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Tomorrow's Answers Today

Tony Kiss

TU Delft

Advanced Process Integration

Reactive Distillation + Dividing-Wall Column

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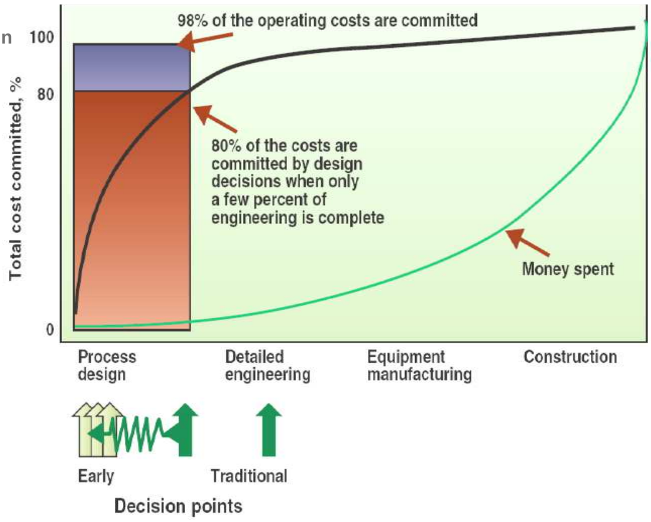
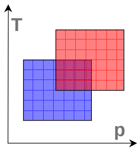
Process design impact on project costs

- ❖ Conceptual process design
- ❖ Steady-state simulations
- ❖ Dynamic simulations
- ❖ Sensitivity analysis
- ❖ Equipment sizing
- ❖ Process control
- ❖ Cost estimates



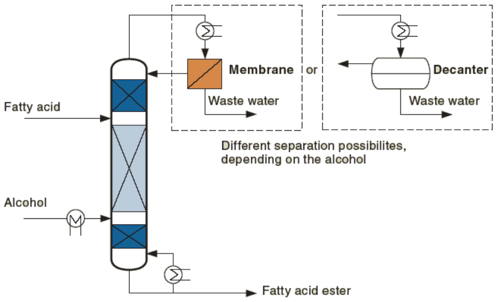
Source: *aspenONE Process Engineering Webinar 2008 - Capitalize on New Technologies for Emerging Energy Processes*

Reactive separation processes



- ➢ Combine reaction and separation into a single unit
- ➢ Match between reaction and distillation parameters
- ➢ Difference in relative volatility of product & one reactant
- ➢ Fast reaction not requiring a large amount of catalyst

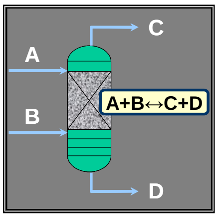
- ❖ Reactive Distillation
- ❖ Reactive Absorption
- ❖ Reactive Extraction
- ❖ Reactive Membrane Separation



Different separation possibilites, depending on the alcohol

Benefits of reactive separation

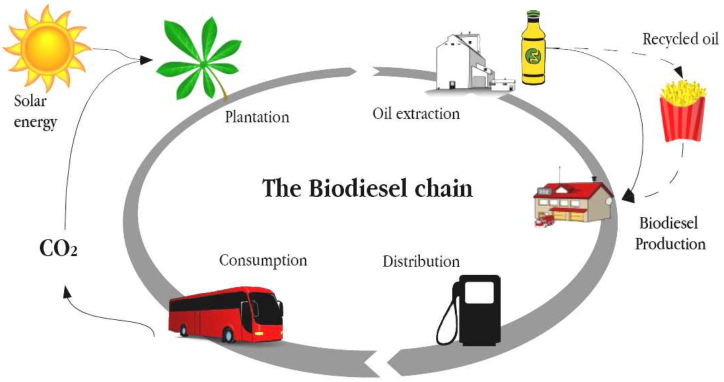
- ➢ Simplify complex processes
- ➢ Lower investment and operating costs
- ➢ Less waste and fewer by-products
- ➢ Improved product quality
- ➢ Reduced degradation of chemicals
- ➢ Surpass equilibrium limitations
- ➢ Enhance rate and conversion
- ➢ Achieve high selectivity
- ➢ Accomplish energy integration
- ➢ Improved separation efficiency
- ➢ Perform difficult separations



Reactive separation applications

- esterification
- trans-esterification
- hydrolysis
- etherification
- acetalization
- hydrogenation
- hydrodesulfurization
- dehydrogenation
- alkylation
- trans-alkylation
- dealkylation
- isomerization
- dimerization
- oligomerization
- hydration / de-hydration
- chlorination
- condensation of aldehydes
- condensation of aldols
- amination and amidation
- neutralization
- recovery and purification

Biodiesel life-cycle



☑ **Biodiesel** = FAME (fatty acids methyl esters) … *and fortune* **$$$**

☑ Very safe (high flash point), renewable, non-toxic, biodegradable

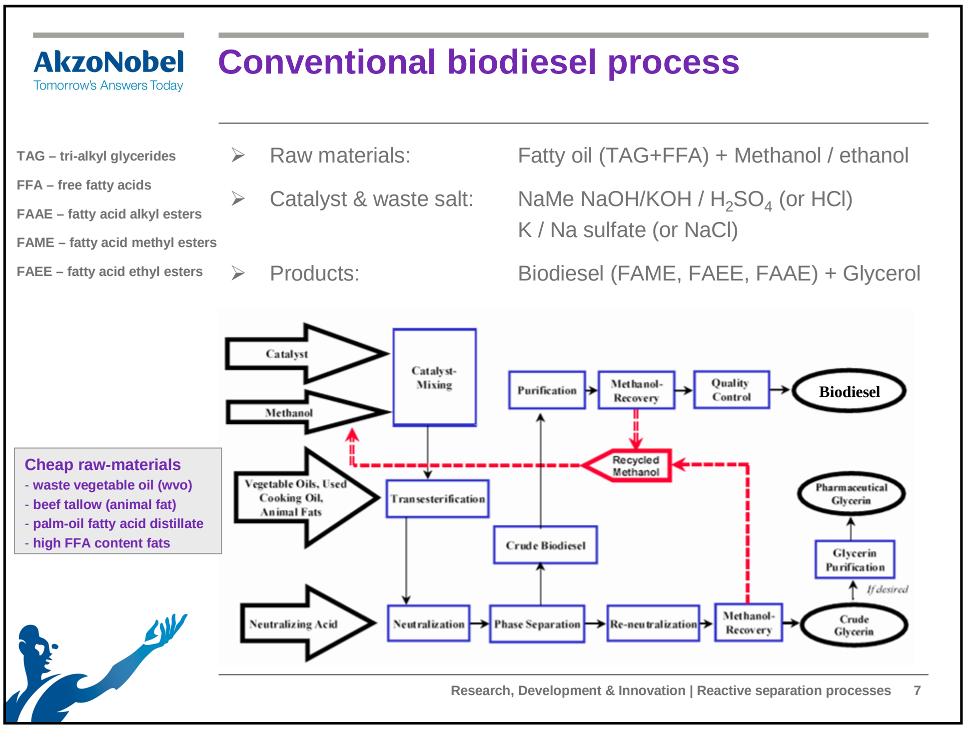
☑ Similar or better performance than petroleum diesel: higher cetane number

☑ **Less emissions than conventional petroleum diesel: –50% CO2, –30% soot**

☑ Blends of biodiesel + diesel usable in existing engines (e.g. B5, B20)

☑ **Raw materials:** vegetable oils, animal fat, waste cooking oils

☑ Positive life cycle energy balance: 3.2 per energy unit



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Conventional biodiesel process

TAG – tri-alkyl glycerides
FFA – free fatty acids
FAAE – fatty acid alkyl esters
FAME – fatty acid methyl esters
FAEE – fatty acid ethyl esters

➢ Raw materials:	Fatty oil (TAG+FFA) + Methanol / ethanol
➢ Catalyst & waste salt:	NaMe NaOH/KOH / H_2SO_4 (or HCl) K / Na sulfate (or NaCl)
➢ Products:	Biodiesel (FAME, FAEE, FAAE) + Glycerol

Cheap raw-materials
- waste vegetable oil (wvo)
- beef tallow (animal fat)
- palm-oil fatty acid distillate
- high FFA content fats

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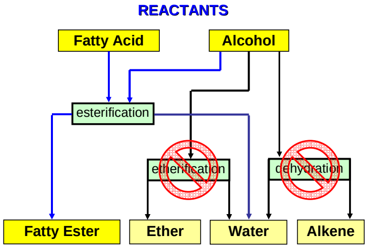
Biodiesel process comparison

Conventional process	Reactive separation process
• (Semi-)Batch esterification or trans-esterification	• Continuous operation at high production rates
• High alcohol / acid ratios	• Stoichiometric ratio
• **Homogeneous catalysis** **- Acid: H_2SO_4** **- Base: KOH, NaOH**	• **Heterogeneous catalysis** **- Solid acid catalyst** **- Solid base catalyst**
• Neutralization of catalyst	• No neutralization
• Salt waste streams	• No salt waste streams
• Difficult and costly separation	• Easy and inexpensive separation
• Large recycle of alcohol	• No recycle of alcohol
• Corrosive catalyst	• Environmentally friendly

The key to success is an active & selective solid acid/base catalyst

Catalyst & reaction pathways

A. A. Kiss, A. C. Dimian, G. Rothenberg,
Solid acid catalysts for biodiesel production - towards sustainable energy,
Advanced Synthesis and Catalysis, 348, 75-81, 2006.



REACTANTS

Fatty Acid **Alcohol**

esterification

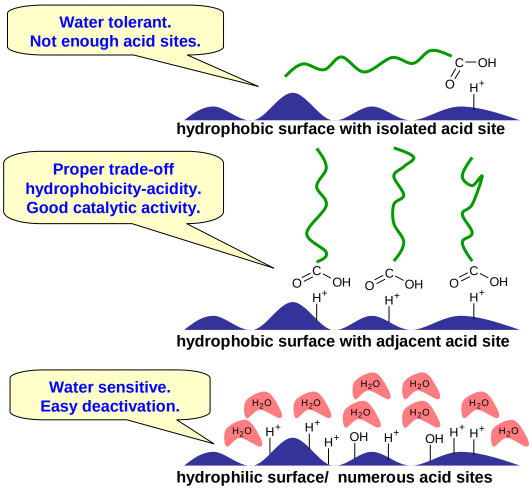
etherification

dehydration

Fatty Ester **Ether** **Water** **Alkene**

Main product

Secondary products



Water tolerant.
Not enough acid sites.

hydrophobic surface with isolated acid site

Proper trade-off
hydrophobicity-acidity.
Good catalytic activity.

hydrophobic surface with adjacent acid site

Water sensitive.
Easy deactivation.

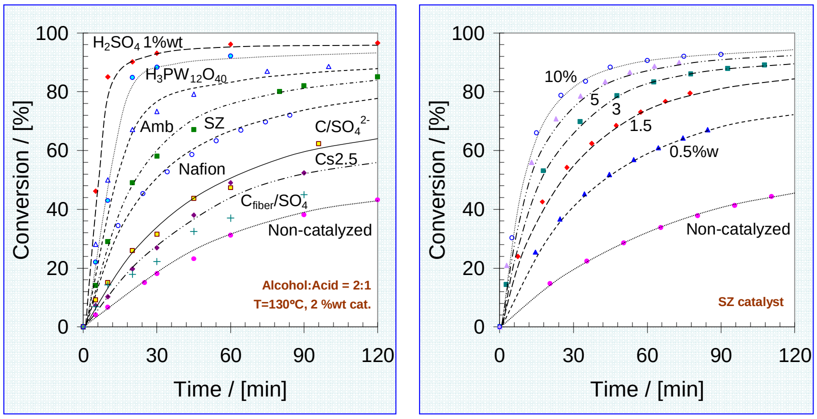
hydrophilic surface/ numerous acid sites

Influence of surface hydrophobicity on catalytic activity.

Catalyst selection

A. A. Kiss, A. C. Dimian, G. Rothenberg,
Solid acid catalysts for biodiesel production - towards sustainable energy,
Advanced Synthesis and Catalysis, 348, 75-81, 2006.

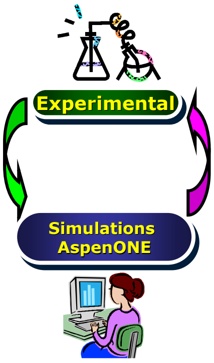
Esterification reaction profiles: FattyAcid + Methanol ↔ FattyEster + Water



Mixed metal oxides are the best choice as solid acid catalysts
Solid base catalysts are also available: calcium m/ethoxide

Simulation methods

A. A. Kiss,
Separative reactors for integrated production of bioethanol and biodiesel,
Computers & Chemical Engineering, 34, 812-820, 2010.



