AACHENER VERFAHRENSTECHNIK

Evaluation of Reaction Pathways for Next-Generation Biofuels

Anna Voll & Wolfgang Marquardt

Aachener Verfahrenstechnik – Process Systems Engineering
RWTH Aachen University, Germany

1st Brazilian BioEnergy Science and Technology Conference
Campos do Jordão
August 14 to 18, 2011

RWTH

TMFB Cluster of Excellence @ RWTH Aachen University

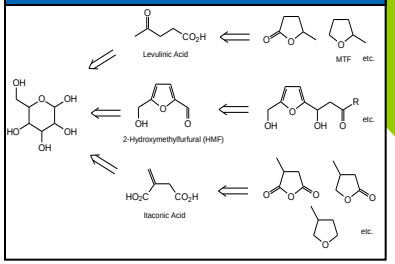
Novel Synthesis and Production Routes

Tailor-Made Fuels from Biomass

solar energy & CO_2 to biomass

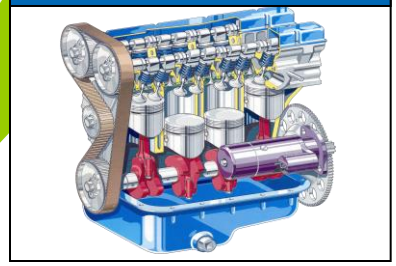
carbon dioxide to atmosphere

Catalytic Conversion



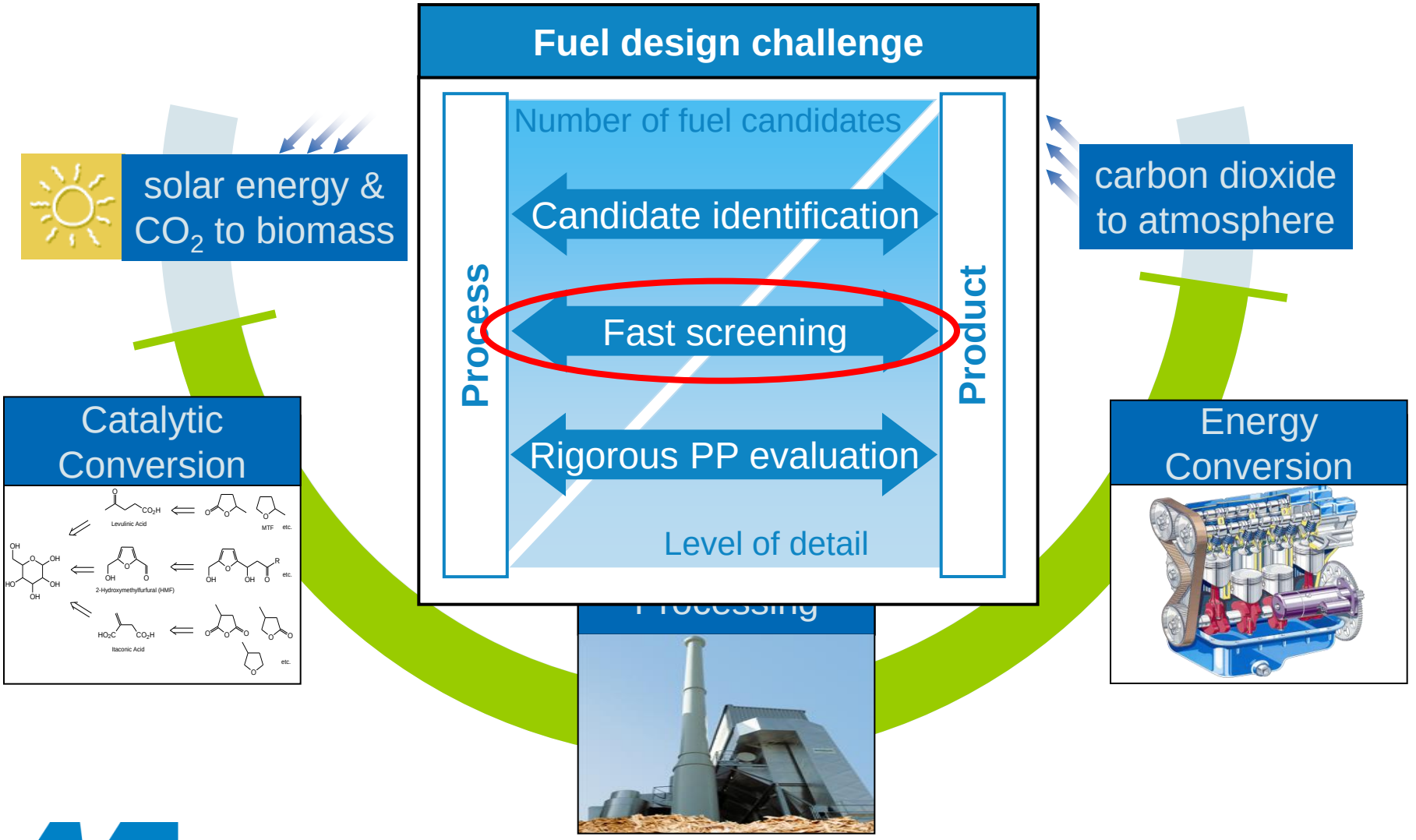
Processing

Energy Conversion

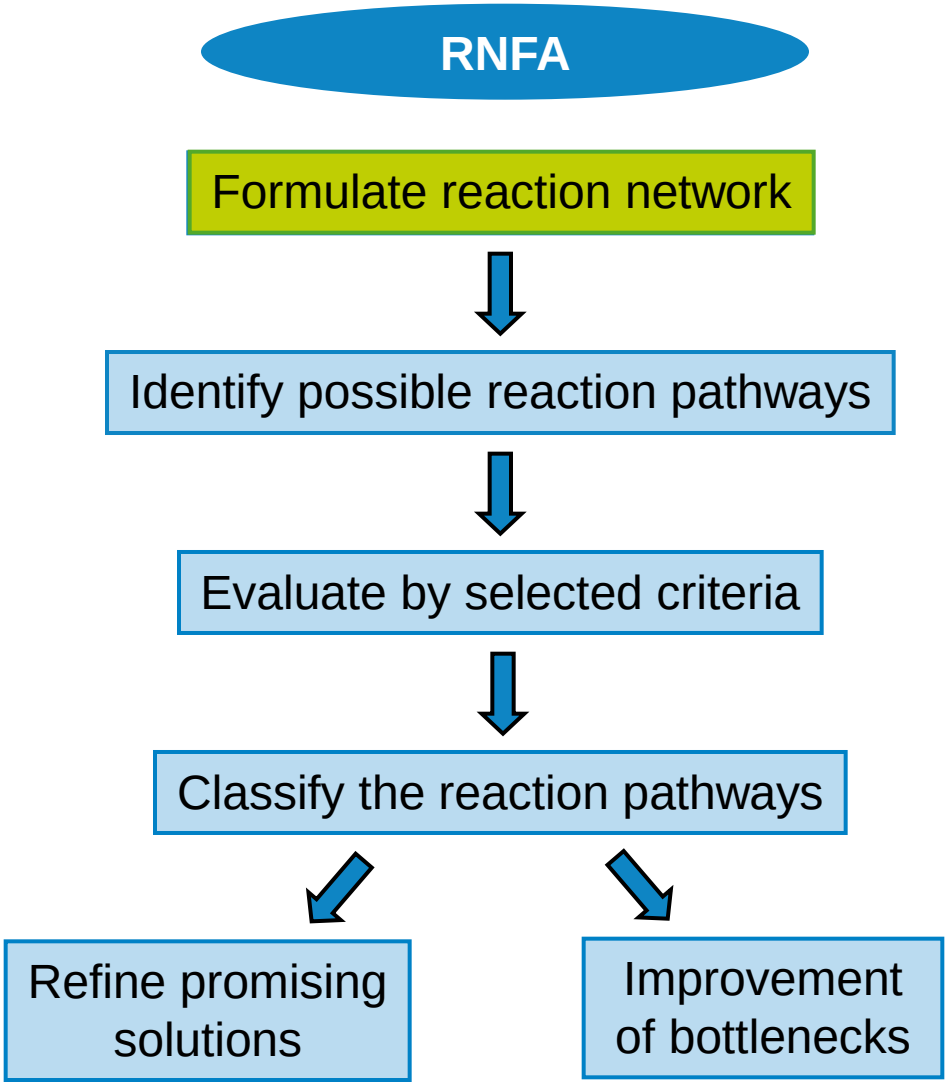


Combustion Characteristics

TMFB Cluster of Excellence @ RWTH Aachen University



Reaction Network Flux Analysis (RNFA)



Representation of network:

- Nodes → molecules
- Arcs → reactions

Network model:

$$\boldsymbol{A} \cdot \boldsymbol{f} = \boldsymbol{b}$$

$$f_j \le Y_j \sum_{k,k \ne j} \nu_k \cdot f_k \quad \forall j$$

$$\boldsymbol{f}, \boldsymbol{b} \ge 0$$

(1)

