F_{gly}: 5, T: 503 K



p: 7.5 MPa, F_{H2}/F_{gly}: 5, X ~ 0.35

Rate coefficient	A	E_a	k_{483}
k_1^{comp}	10^{15}	78.5 ± 2.15	3.2 x 10^6
k_2^{comp}	10^{13}	59.8 ± 1.07	3.4 x 10^6
k_3	10^{13}	98.9 ± 11.2	2.0 x 10^2
k_4	10^{13}	93.8 ± 11.1	7.1 x 10^2
k_5	10^{14}	91.6 ± 1.26	1.2 x 10^4
k_6	10^{14}	91.6 ± 0.97	1.3 x 10^4
k_7	10^{14}	88.8 ± 1.18	2.5 x 10^4
k_8	10^{12}	112.4 ± 3.51	0.70
Adsorption coefficient	ΔS^0	$-\Delta H^0$	K_{483}
K_G	-168	71.2 ± 1.09	8.4 x 10^{-2}
K_A	-166	68.0 ± 3.97	4.8 x 10^{-2}
K_{PG}	-143	53.6 ± 1.45	2.1 x 10^{-2}
K_H	-136	64.8 ± 10.6	8.0 x 10^{-1}
K_{H2O}	-154	53.3 ± 1.27	5.3 x 10^{-3}
Equilibrium coefficient	ΔS^0	$-\Delta H^0$	K_{483}
K_{AH}	0	5.3 ± 1.8	1.00
F value	1.7 x 10^5 (F_{tab} : 2.79)		

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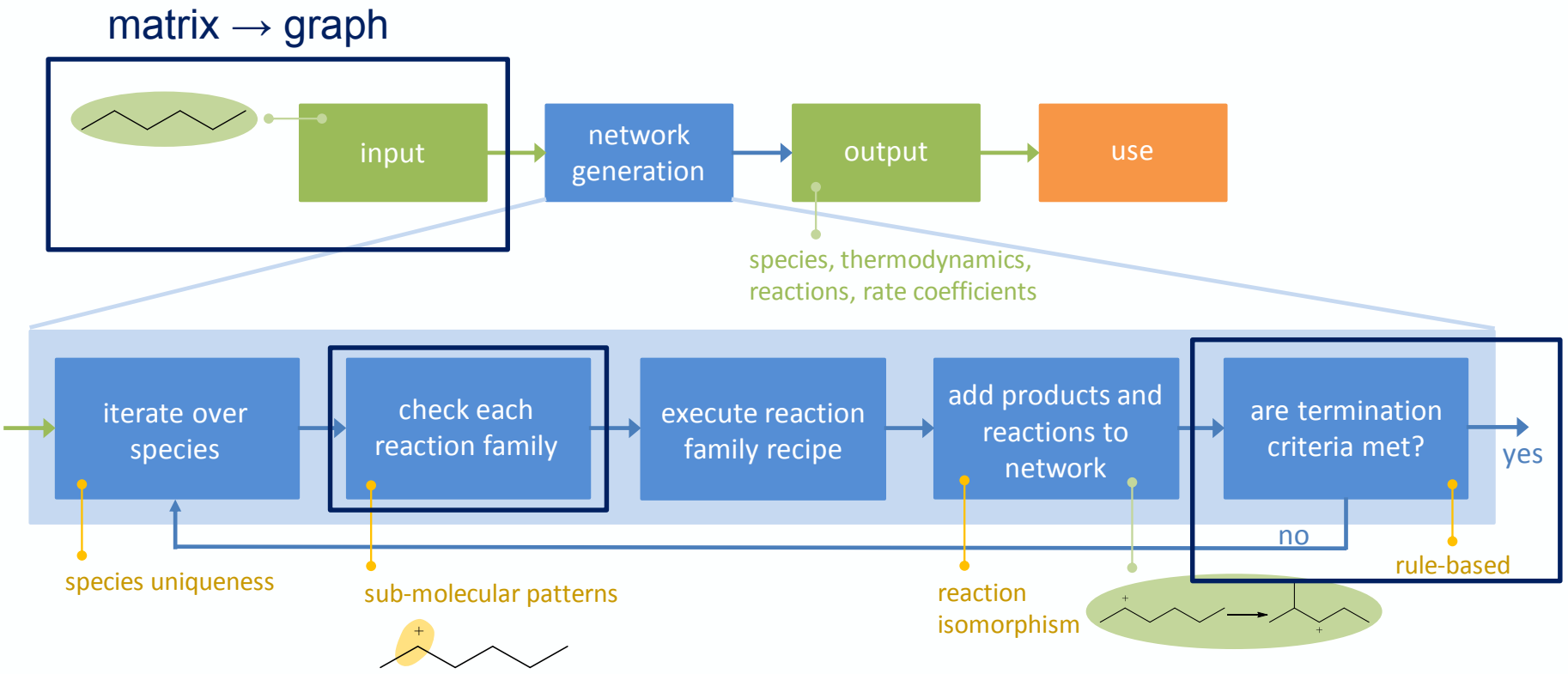
network generation algorithm



- accounting for heteroatoms
- new functions → new reaction families, next nearest neighbour effects
- adaptive network size control

conclusions

- elementary kinetics based models
  - detailed insight in reaction mechanism
  - information driven catalyst and reactor design
- complex mixtures → automated assessment
  - reaction families
  - kinetic and thermodynamic parameter estimation and calculation
- transition from conventional to renewable feeds
  - hetero-atoms (oxygen, nitrogen, sulfur)
  - reaction family definition, (next) nearest neighbour effects
  - species representation and reaction generation
  - network size control

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