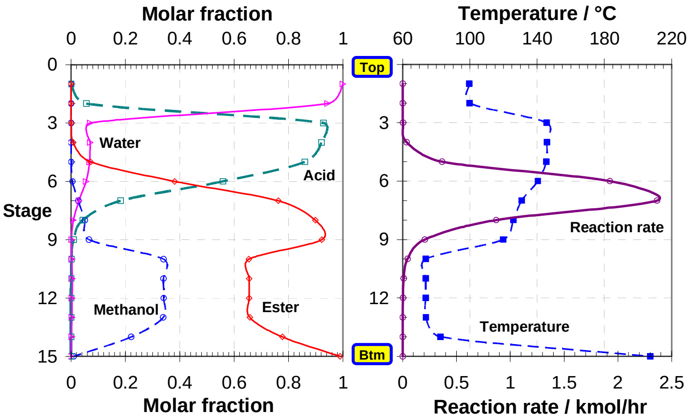
	Rigorous method	Shortcut method	Hybrid method
Requirements	Properties for all species. VLL data and BIP's for all pairs of components. Kinetic parameters for all reactions possible.	Properties for single fatty acid/ester/tri-glyceride. VLL data for the system ester/glycerol/alcohol. Asumed conversion (no kinetic parameters).	Single or reduced list of fatty acid/ester/TG. Short list of VLL data and BIP's for components. Reduced list of kinetic parameters, few reactions.
Benefits	Easy optimization of reaction and separation. High fidelity model. Usable for many plants. Easy comparison for various feedstocks.	Simple model. Fast simulations. Easy-to-build mass and energy balance. No data needed for all species present.	Optimization possible for reaction and separation. Certain ability to compare various feedstocks. Better model fidelity. Fast simulations for RTO.
Drawbacks	Slow simulations and convergence problems. Expensive measurements. Limited RTO and model based control usage.	No comparison possible for various feedstocks. Low-fidelity model. Less ability to use RTO.	More effort to build component list and get kinetic parameters. More work to find VLL data and regress BIP's.

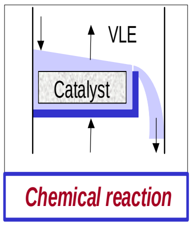
Linking experiments with modeling is imperative!
Optimal experimental design / Minimum kinetic requirements

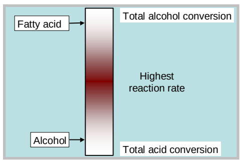
RD column profiles

A. A. Kiss, A. C. Dimian, G. Rothenberg,
Biodiesel by Reactive Distillation Powered by Metal Oxides,
Energy & Fuels, 22, 598-604, 2008.

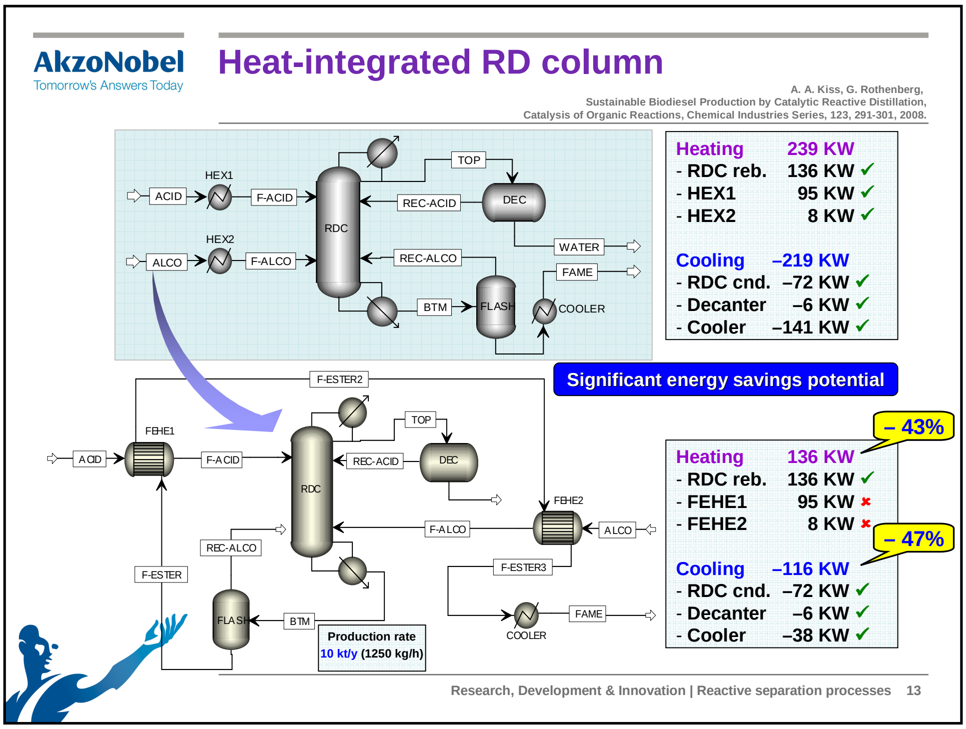
Esterification of fatty acid with methanol







Composition and temperature profiles in the reactive distillation column



Heat-integrated RD column

A. A. Kiss, G. Rothenberg,
Sustainable Biodiesel Production by Catalytic Reactive Distillation,
Catalysis of Organic Reactions, Chemical Industries Series, 123, 291-301, 2008.

Heating	**239 KW**
- RDC reb.	136 KW ✓
- HEX1	95 KW ✓
- HEX2	8 KW ✓
Cooling	**–219 KW**
- RDC cnd.	–72 KW ✓
- Decanter	–6 KW ✓
- Cooler	–141 KW ✓

Significant energy savings potential

– 43%

– 47%

Heating	**136 KW**
- RDC reb.	136 KW ✓
- FEHE1	95 KW ✗
- FEHE2	8 KW ✗
Cooling	**–116 KW**
- RDC cnd.	–72 KW ✓
- Decanter	–6 KW ✓
- Cooler	–38 KW ✓

Production rate
10 kt/y (1250 kg/h)

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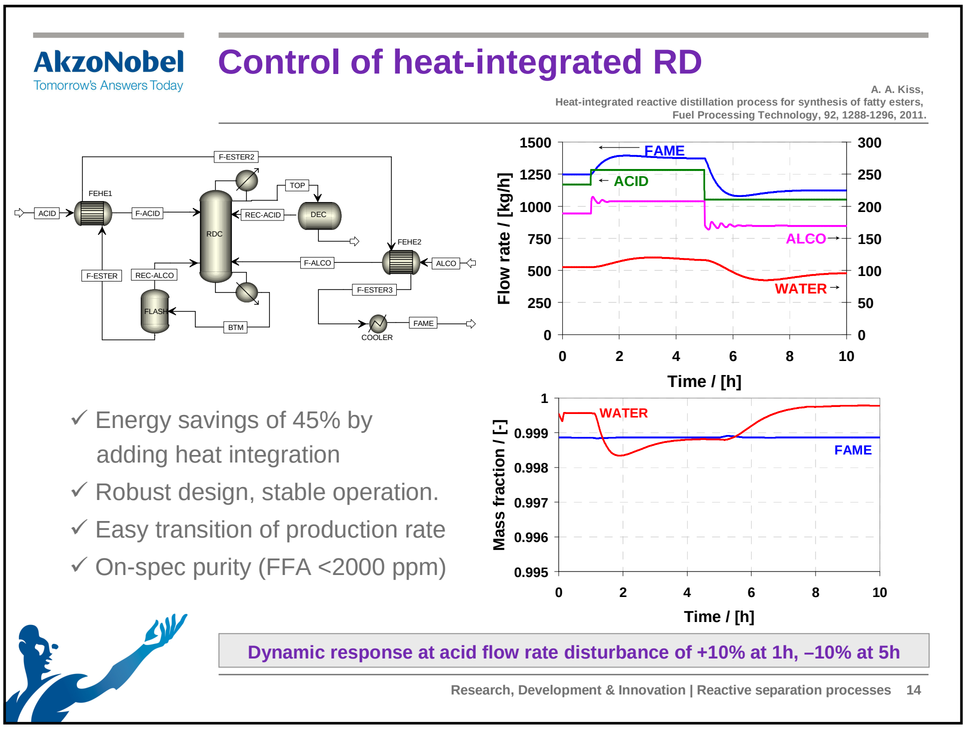

Control of heat-integrated RD

A. A. Kiss,
Heat-integrated reactive distillation process for synthesis of fatty esters,
Fuel Processing Technology, 92, 1288-1296, 2011.

- ✓ Energy savings of 45% by adding heat integration
- ✓ Robust design, stable operation.
- ✓ Easy transition of production rate
- ✓ On-spec purity (FFA <2000 ppm)

Dynamic response at acid flow rate disturbance of +10% at 1h, –10% at 5h

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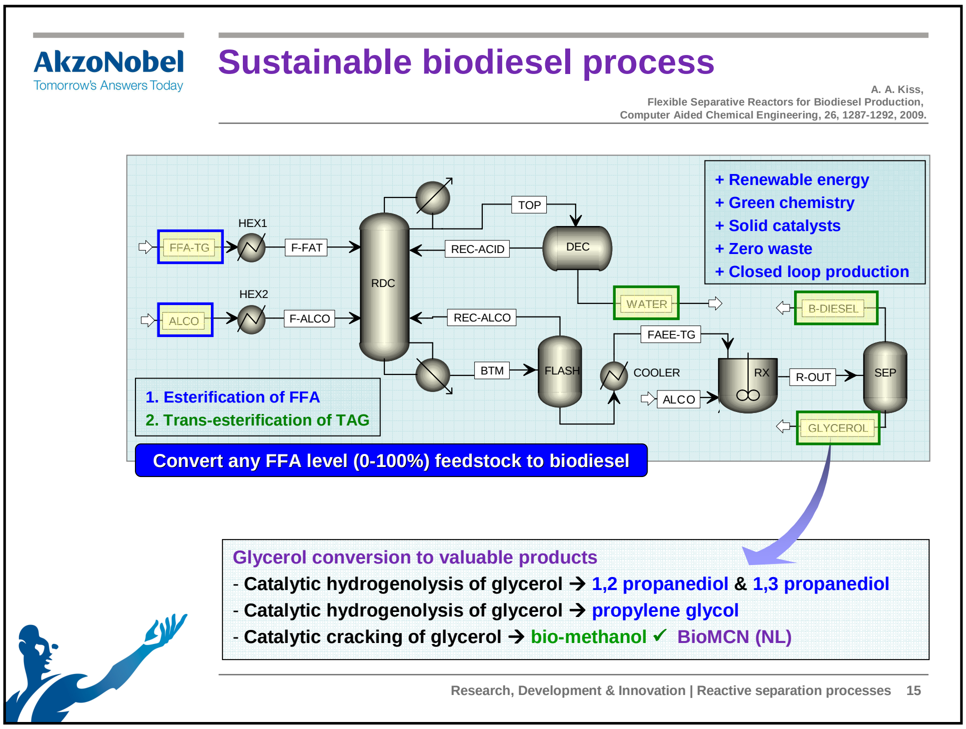


Sustainable biodiesel process

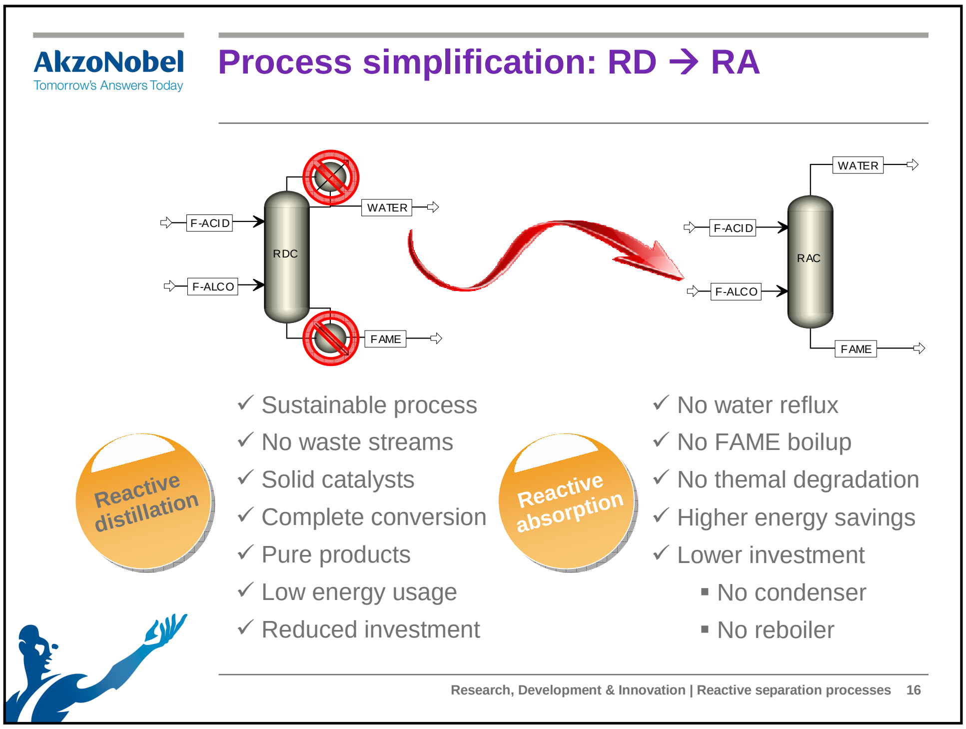
A. A. Kiss,
Flexible Separative Reactors for Biodiesel Production,
Computer Aided Chemical Engineering, 26, 1287-1292, 2009.