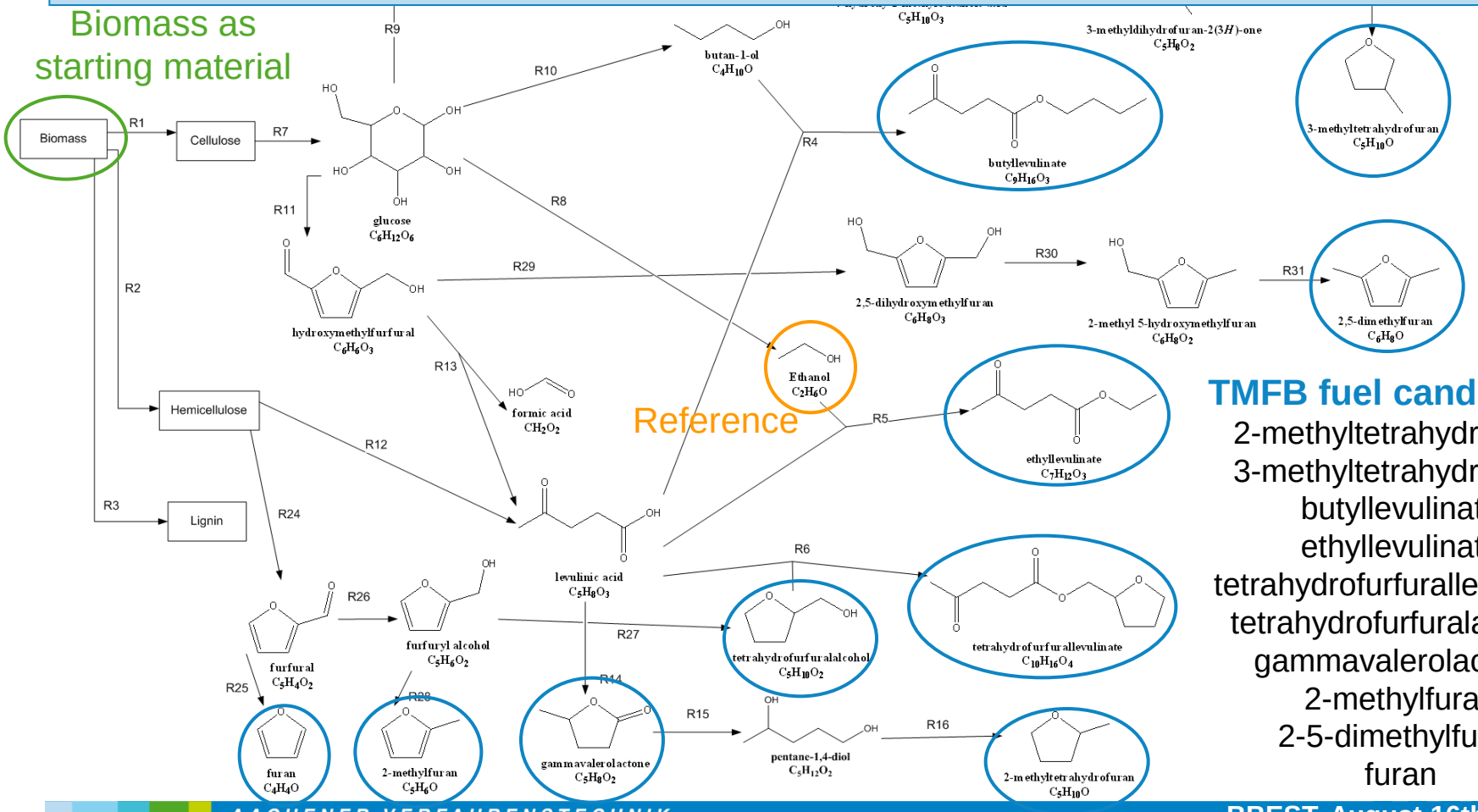
$\boldsymbol{A}$ Matrix of stoichiometric coefficients
$\boldsymbol{f}$ Flux vector
$\boldsymbol{b}$ Production vector
$\boldsymbol{Y}$ Yield coefficient
ν Stoichiometric coefficient

Voll, Marquardt, AIChE J. (2011), in press

Reaction Network for Fuel Candidates

- Case study: **Comparison of 10 TMFB fuel candidates**
  - Same amount of fuel energy should be produced.
  - Reference: production of 100 000 t/yr cellulosic ethanol.

Biomass as starting material

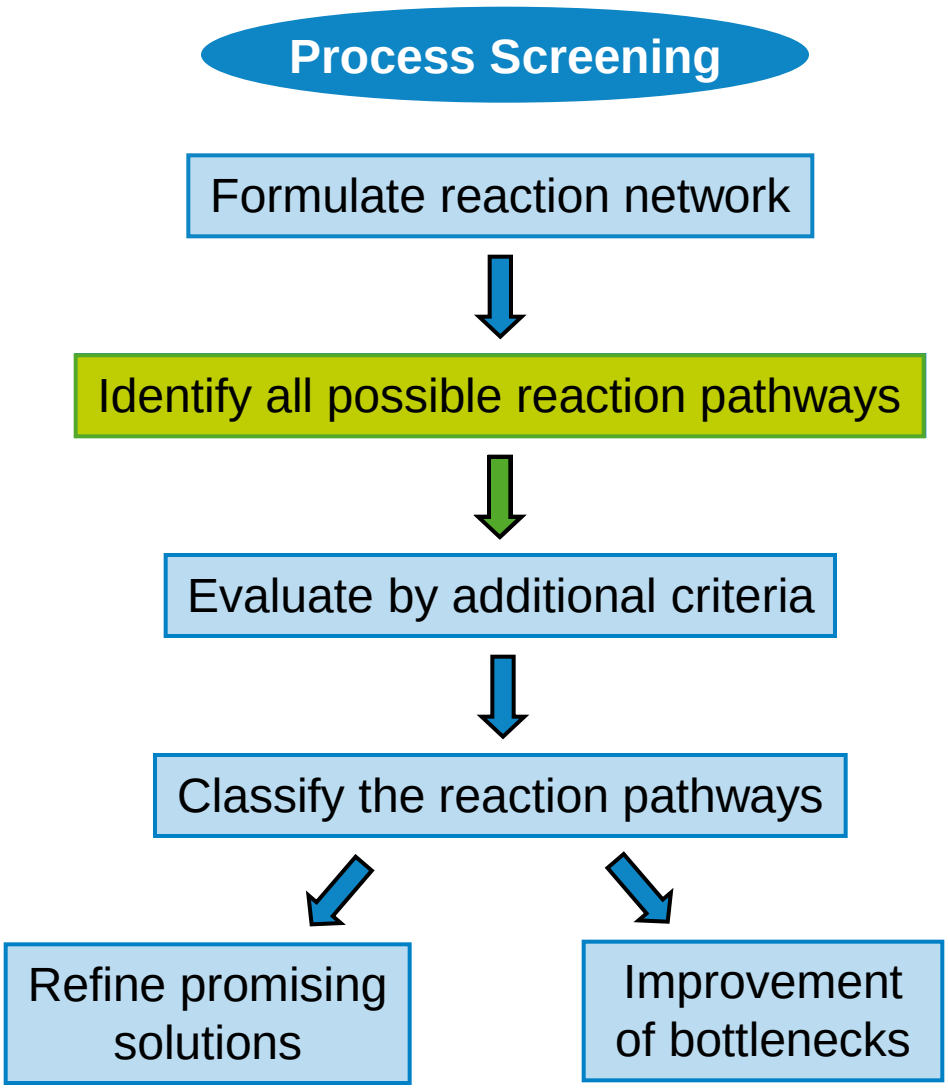


TMFB fuel candidates:

2-methyltetrahydrofuran
3-methyltetrahydrofuran
butyllevulinate
ethyllevulinate
tetrahydrofurfurallevulinate
tetrahydrofurfuralalcohol
gammavalerolactone
2-methylfuran
2-5-dimethylfuran
furan

Huber et al. (2006), Corma et al. (2007), Kamm (2005), Geilen et al. (2010)

Reaction Network Flux Analysis (RNFA)