- + Renewable energy
- + Green chemistry
- + Solid catalysts
- + Zero waste
- + Closed loop production

1. Esterification of FFA
2. Trans-esterification of TAG

Convert any FFA level (0-100%) feedstock to biodiesel

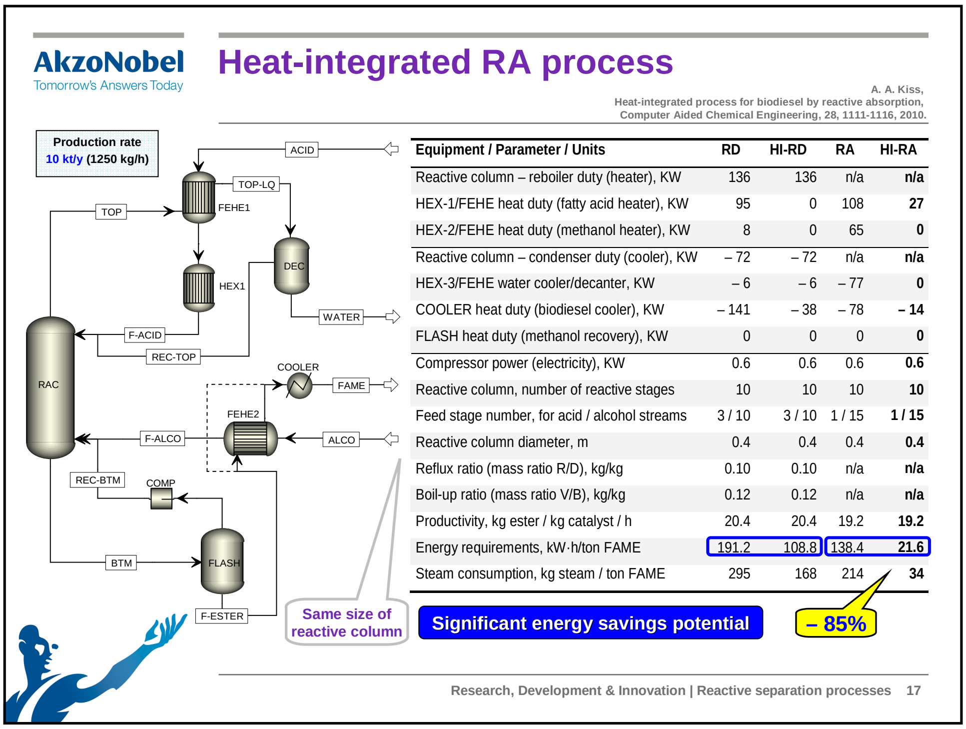
Glycerol conversion to valuable products
- Catalytic hydrogenolysis of glycerol → 1,2 propanediol & 1,3 propanediol
- Catalytic hydrogenolysis of glycerol → propylene glycol
- Catalytic cracking of glycerol → bio-methanol ✓ BioMCN (NL)



Process simplification: RD → RA

- ✓ Sustainable process
- ✓ No waste streams
- ✓ Solid catalysts
- ✓ Complete conversion
- ✓ Pure products
- ✓ Low energy usage
- ✓ Reduced investment

- ✓ No water reflux
- ✓ No FAME boilup
- ✓ No themal degradation
- ✓ Higher energy savings
- ✓ Lower investment
  - No condenser
  - No reboiler



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Heat-integrated RA process

A. A. Kiss,
Heat-integrated process for biodiesel by reactive absorption,
Computer Aided Chemical Engineering, 28, 1111-1116, 2010.

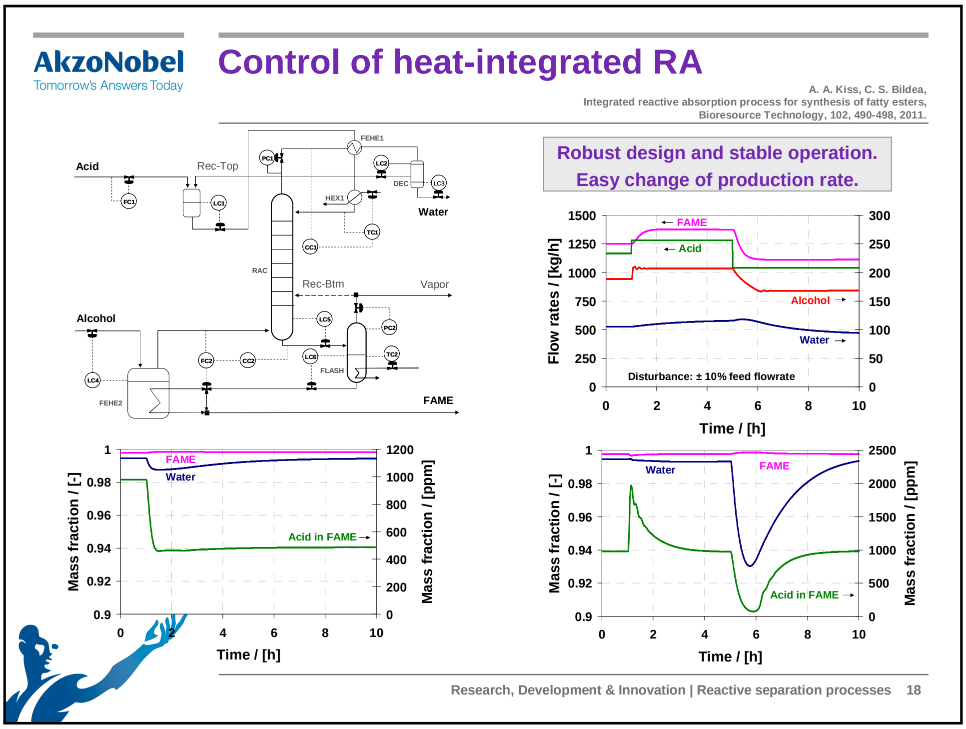
Production rate
10 kt/y (1250 kg/h)

Equipment / Parameter / Units	RD	HI-RD	RA	HI-RA
Reactive column – reboiler duty (heater), KW	136	136	n/a	**n/a**
HEX-1/FEHE heat duty (fatty acid heater), KW	95	0	108	**27**
HEX-2/FEHE heat duty (methanol heater), KW	8	0	65	**0**
Reactive column – condenser duty (cooler), KW	– 72	– 72	n/a	**n/a**
HEX-3/FEHE water cooler/decanter, KW	– 6	– 6	– 77	**0**
COOLER heat duty (biodiesel cooler), KW	– 141	– 38	– 78	**– 14**
FLASH heat duty (methanol recovery), KW	0	0	0	**0**
Compressor power (electricity), KW	0.6	0.6	0.6	**0.6**
Reactive column, number of reactive stages	10	10	10	**10**
Feed stage number, for acid / alcohol streams	3 / 10	3 / 10	1 / 15	**1 / 15**
Reactive column diameter, m	0.4	0.4	0.4	**0.4**
Reflux ratio (mass ratio R/D), kg/kg	0.10	0.10	n/a	**n/a**
Boil-up ratio (mass ratio V/B), kg/kg	0.12	0.12	n/a	**n/a**
Productivity, kg ester / kg catalyst / h	20.4	20.4	19.2	**19.2**
Energy requirements, kW·h/ton FAME	191.2	108.8	138.4	**21.6**
Steam consumption, kg steam / ton FAME	295	168	214	**34**

Same size of reactive column

Significant energy savings potential

– 85%



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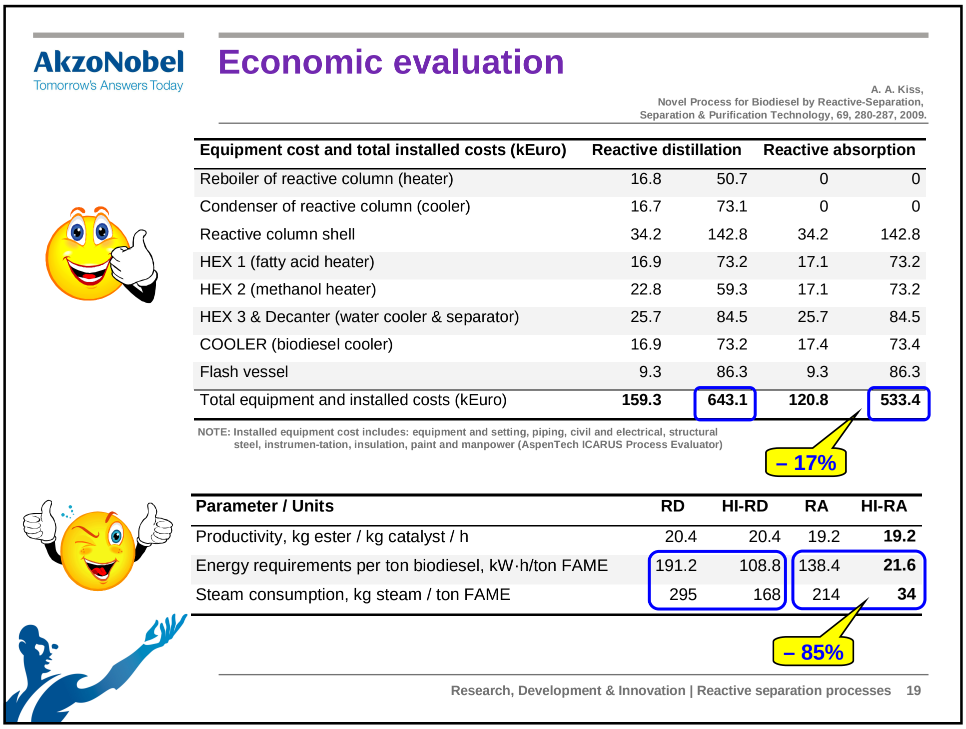
Control of heat-integrated RA

A. A. Kiss, C. S. Bildea,
Integrated reactive absorption process for synthesis of fatty esters,
Bioresource Technology, 102, 490-498, 2011.

Robust design and stable operation.
Easy change of production rate.