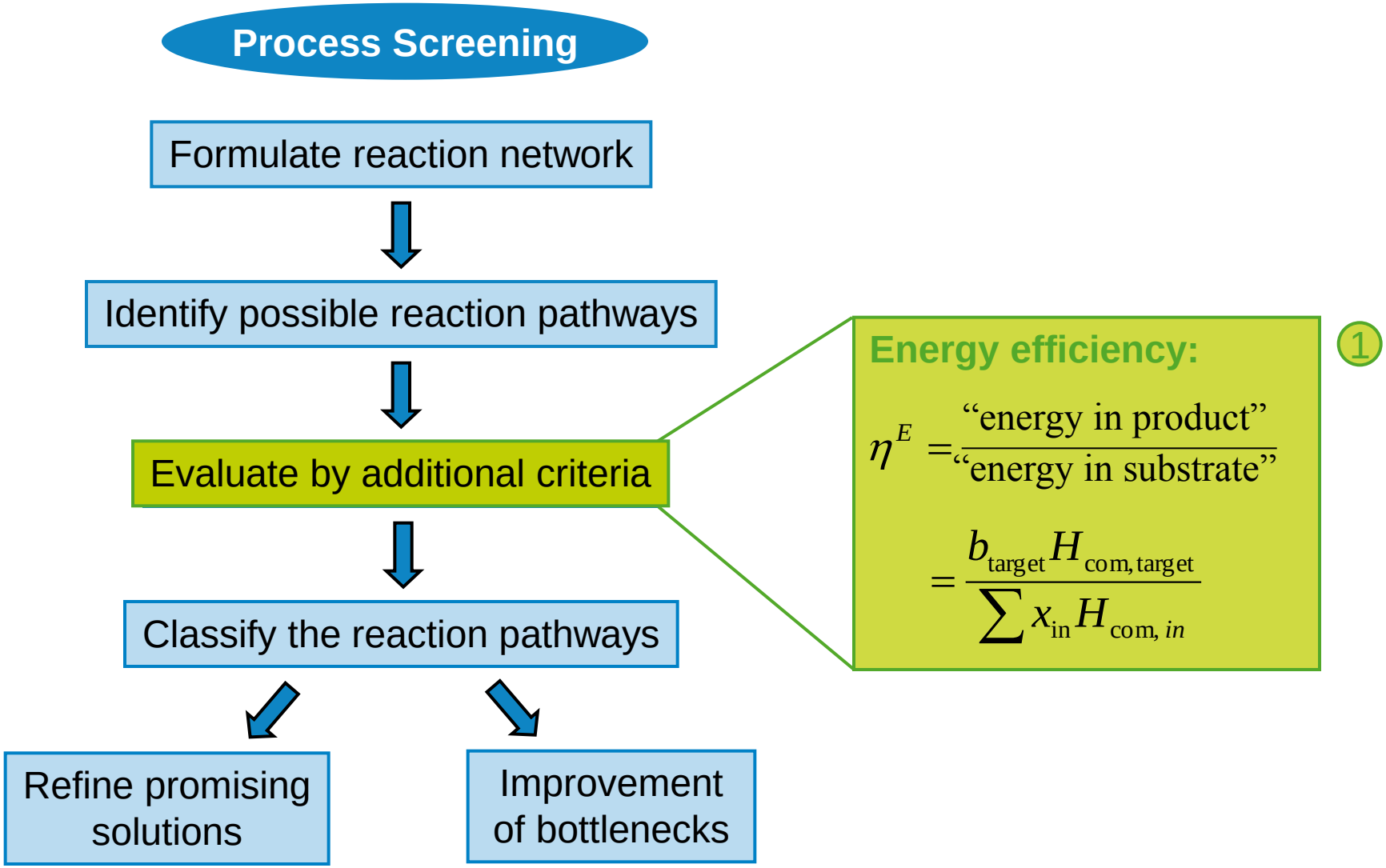


Mass balance related criteria:

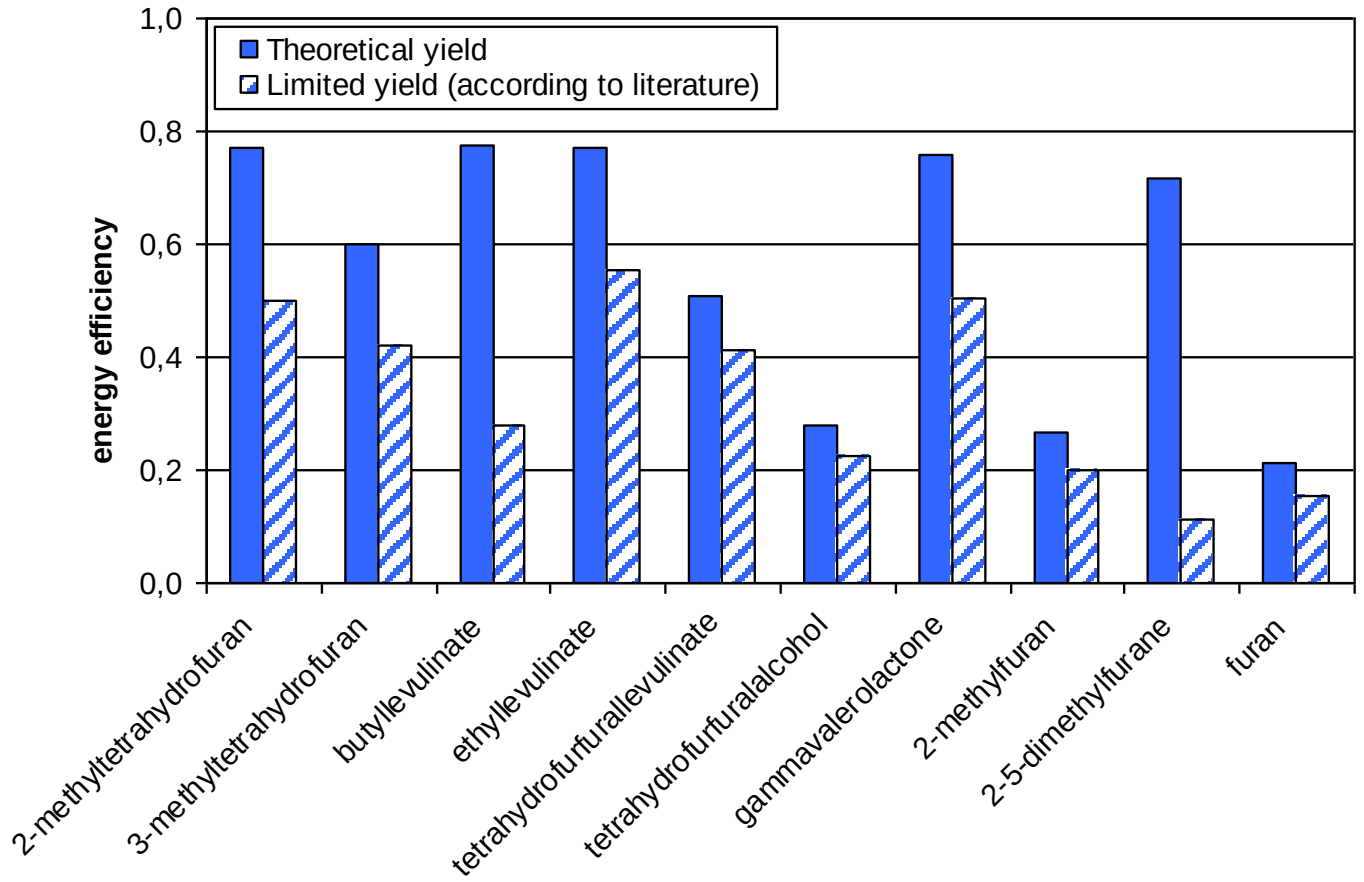
- **Product yield**
- By-product formation
- Need of additional reactants
- Carbon efficiency
- Energy efficiency

Voll, Marquardt, AIChE J. (2011), in press

Reaction Network Flux Analysis (RNFA)



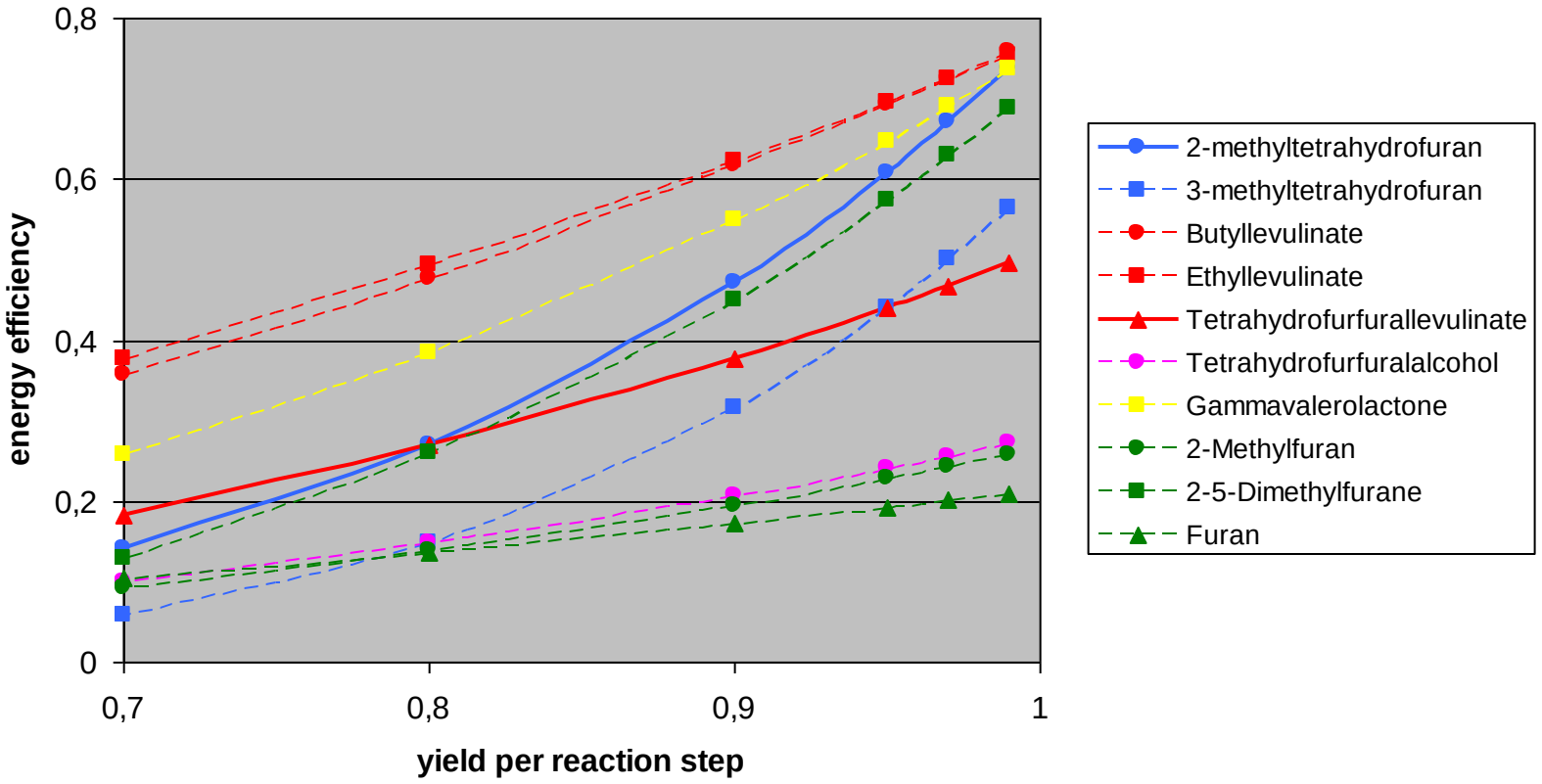
Comparison of Energy Efficiencies



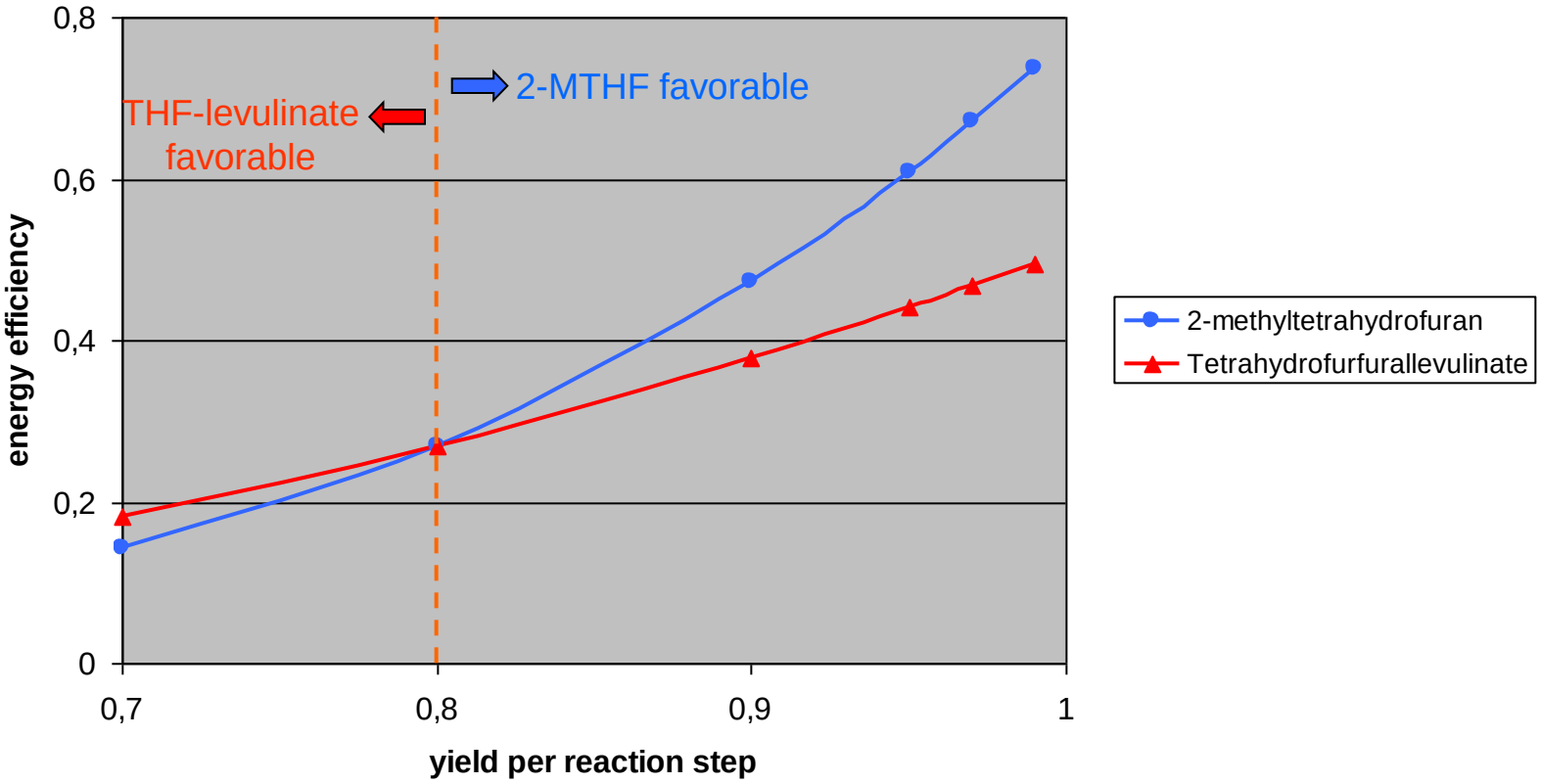
Reaction yields

- have a significant effect on the evaluation results,
- but are often subject to significant uncertainty.