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Economic evaluation

A. A. Kiss,
Novel Process for Biodiesel by Reactive-Separation,
Separation & Purification Technology, 69, 280-287, 2009.

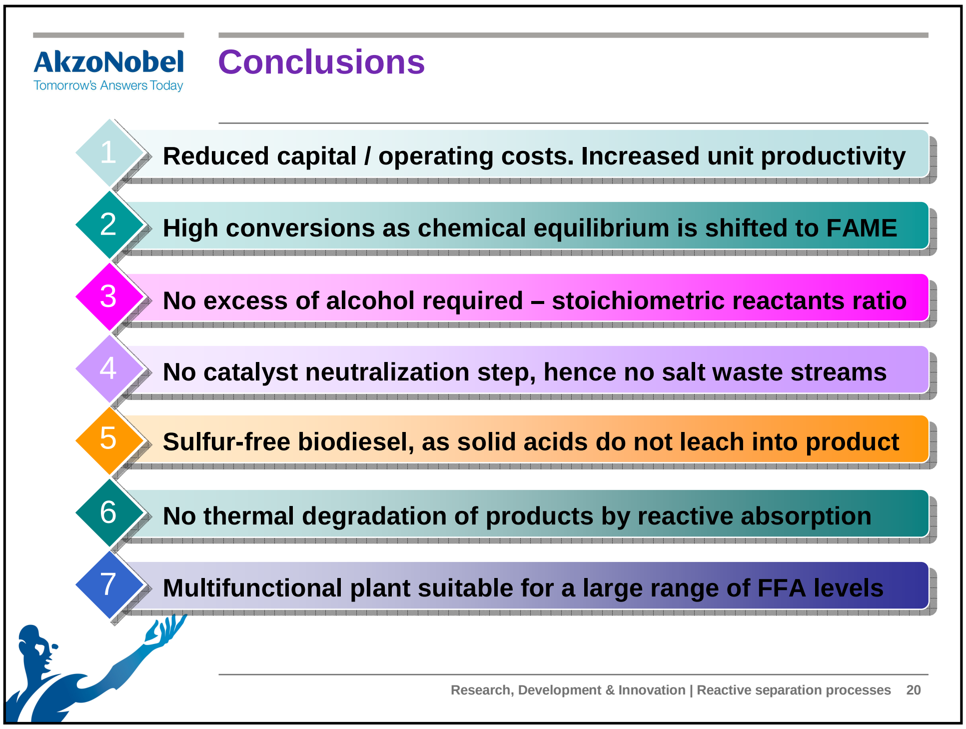
Equipment cost and total installed costs (kEuro)	Reactive distillation		Reactive absorption	
Reboiler of reactive column (heater)	16.8	50.7	0	0
Condenser of reactive column (cooler)	16.7	73.1	0	0
Reactive column shell	34.2	142.8	34.2	142.8
HEX 1 (fatty acid heater)	16.9	73.2	17.1	73.2
HEX 2 (methanol heater)	22.8	59.3	17.1	73.2
HEX 3 & Decanter (water cooler & separator)	25.7	84.5	25.7	84.5
COOLER (biodiesel cooler)	16.9	73.2	17.4	73.4
Flash vessel	9.3	86.3	9.3	86.3
Total equipment and installed costs (kEuro)	**159.3**	**643.1**	**120.8**	**533.4**

NOTE: Installed equipment cost includes: equipment and setting, piping, civil and electrical, structural steel, instrumen-tation, insulation, paint and manpower (AspenTech ICARUS Process Evaluator)

– 17%

Parameter / Units	RD	HI-RD	RA	HI-RA
Productivity, kg ester / kg catalyst / h	20.4	20.4	19.2	**19.2**
Energy requirements per ton biodiesel, kW·h/ton FAME	191.2	108.8	138.4	**21.6**
Steam consumption, kg steam / ton FAME	295	168	214	**34**

– 85%



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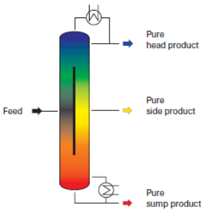
Conclusions

1. Reduced capital / operating costs. Increased unit productivity
2. High conversions as chemical equilibrium is shifted to FAME
3. No excess of alcohol required – stoichiometric reactants ratio
4. No catalyst neutralization step, hence no salt waste streams
5. Sulfur-free biodiesel, as solid acids do not leach into product
6. No thermal degradation of products by reactive absorption
7. Multifunctional plant suitable for a large range of FFA levels

Dividing-Wall Column – timeline

I. Dejanovic, Lj. Matijasevic, Z. Olujic,
Dividing wall column - A breakthrough towards sustainable distilling,
Chemical Engineering and Processing: Process Intensification, 49, 559-580, 2010.



- 1935 – Patent by D.A. Monro (US 2,134,882 / 1938)
- 1936 – Patent by A.J. Brugma (US 2,295,256 / 1942)
- 1946 – Patent by R.O. Wright (US 2,471,134 / 1949)
- 1965 – First theoretical work by F. Petlyuk
- 1985 – First built dividing-wall column (BASF, G. Kaibel)
- 2000 – Largest application for hexane plant (Linde AG)
  Sasol plant (~70-80m height, 5-6m diameter)
- 2010 – BASF operates ~70 dividing wall columns
  Julius Montz GmbH – world leading supplier of DWC (>100)
  Engineering know-how developed by Linde AG, Uhde, UOP
  Sulzer Chemtech & Koch-Glitsch are also active in this field

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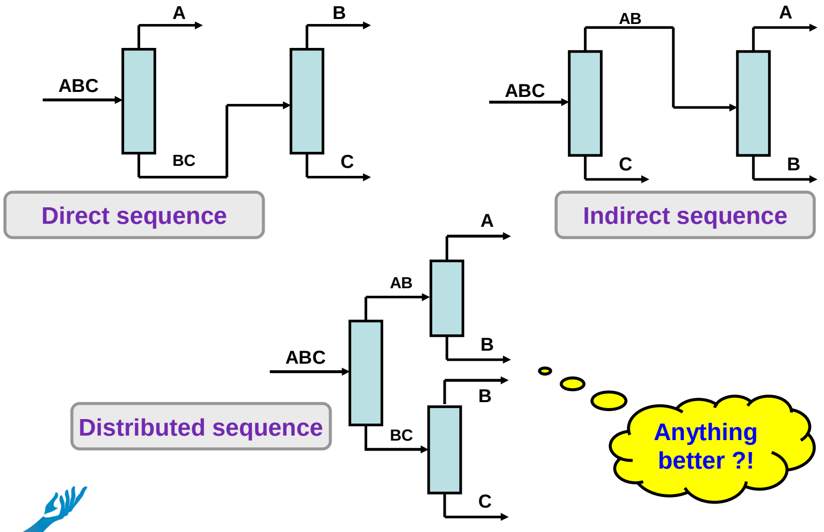
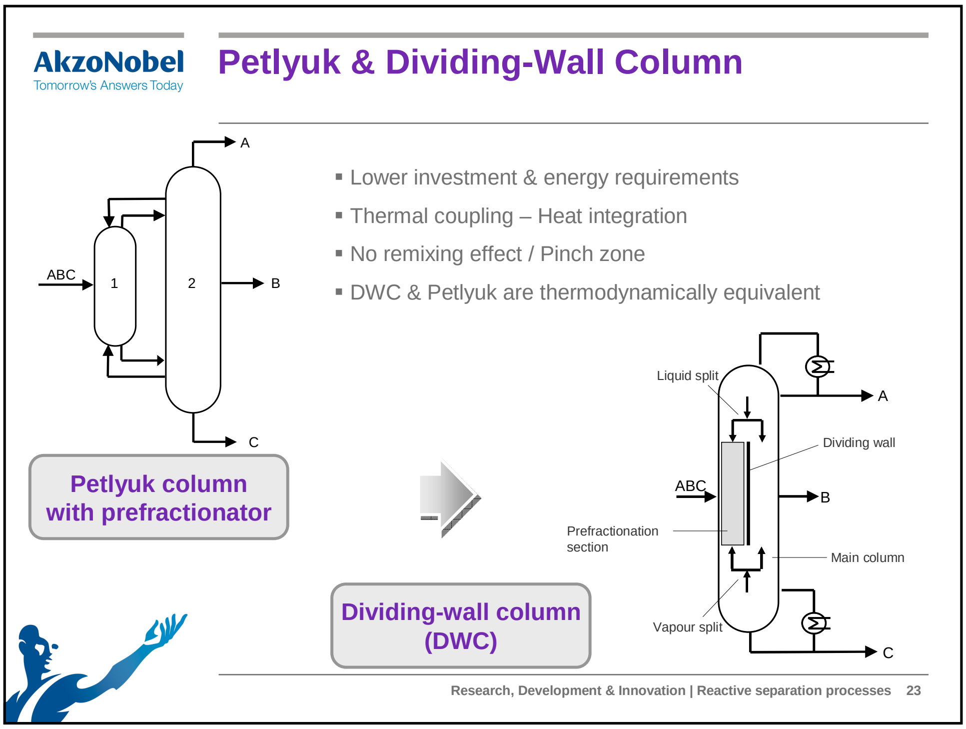
Ternary separation systems

$\alpha_A > \alpha_B > \alpha_C$





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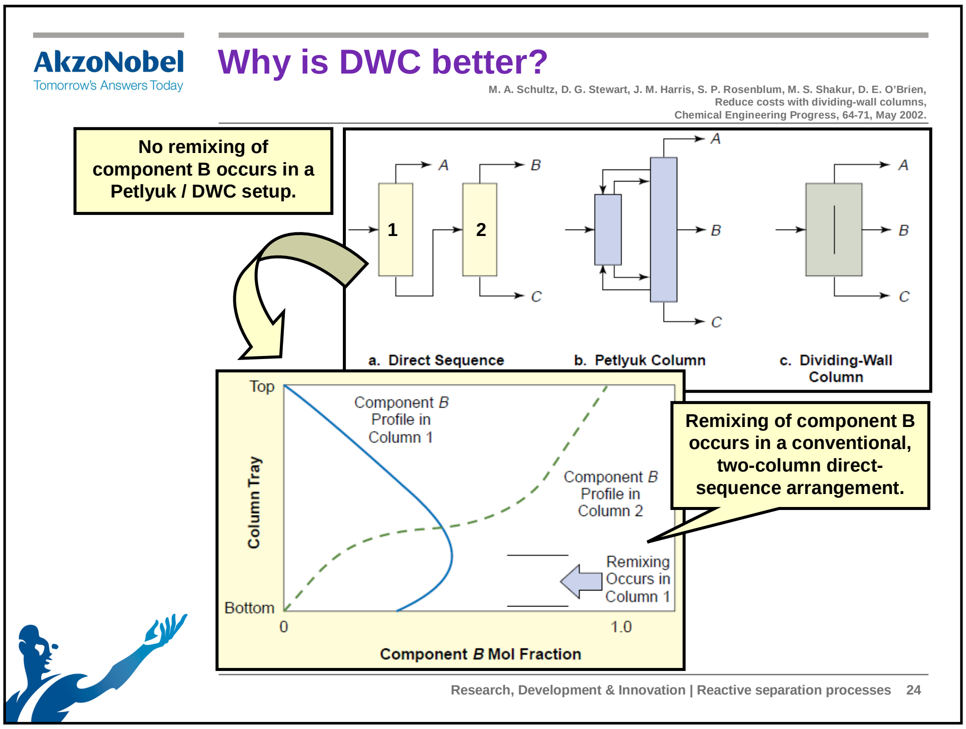
Petlyuk & Dividing-Wall Column

- Lower investment & energy requirements
- Thermal coupling – Heat integration
- No remixing effect / Pinch zone
- DWC & Petlyuk are thermodynamically equivalent

Petlyuk column with prefractionator

Dividing-wall column (DWC)



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Why is DWC better?

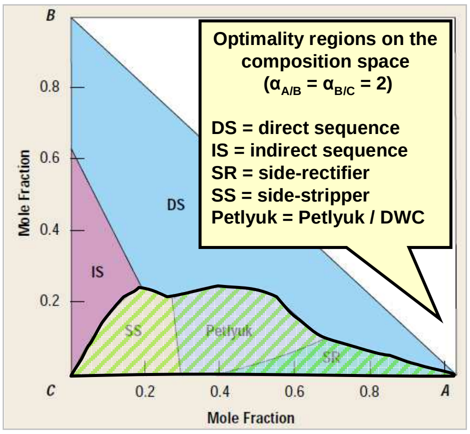
M. A. Schultz, D. G. Stewart, J. M. Harris, S. P. Rosenblum, M. S. Shakur, D. E. O'Brien,
Reduce costs with dividing-wall columns,
Chemical Engineering Progress, 64-71, May 2002.

No remixing of component B occurs in a Petlyuk / DWC setup.

Remixing of component B occurs in a conventional, two-column direct-sequence arrangement.

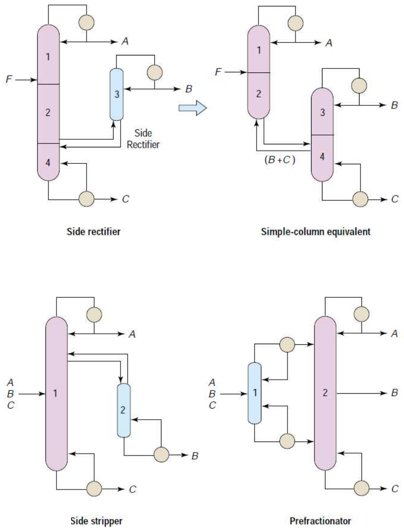
DWC – when can it be used?