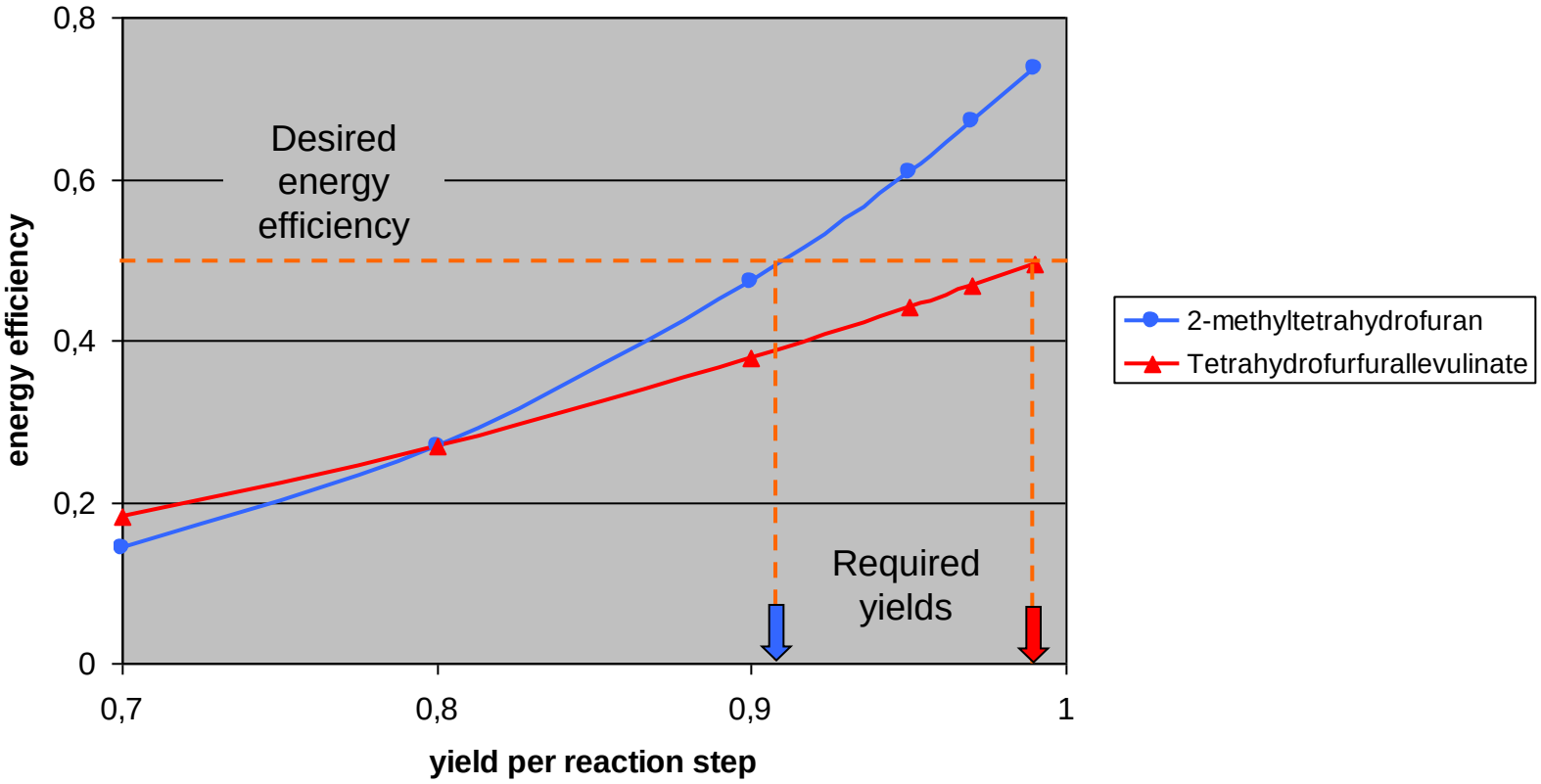
Variation of Yield Coefficients



Variation of Yield Coefficients



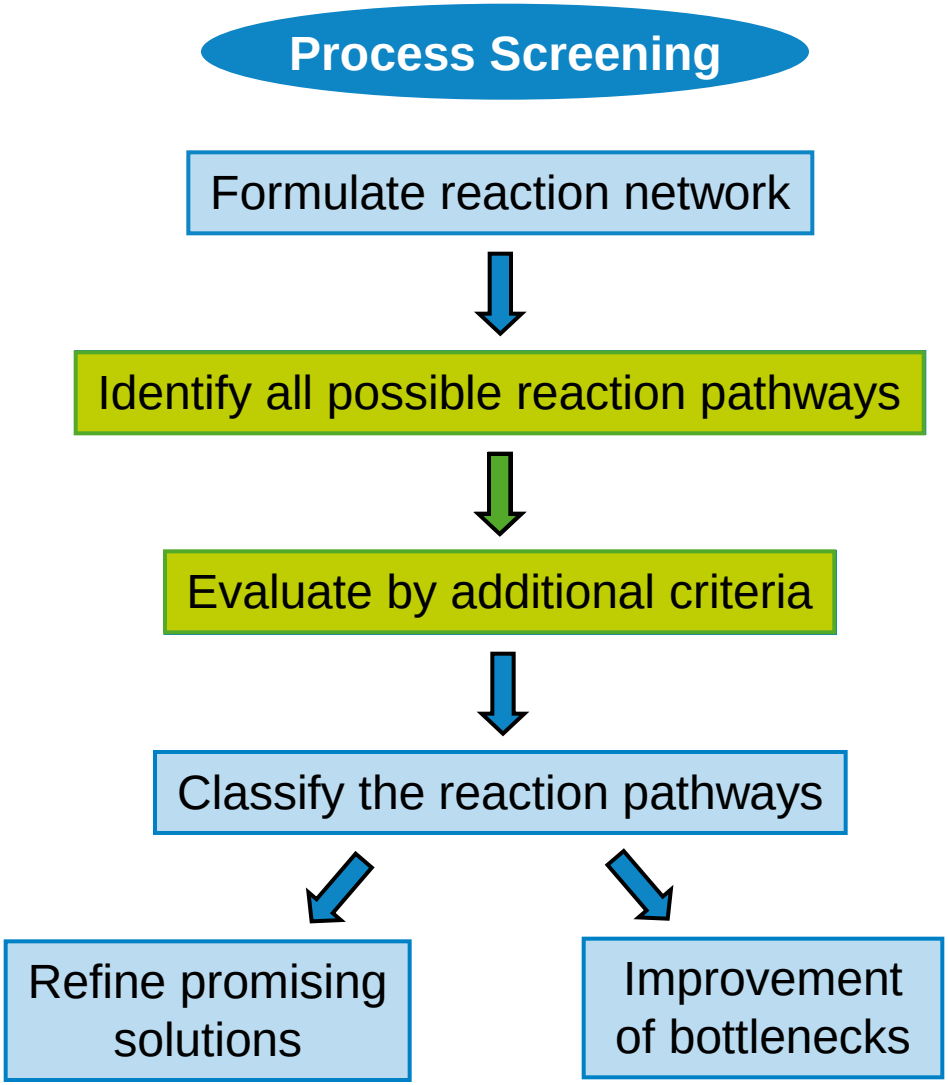
Variation of Yield Coefficients



Targets

- can be set based on yield sensitivity analysis.

Reaction Network Flux Analysis (RNFA)



Mass balance related criteria:

- Product yield
- By-product formation
- Need of additional reactants
- Carbon efficiency
- Energy efficiency

Voll, Marquardt, AIChE J. (2011), in press

Total Annualized Cost (TAC)

- TAC are composed of two parts:
  - Total raw material cost (C_{Raw})
  - Investment cost (IC in M$)*

- Realization within RNFA:

$$TAC = C_{Raw} + \frac{IC \cdot i}{1-(1+i)^{-n}}$$

$$C_{Raw} = \sum_{i=1}^{s} (\boldsymbol{A_1 f_1})_i M_i C_i$$

$$IC = 3 \cdot 10^6 (\Delta E)^{0.84}$$

(2)

i	Interest rate (8%)
n	Plant lifetime (10 years)
$\boldsymbol{C}$	Raw material prices
ΔE	Energy loss

* Lange (2001)

Environmental Impact (EI)

- Eco-Efficiency Analysis* covering the following aspects:
  - Energy consumption (EC)
  - Resource consumption (RC)
  - CO_2 emission impact (Em)
  - Toxicity potential (TP)

- Adapted to be integrated in RNFA:

$$EI = \frac{EC}{\|EC\|_\infty} + \frac{RC}{\|RC\|_\infty} + \frac{Em}{\|Em\|_\infty} + \frac{TP}{\|TP\|_\infty} \qquad (3)$$

$$EC = \frac{\Delta E}{M_{target} b_{target}} \qquad RC = \frac{\sum_{i=1}^{s} (\mathbf{A_1 f_1})_i M_i}{M_{target} b_{target}}$$

$$Em = \frac{M_{CO2} b_{CO2}}{M_{target} b_{target}} \qquad TP = M_{target} b_{target} TS_{target}$$

$\boldsymbol{M}$ Molar mass
$\boldsymbol{TS}$ Toxicity scale

* Saling et al.(2002)

Multi-Objective Optimization Problem

$$\min_{f,b} \begin{Bmatrix} TAC \\ EI \end{Bmatrix}$$

s.t. *Mass balance* ①

Total annualized cost ②

Environmental impact ③

ε-constraint method

$$\min_{f,b} TAC$$

$$s.t. \quad EI \leq \varepsilon$$

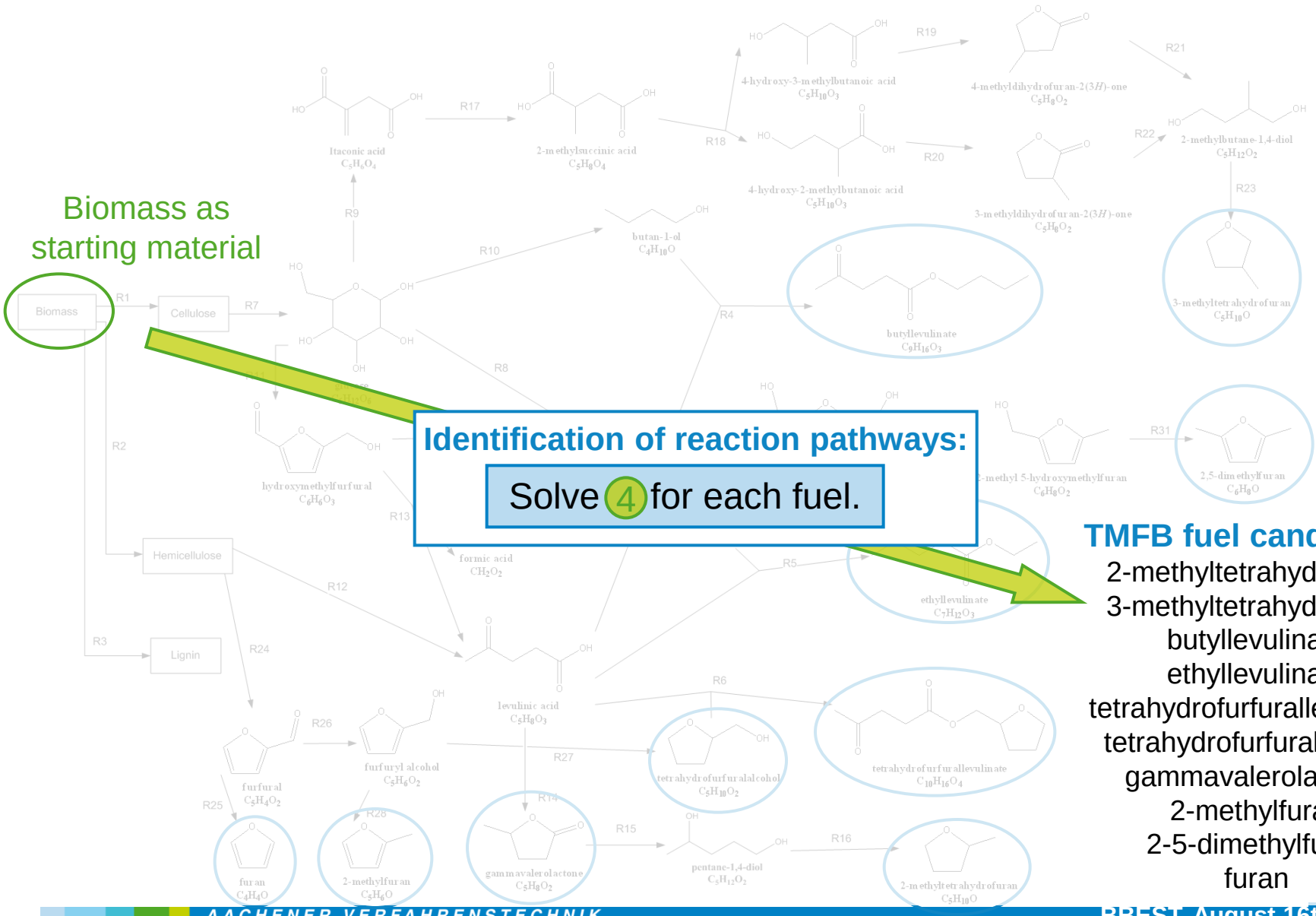
Mass balance ①

Total annualized cost ②

Environmental impact ③

④

Reaction Network for Fuel Candidates



Identification of reaction pathways:

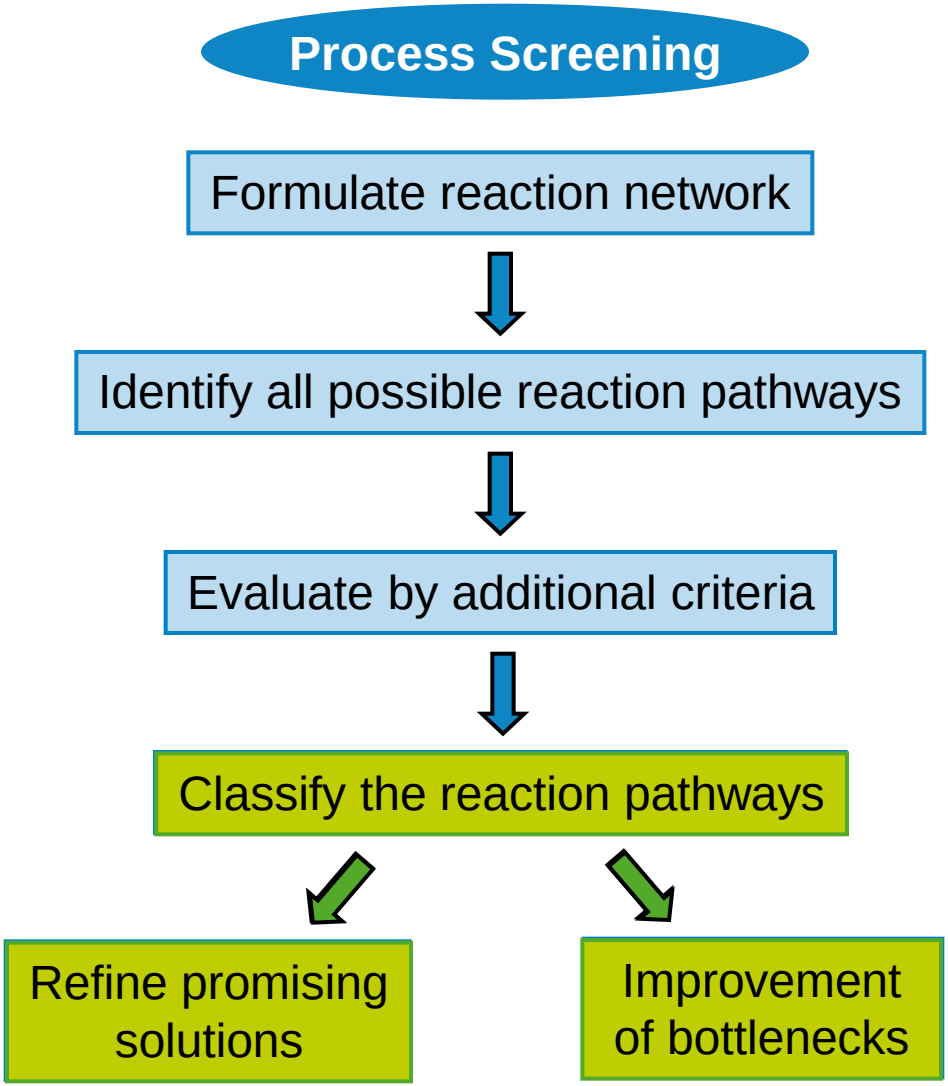
Solve 4 for each fuel.

TMFB fuel candidates:

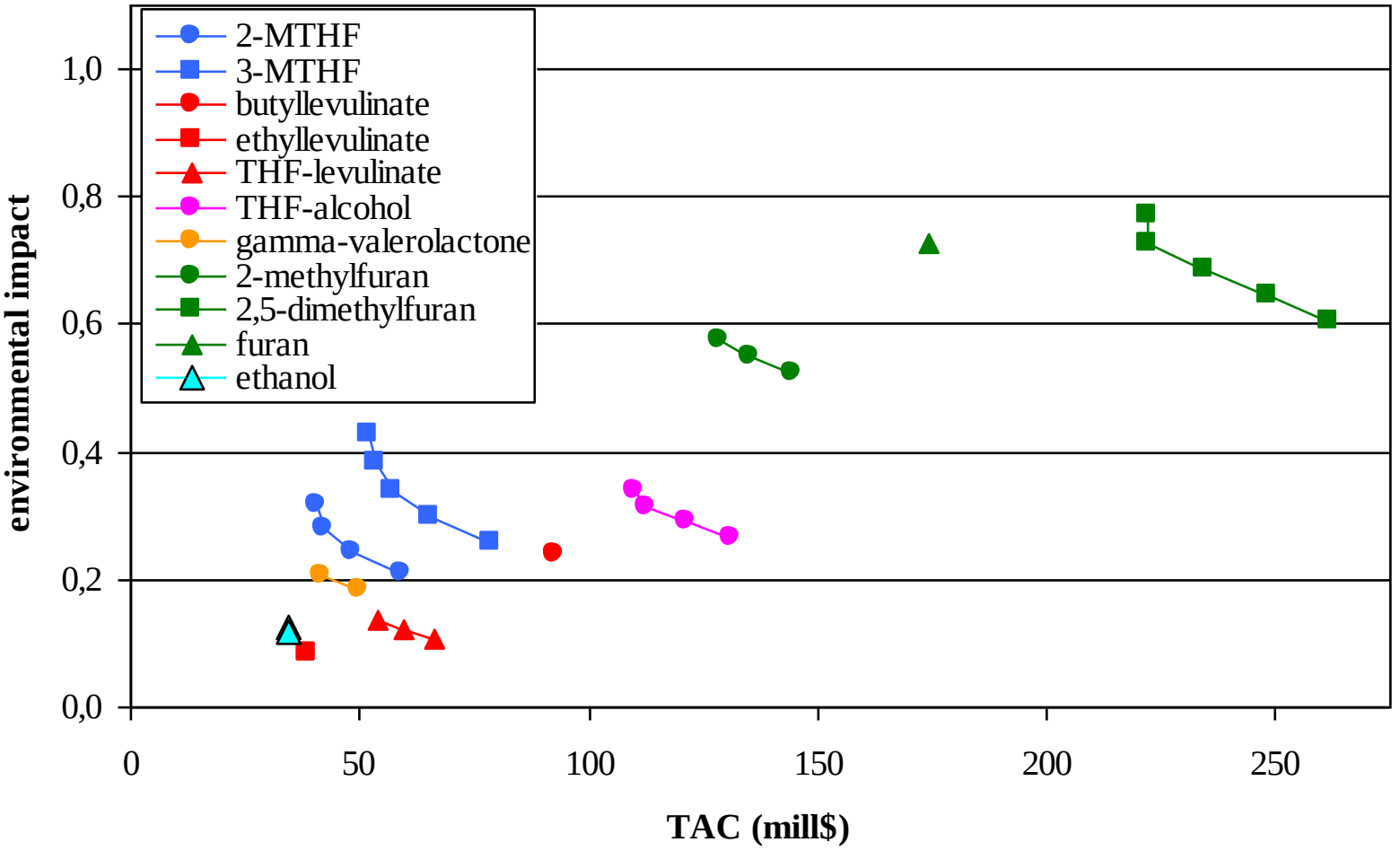
2-methyltetrahydrofuran
3-methyltetrahydrofuran
butyllevulinate
ethyllevulinate
tetrahydrofurfurallevulinate
tetrahydrofurfuralalcohol
gammavalerolactone
2-methylfuran
2-5-dimethylfuran
furan