P. B. Shah,
Squeeze more out of complex columns,
Chemical Engineering Progress, 46-55, July 2002.



Optimality regions on the composition space
($\alpha_{A/B} = \alpha_{B/C} = 2$)

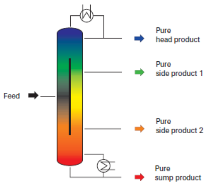
DS = direct sequence
IS = indirect sequence
SR = side-rectifier
SS = side-stripper
Petlyuk = Petlyuk / DWC

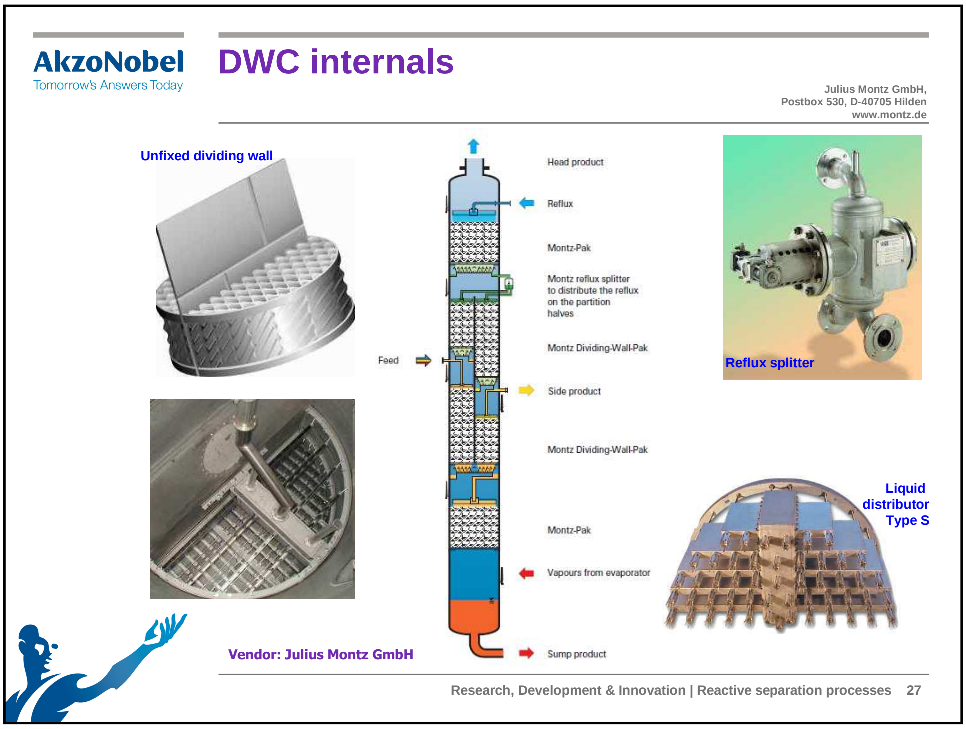


DWC advantages & drawbacks

I. Dejanovic, Lj. Matijasevic, Z. Olujic,
Dividing wall column - A breakthrough towards sustainable distilling,
Chemical Engineering and Processing: Process Intensification, 49, 559-580, 2010.

- Improved thermodynamic efficiency
- High purity also for the middle product
- Compact configuration: 2 columns in 1 shell
- Around 25-30% energy savings (no remixing effect)
- Reduce capital investment by 20-30%
  due to the use of only 1 reboiler + 1 condenser
- Effectively applicable to many processes
- Large range of applications
  - D = 0.04 – 6 m, H = 2.5 – 80+ m
  - P = 10 mbar – 10 bar, up to 100 trays, purity levels ~1 ppm
- **Drawbacks**
  - One operating pressure
  - Higher pressure drop
  - Higher temperature difference

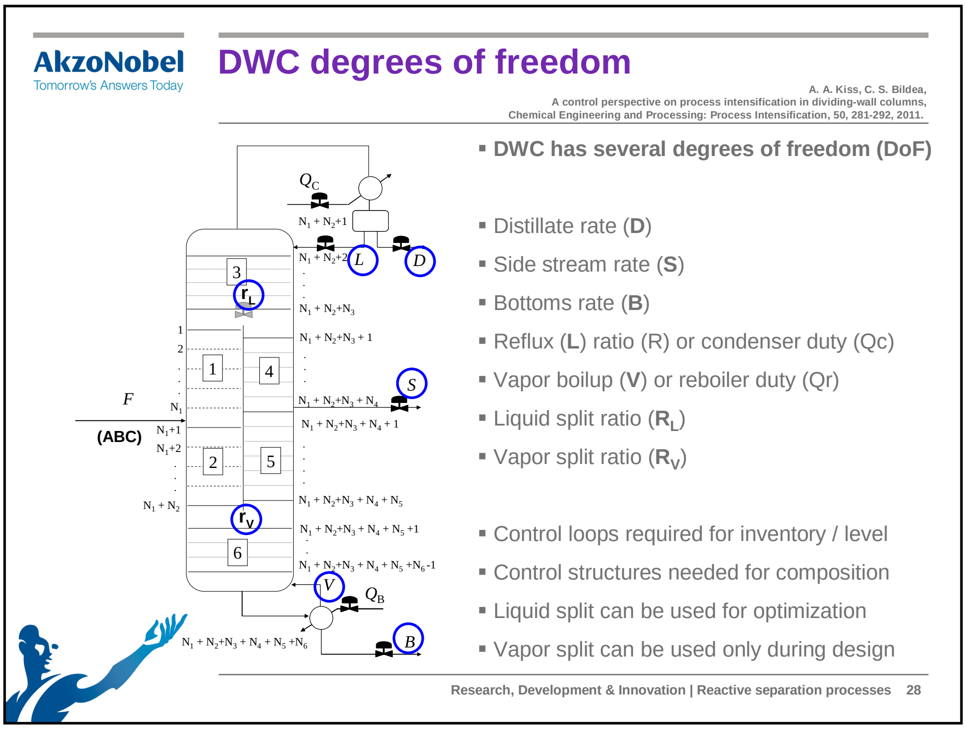




DWC internals

Julius Montz GmbH,
Postbox 530, D-40705 Hilden
www.montz.de

Vendor: Julius Montz GmbH



DWC degrees of freedom

A. A. Kiss, C. S. Bildea,
A control perspective on process intensification in dividing-wall columns,
Chemical Engineering and Processing: Process Intensification, 50, 281-292, 2011.

- **DWC has several degrees of freedom (DoF)**

- Distillate rate (**D**)
- Side stream rate (**S**)
- Bottoms rate (**B**)
- Reflux (**L**) ratio (R) or condenser duty (Qc)
- Vapor boilup (**V**) or reboiler duty (Qr)
- Liquid split ratio (**R_L**)
- Vapor split ratio (**R_V**)

- Control loops required for inventory / level
- Control structures needed for composition
- Liquid split can be used for optimization
- Vapor split can be used only during design

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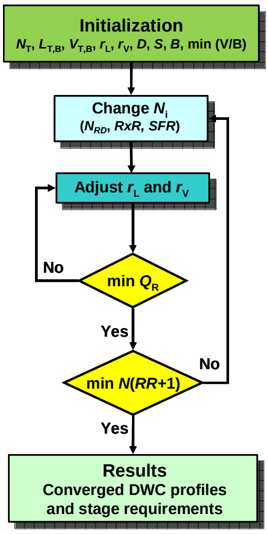
DWC design procedure

Dejanović I., Matijašević Lj., Olujic Z.,
An effective method for establishing the stage and reflux requirement of three-product dividing wall columns,
Chemical and Biochemical Engineering Quarterly, 25 (2011), 147-157.



Initialization
N_T, $L_{T,B}$, $V_{T,B}$, r_L, r_V, D, S, B, min (V/B)

Change N_i
(N_{RD}, *RxR*, *SFR*)

Adjust r_L and r_V

min Q_R

No

Yes

min *N*(*RR*+1)

No

Yes

Results
Converged DWC profiles and stage requirements

Algorithm of the detailed DWC model

1. Define separation task: feed composition and state, recoveries of key components.

2. Calculate reboiler vapour flow rate and distillate flow rate for every possible binary split of key components, for $N_T > 4N_{min}$ (as using Fenske equation to estimate the N_{min})

3. Construct V_{min} diagram and calculate product flow rates, as well as internal liquid and vapour flow rates.

4. Initialize rigorous sequential simulation using values from V_{min} diagram.

5. Optimize vapour and liquid split ratios until Q_R is minimized, while maintaining product purities.

6. Repeat calculation gradually reducing the number of stages in each section until N(RR+1) is minimized.

The procedure can be extended also to:
R-DWC, E-DWC and A-DWC

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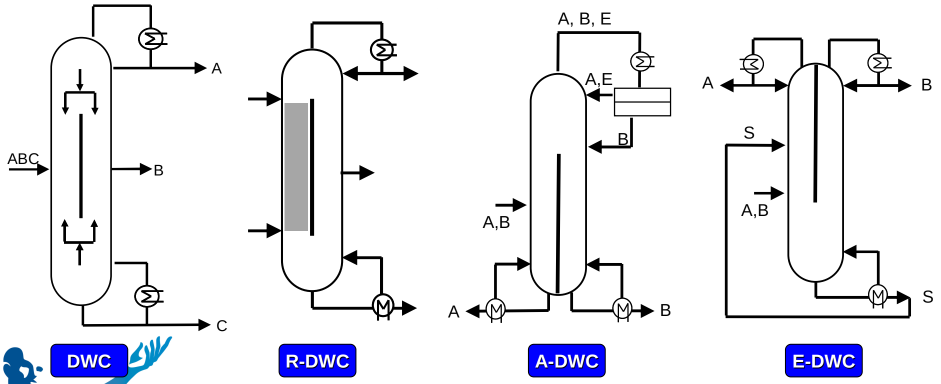
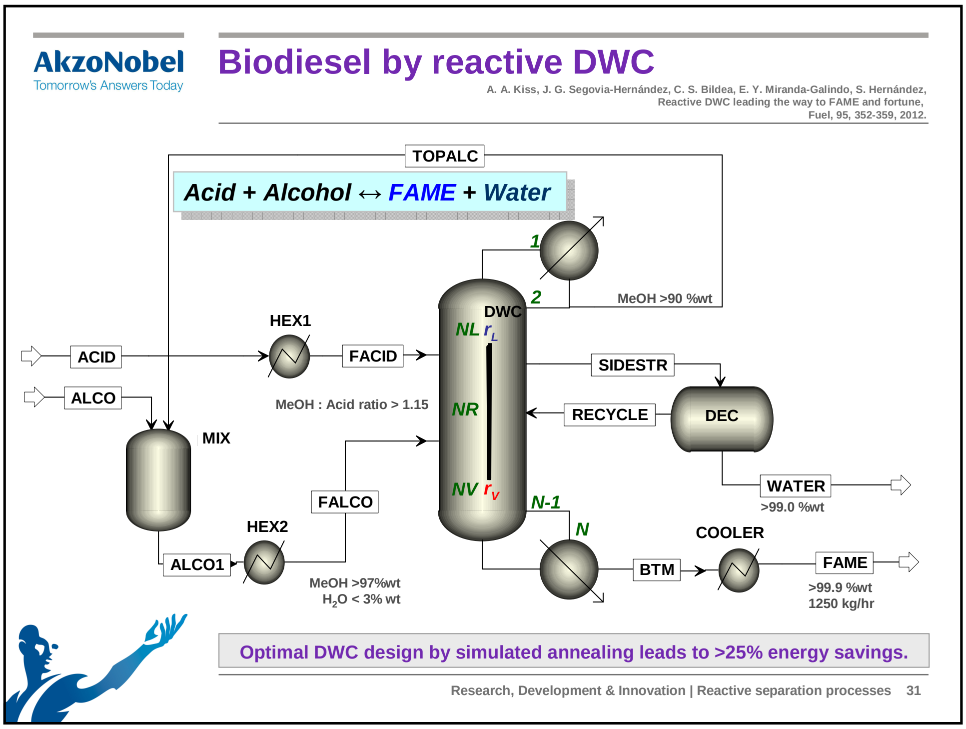
DWC applications

O. Yildirim, A. A. Kiss, E. Y. Kenig,
Dividing-wall columns in chemical process industry: A review on current activities,
Separation & Purification Technology, 80, 403-417, 2011.