Huber et al. (2006), Corma et al. (2007), Kamm (2005), Geilen et al. (2010)

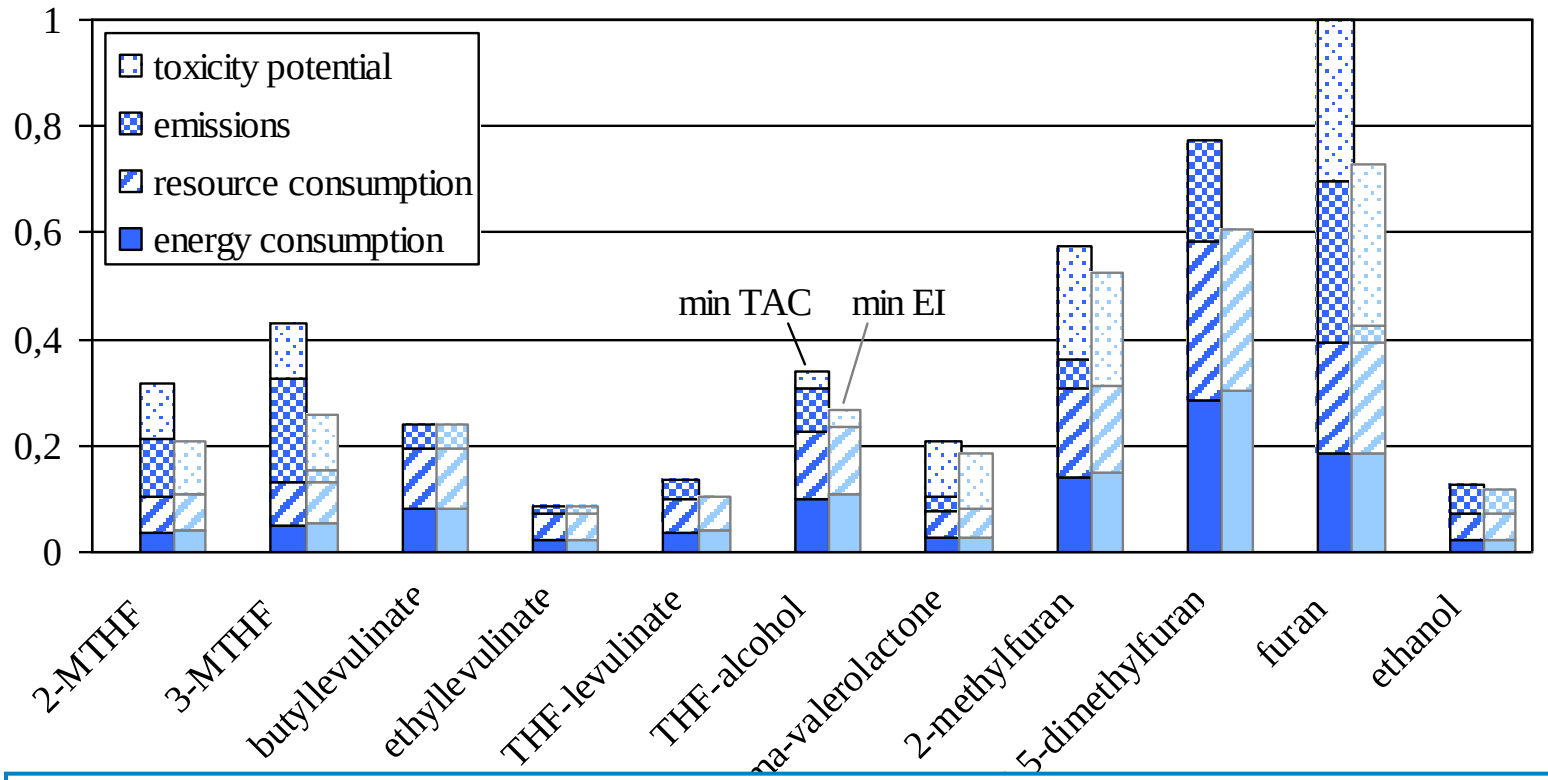
Reaction Network Flux Analysis (RNFA)



Results – Pareto Fronts



Results – Environmental Impact



Hydrogen source trade-off:

- **min TAC:** Gasification of biomass residuals: higher CO_2 emissions
- **min EI:** External carbon neutral supply: higher energy/resources consumption and cost

Reaction Network Flux Analysis (RNFA)