- Multi-component separations (DWC)
- Reactive distillation (R-DWC)
- Azeotropic distillation (A-DWC)
- Extractive distillation (E-DWC)



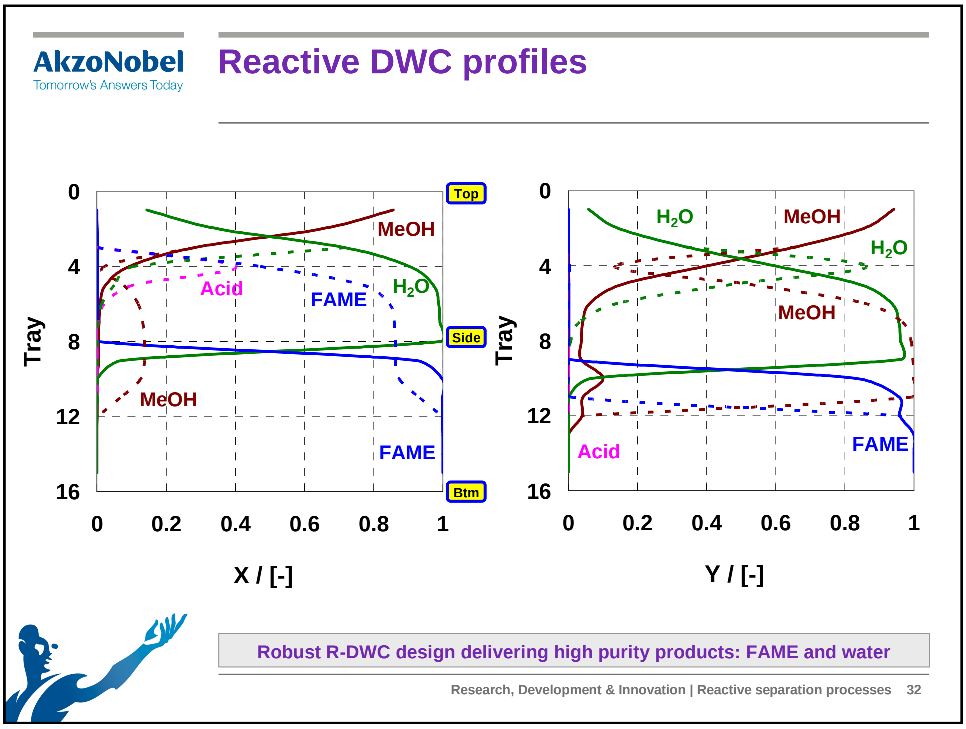


Biodiesel by reactive DWC

A. A. Kiss, J. G. Segovia-Hernández, C. S. Bildea, E. Y. Miranda-Galindo, S. Hernández,
Reactive DWC leading the way to FAME and fortune,
Fuel, 95, 352-359, 2012.

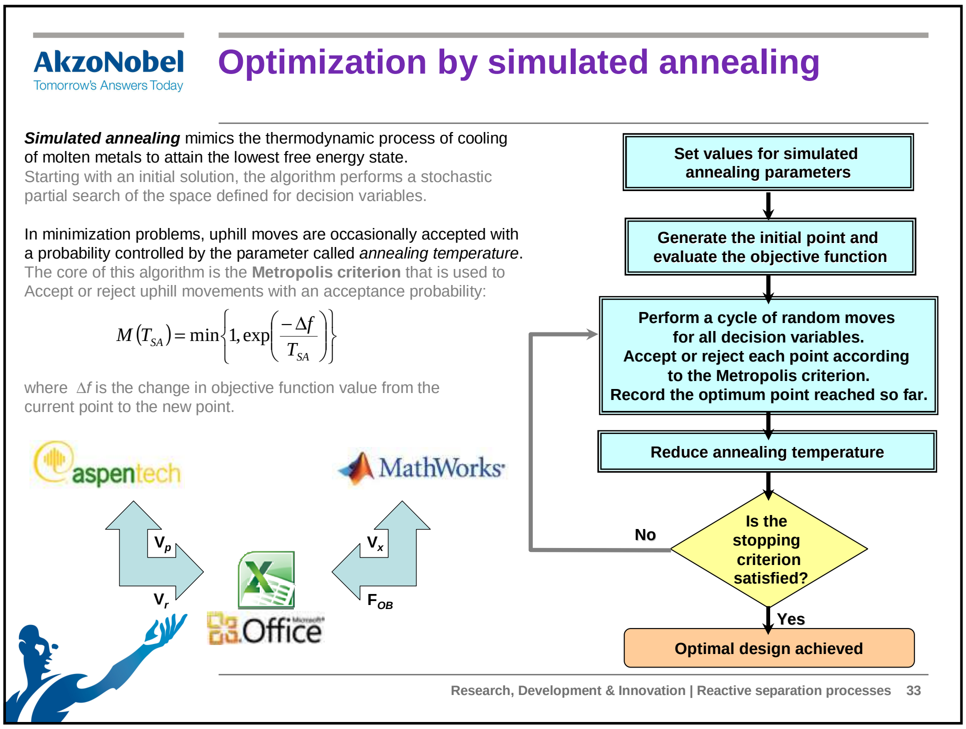
Acid + Alcohol ↔ FAME + Water

Optimal DWC design by simulated annealing leads to >25% energy savings.



Reactive DWC profiles

Robust R-DWC design delivering high purity products: FAME and water



Optimization by simulated annealing

Simulated annealing mimics the thermodynamic process of cooling of molten metals to attain the lowest free energy state.
Starting with an initial solution, the algorithm performs a stochastic partial search of the space defined for decision variables.

In minimization problems, uphill moves are occasionally accepted with a probability controlled by the parameter called *annealing temperature*.
The core of this algorithm is the **Metropolis criterion** that is used to Accept or reject uphill movements with an acceptance probability:

$$M\left(T_{SA}\right)=\min\left\{1,\exp\left(\frac{-\Delta f}{T_{SA}}\right)\right\}$$

where Δf is the change in objective function value from the current point to the new point.

Set values for simulated annealing parameters

Generate the initial point and evaluate the objective function

**Perform a cycle of random moves for all decision variables.
Accept or reject each point according to the Metropolis criterion.
Record the optimum point reached so far.**

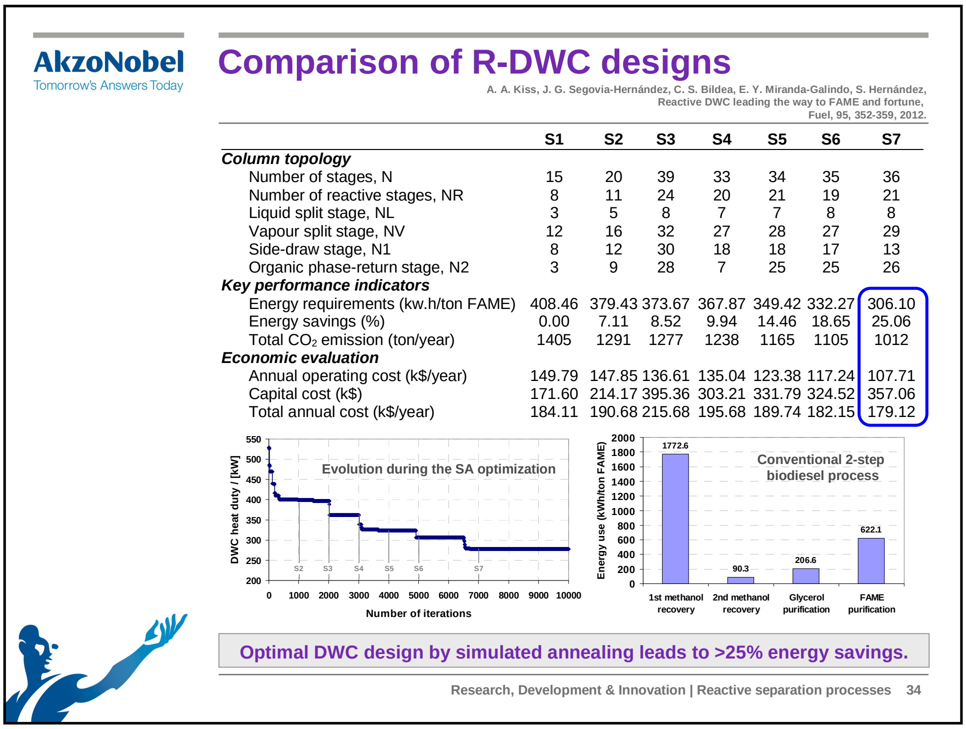
Reduce annealing temperature

Is the stopping criterion satisfied?

No

Yes

Optimal design achieved



Comparison of R-DWC designs

A. A. Kiss, J. G. Segovia-Hernández, C. S. Bildea, E. Y. Miranda-Galindo, S. Hernández,
Reactive DWC leading the way to FAME and fortune,
Fuel, 95, 352-359, 2012.

	S1	S2	S3	S4	S5	S6	S7
Column topology							
Number of stages, N	15	20	39	33	34	35	36
Number of reactive stages, NR	8	11	24	20	21	19	21
Liquid split stage, NL	3	5	8	7	7	8	8
Vapour split stage, NV	12	16	32	27	28	27	29
Side-draw stage, N1	8	12	30	18	18	17	13
Organic phase-return stage, N2	3	9	28	7	25	25	26
Key performance indicators							
Energy requirements (kw.h/ton FAME)	408.46	379.43	373.67	367.87	349.42	332.27	306.10
Energy savings (%)	0.00	7.11	8.52	9.94	14.46	18.65	25.06
Total CO_2 emission (ton/year)	1405	1291	1277	1238	1165	1105	1012
Economic evaluation							
Annual operating cost (k$/year)	149.79	147.85	136.61	135.04	123.38	117.24	107.71
Capital cost (k$)	171.60	214.17	395.36	303.21	331.79	324.52	357.06
Total annual cost (k$/year)	184.11	190.68	215.68	195.68	189.74	182.15	179.12

Optimal DWC design by simulated annealing leads to >25% energy savings.

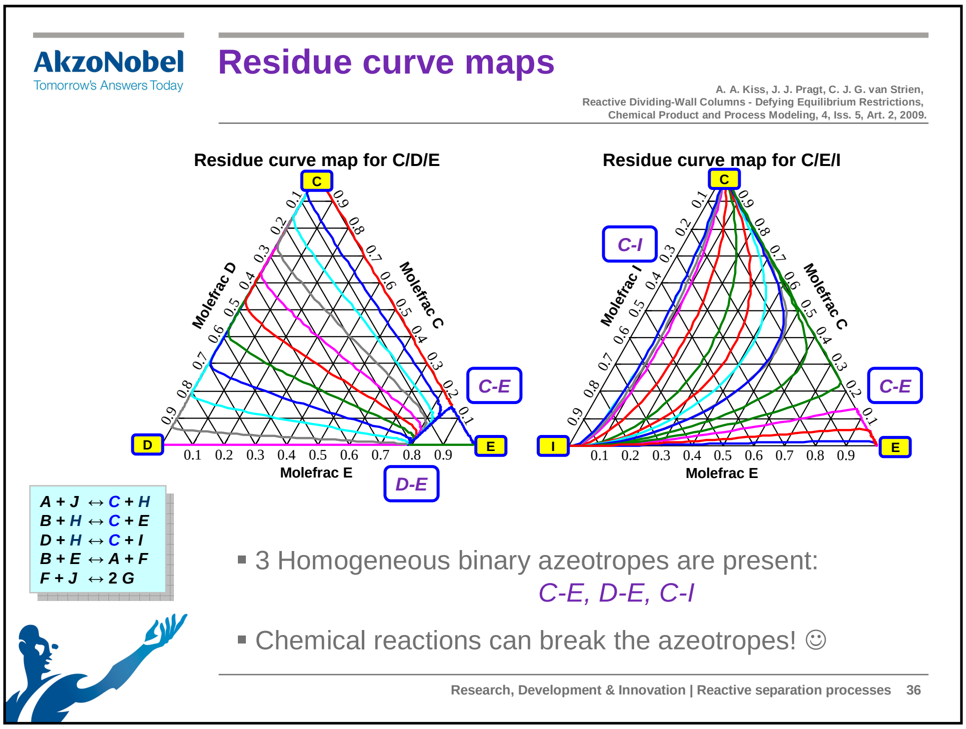
AN industrial case study

A. A. Kiss, J. J. Pragt, C. J. G. van Strien,
Reactive Dividing-Wall Columns - How to get more with less resources?,
Chemical Engineering Communications, 196, 1366-1374, 2009.