RNFA

Formulate reacti

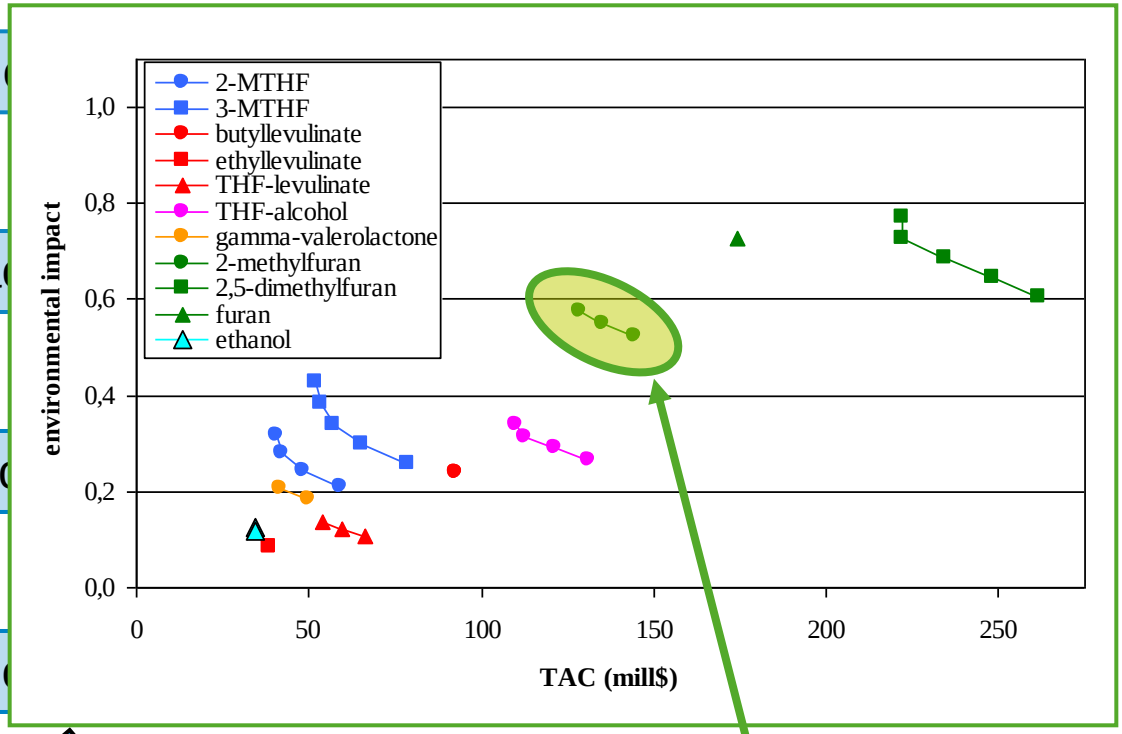
Identify possible rea

Evaluate by selec

Classify the reacti

Refine promising solutions

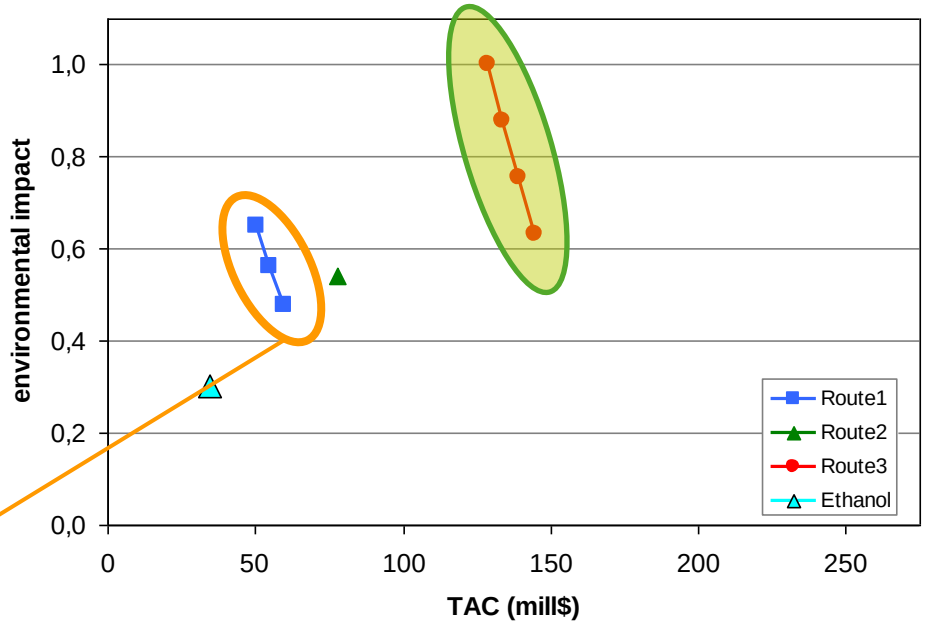
Improvement of bottlenecks



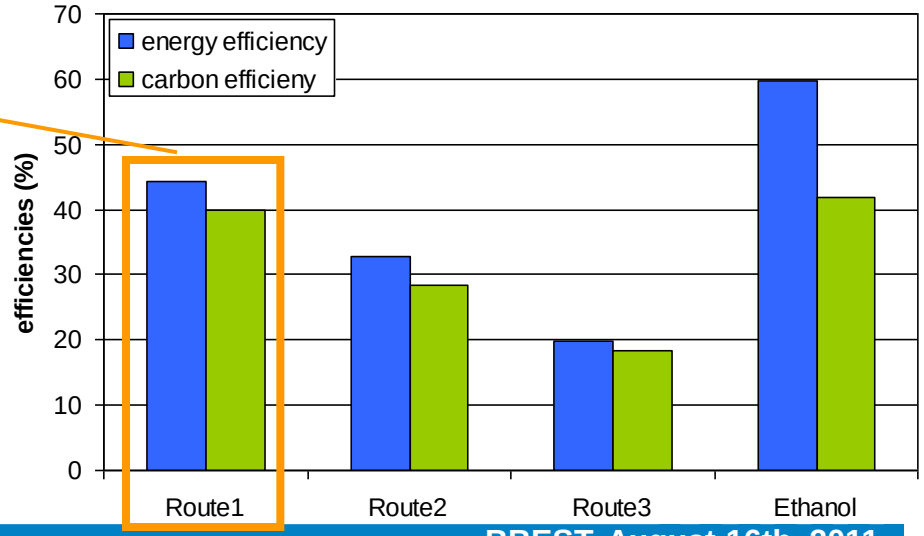
2-methylfuran – not an attractive fuel?

Focus on 2-Methylfuran Synthesis

- Comparison of **3 catalytical concepts** for the production of 2-methyl-furan from biomass.
- Performance can be increased significantly by novel catalysis routes.
- 2-methylfuran is a promising fuel candidate!!



TMFB approach (Leitner group)



Concluding Remarks

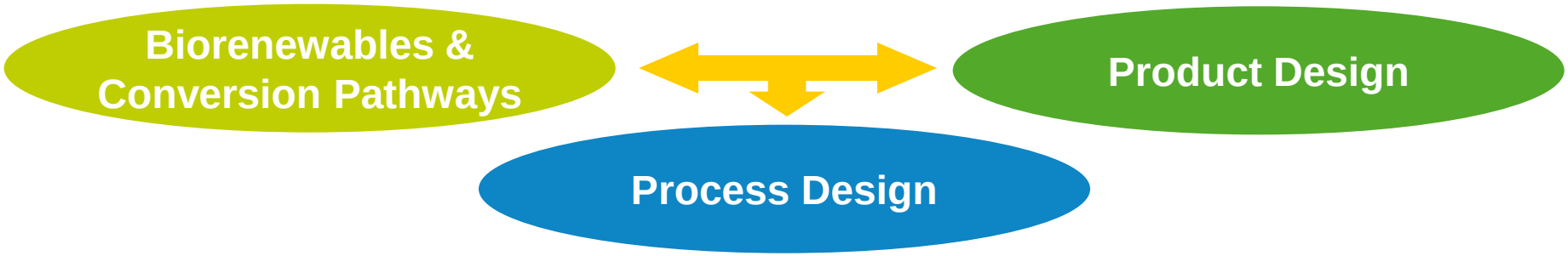
Reaction Network Flux Analysis (RNFA)

- motivated by Metabolic Flux Analysis (Schilling & Palsson, 1998);
- enables an early screening of biofuel processes based on
  - the mass balances,
  - **economic** and **ecological** criteria;
- can be extended to a multi-criteria evaluation;
- can be integrated with product design (Hechinger et al., 2010).

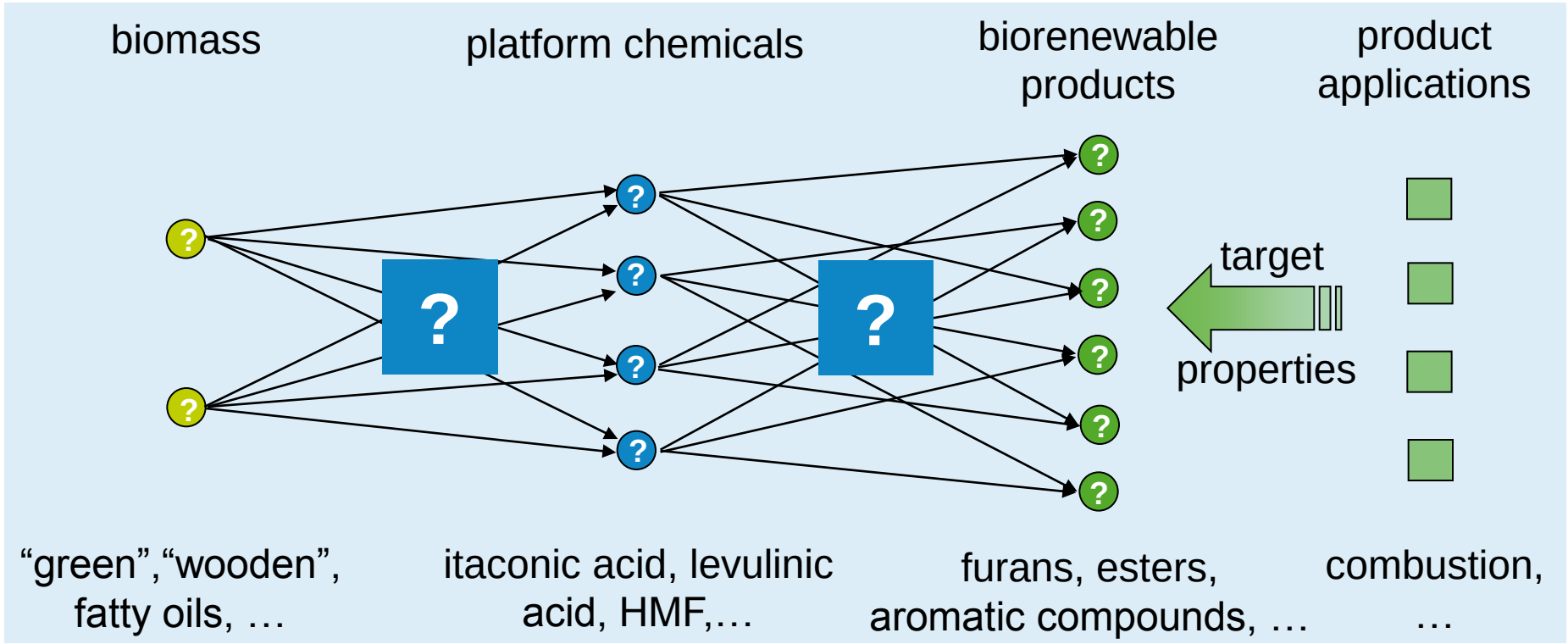
Reaction Network Flux Analysis (RNFA)

- guides the discovery of accessible biofuels and research in catalysis
- forms the starting point for model-based process synthesis and process integration.

The Whole Picture …



➢ **Which are the best raw materials and conversion pathways?**



NGP² - Next-Generation Processes and Products

ChemE fundamentals for next generation industrial value chains based on regenerative carbon resources (biomass, CO_2)…

AACHENER VERFAHRENSTECHNIK

Thank you for your attention.

Questions?

This work was performed as part of the Cluster of Excellence "Tailor-Made Fuels from Biomass“.

RWTH