- Fast equilibrium of 10 components
- Homogeneous catalyst
- 3 Homogeneous binary azeotropes
- Relative volatility: *A* > *B* > … > *H* > *I*

$A + J \leftrightarrow C + H$
$B + H \leftrightarrow C + E$
$D + H \leftrightarrow C + I$
$B + E \leftrightarrow A + F$
$F + J \leftrightarrow 2\,G$

- Due to market changes one by-product C becomes more expensive than main product H
- Current plant not suitable for production of C
- Reactive DWC design reduces costs by ~35%
- Energy savings of 15% are also possible
- Simulation results show feasible implementation

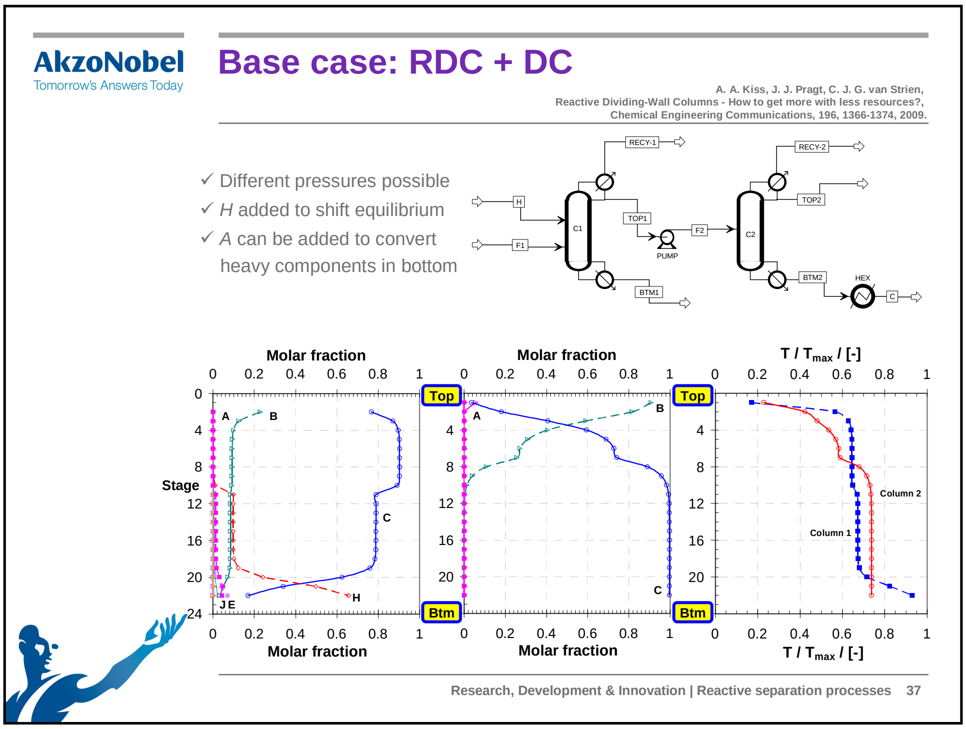


Residue curve maps

A. A. Kiss, J. J. Pragt, C. J. G. van Strien,
Reactive Dividing-Wall Columns - Defying Equilibrium Restrictions,
Chemical Product and Process Modeling, 4, Iss. 5, Art. 2, 2009.

$A + J \leftrightarrow C + H$
$B + H \leftrightarrow C + E$
$D + H \leftrightarrow C + I$
$B + E \leftrightarrow A + F$
$F + J \leftrightarrow 2\,G$

- 3 Homogeneous binary azeotropes are present:
  C-E, D-E, C-I
- Chemical reactions can break the azeotropes! ☺



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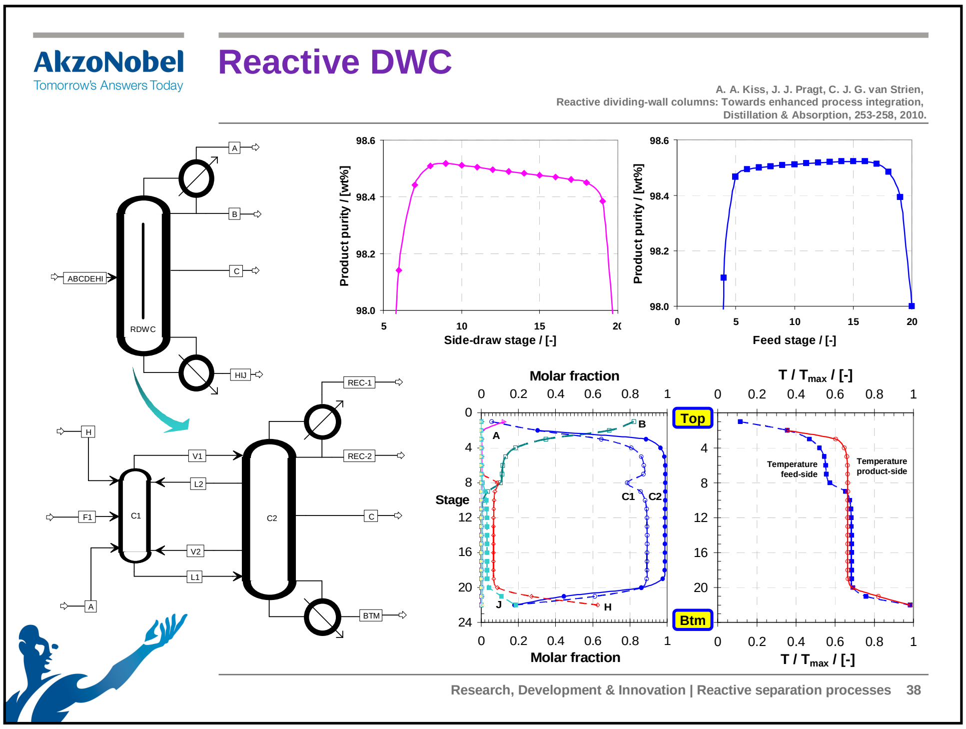
Base case: RDC + DC

A. A. Kiss, J. J. Pragt, C. J. G. van Strien,
Reactive Dividing-Wall Columns - How to get more with less resources?,
Chemical Engineering Communications, 196, 1366-1374, 2009.

- ✓ Different pressures possible
- ✓ *H* added to shift equilibrium
- ✓ *A* can be added to convert heavy components in bottom

Research, Development & Innovation | Reactive separation processes 37



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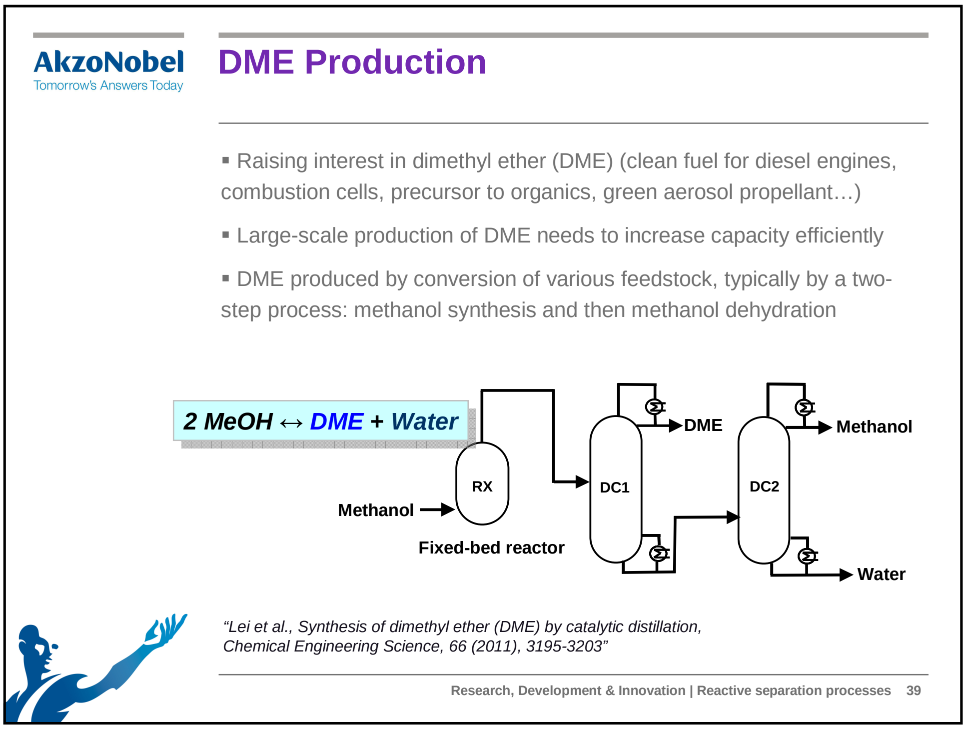
Reactive DWC

A. A. Kiss, J. J. Pragt, C. J. G. van Strien,
Reactive dividing-wall columns: Towards enhanced process integration,
Distillation & Absorption, 253-258, 2010.

Research, Development & Innovation | Reactive separation processes 38



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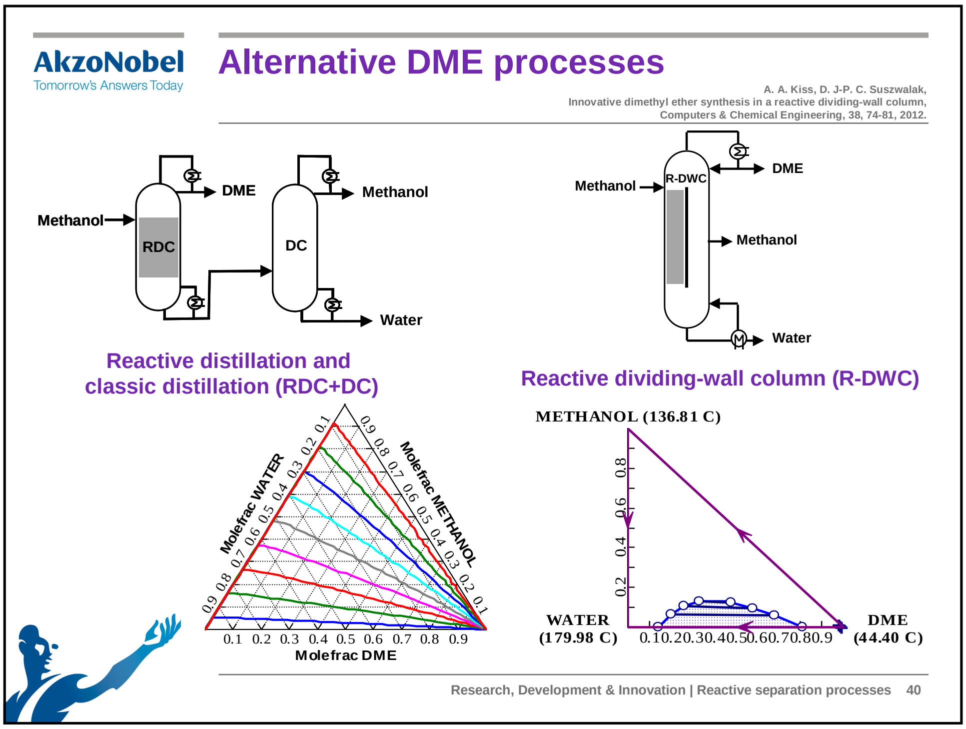
DME Production

- Raising interest in dimethyl ether (DME) (clean fuel for diesel engines, combustion cells, precursor to organics, green aerosol propellant…)
- Large-scale production of DME needs to increase capacity efficiently
- DME produced by conversion of various feedstock, typically by a two-step process: methanol synthesis and then methanol dehydration

2 MeOH ↔ DME + Water

"Lei et al., Synthesis of dimethyl ether (DME) by catalytic distillation, Chemical Engineering Science, 66 (2011), 3195-3203"



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Alternative DME processes

A. A. Kiss, D. J-P. C. Suszwalak,
Innovative dimethyl ether synthesis in a reactive dividing-wall column,
Computers & Chemical Engineering, 38, 74-81, 2012.

Reactive distillation and classic distillation (RDC+DC)

Reactive dividing-wall column (R-DWC)

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Optimization approach

- Approach: simulation and optimization of the processes via the sequential quadratic programming (SQP) method from Aspen Plus
- Fair comparison between an optimal conventional sequence and the optimized RDC+DC and DWC alternatives

➢ Sequential quadratic programming (SQP) is an iterative method for nonlinear optimization.

➢ SQP methods solve a sequence of optimization sub-problems, each optimizing a quadratic model of the objective subject to a linearization of the constraints.

$$\text{Min}\ (Q) = f\ (N_T, N_F, N_R, N_{RZ}, N_{DWS}, N_{DWC}, N_{SS}, RR, V, F_{SS}, r_V, r_L)$$

$$\text{Subject to}\ \vec{y}_m \geq \vec{x}_m$$

➢ Discrete variables: N_T, N_F, N_R, N_{RZ}, N_{DWS}, N_{DWC}, N_{SS}
➢ Continuous variables: RR, V, F_{SS}, r_V, r_L
➢ y_m & x_m: vectors of obtained & required purities for products m

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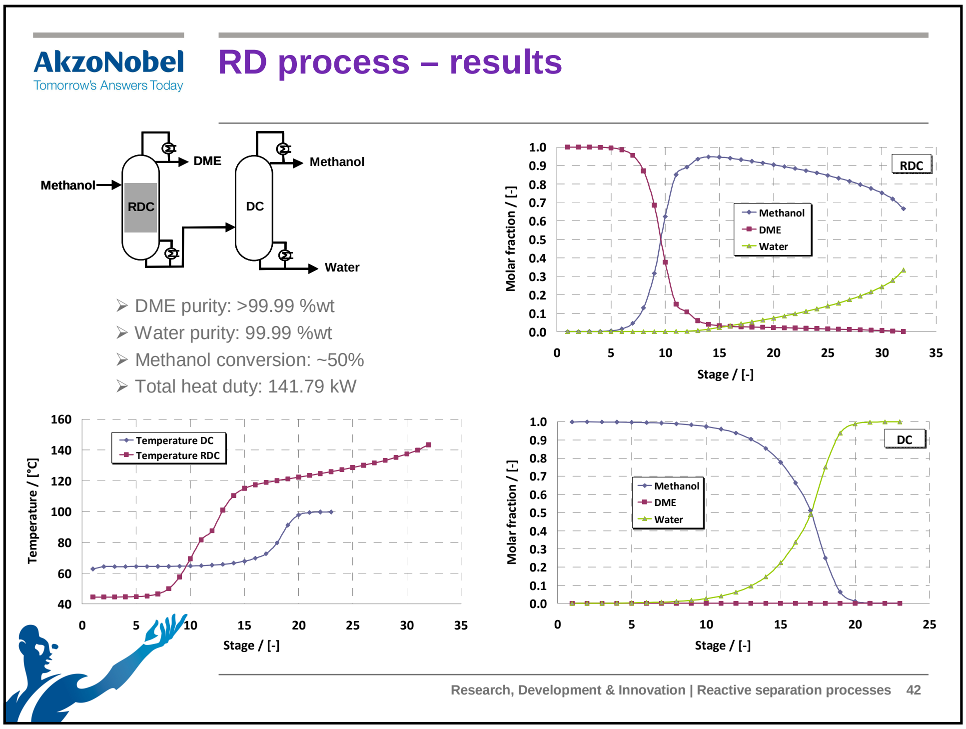

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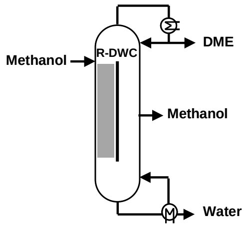
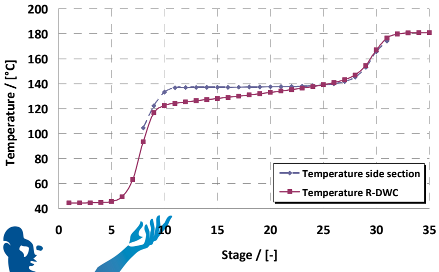
RD process – results

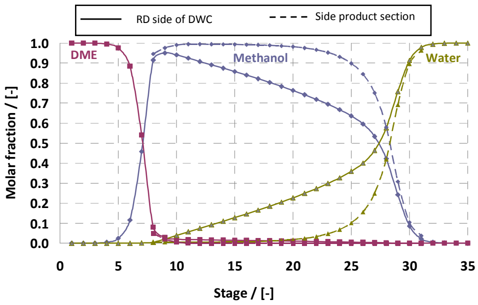
➢ DME purity: >99.99 %wt
➢ Water purity: 99.99 %wt
➢ Methanol conversion: ~50%
➢ Total heat duty: 141.79 kW

R-DWC process – results



- Solid catalyst (IEX resin)
- DME purity: >99.99 %wt
- Water purity: 99.99 %wt
- Methanol conversion: ~50%
- Total heat duty: 58.70 kW



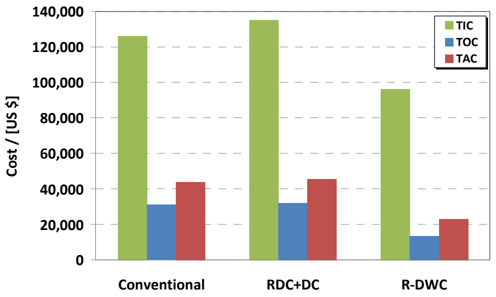


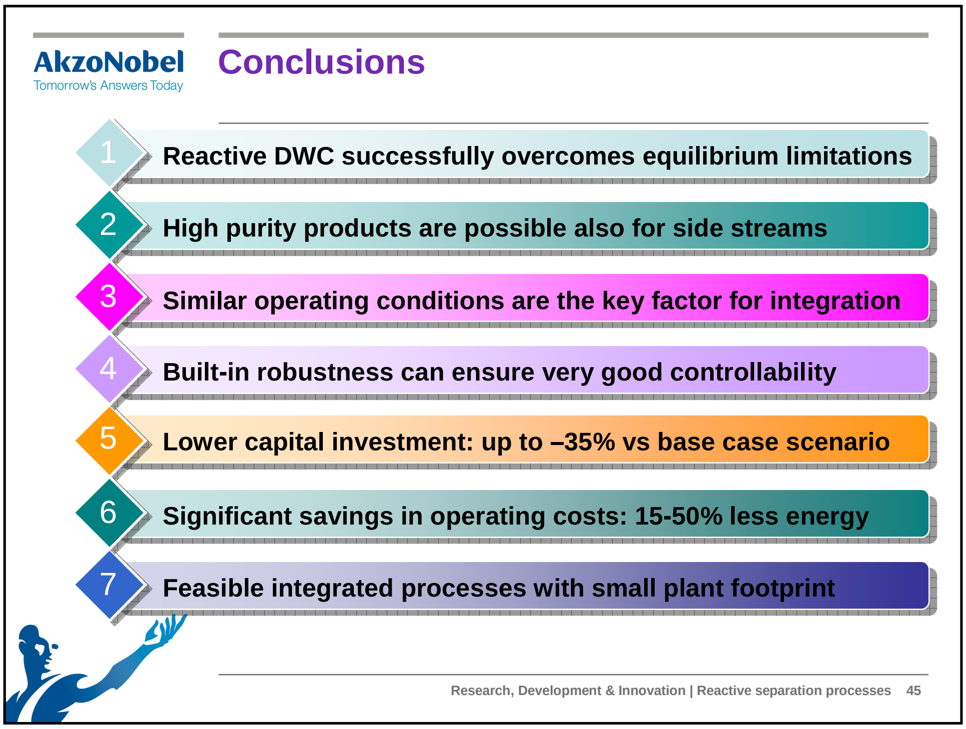
Comparison of DME processes

A. A. Kiss, D. J-P. C. Suszwalak,
Innovative dimethyl ether synthesis in a reactive dividing-wall column,
Computers & Chemical Engineering, 38, 74-81, 2012.

Key performance indicators	**Conventional process**	**Reactive distillation**	**Reactive DWC**
Total investment cost (TIC)	$126,075	$135,260	$96,531
Total operating costs (TOC)	$31,233	$32,186	$13,988
Total annual costs (TAC)	$43,840	$45,712	$23,641
Specific energy requirements (kW·h/ton DME)	640.5	1367.9	566.4
CO_2 emissions (kg CO_2/h·ton DME)	89.57	191.28	79.20

- Energy savings of up to 60%
- Significantly reduced TIC and TAC
- Much lower plant footprint





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Conclusions

1 Reactive DWC successfully overcomes equilibrium limitations

2 High purity products are possible also for side streams

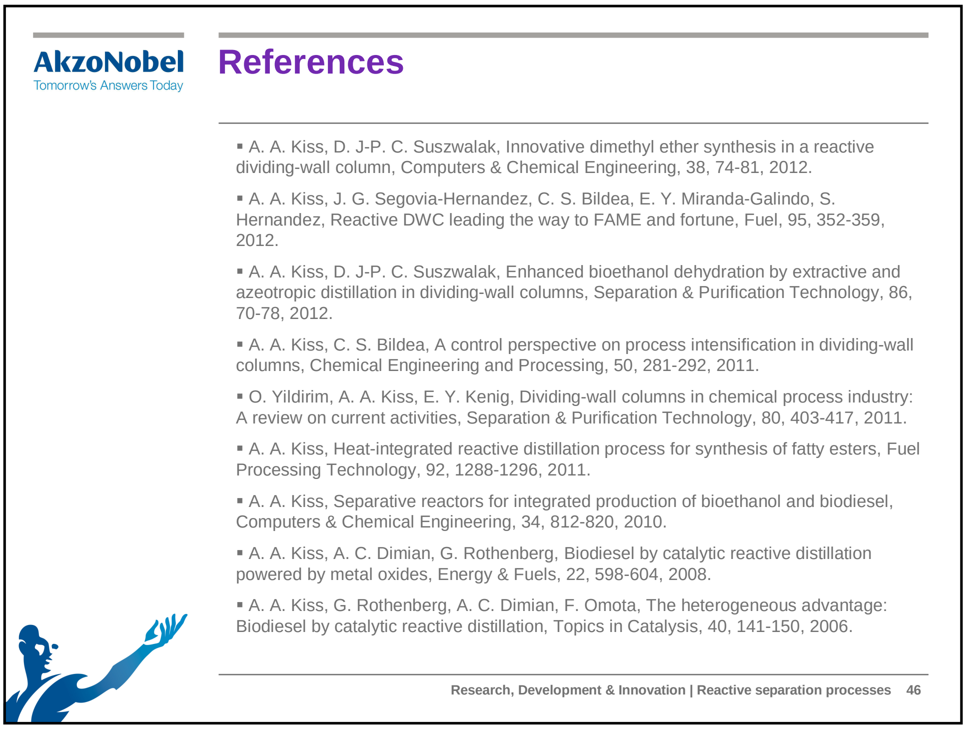
3 Similar operating conditions are the key factor for integration

4 Built-in robustness can ensure very good controllability

5 Lower capital investment: up to –35% vs base case scenario

6 Significant savings in operating costs: 15-50% less energy

7 Feasible integrated processes with small plant footprint



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References

- A. A. Kiss, D. J-P. C. Suszwalak, Innovative dimethyl ether synthesis in a reactive dividing-wall column, Computers & Chemical Engineering, 38, 74-81, 2012.
- A. A. Kiss, J. G. Segovia-Hernandez, C. S. Bildea, E. Y. Miranda-Galindo, S. Hernandez, Reactive DWC leading the way to FAME and fortune, Fuel, 95, 352-359, 2012.
- A. A. Kiss, D. J-P. C. Suszwalak, Enhanced bioethanol dehydration by extractive and azeotropic distillation in dividing-wall columns, Separation & Purification Technology, 86, 70-78, 2012.
- A. A. Kiss, C. S. Bildea, A control perspective on process intensification in dividing-wall columns, Chemical Engineering and Processing, 50, 281-292, 2011.
- O. Yildirim, A. A. Kiss, E. Y. Kenig, Dividing-wall columns in chemical process industry: A review on current activities, Separation & Purification Technology, 80, 403-417, 2011.
- A. A. Kiss, Heat-integrated reactive distillation process for synthesis of fatty esters, Fuel Processing Technology, 92, 1288-1296, 2011.
- A. A. Kiss, Separative reactors for integrated production of bioethanol and biodiesel, Computers & Chemical Engineering, 34, 812-820, 2010.
- A. A. Kiss, A. C. Dimian, G. Rothenberg, Biodiesel by catalytic reactive distillation powered by metal oxides, Energy & Fuels, 22, 598-604, 2008.
- A. A. Kiss, G. Rothenberg, A. C. Dimian, F. Omota, The heterogeneous advantage: Biodiesel by catalytic reactive distillation, Topics in Catalysis, 40, 141-150, 2006.