Reactive Chromatography for Biodiesel Production

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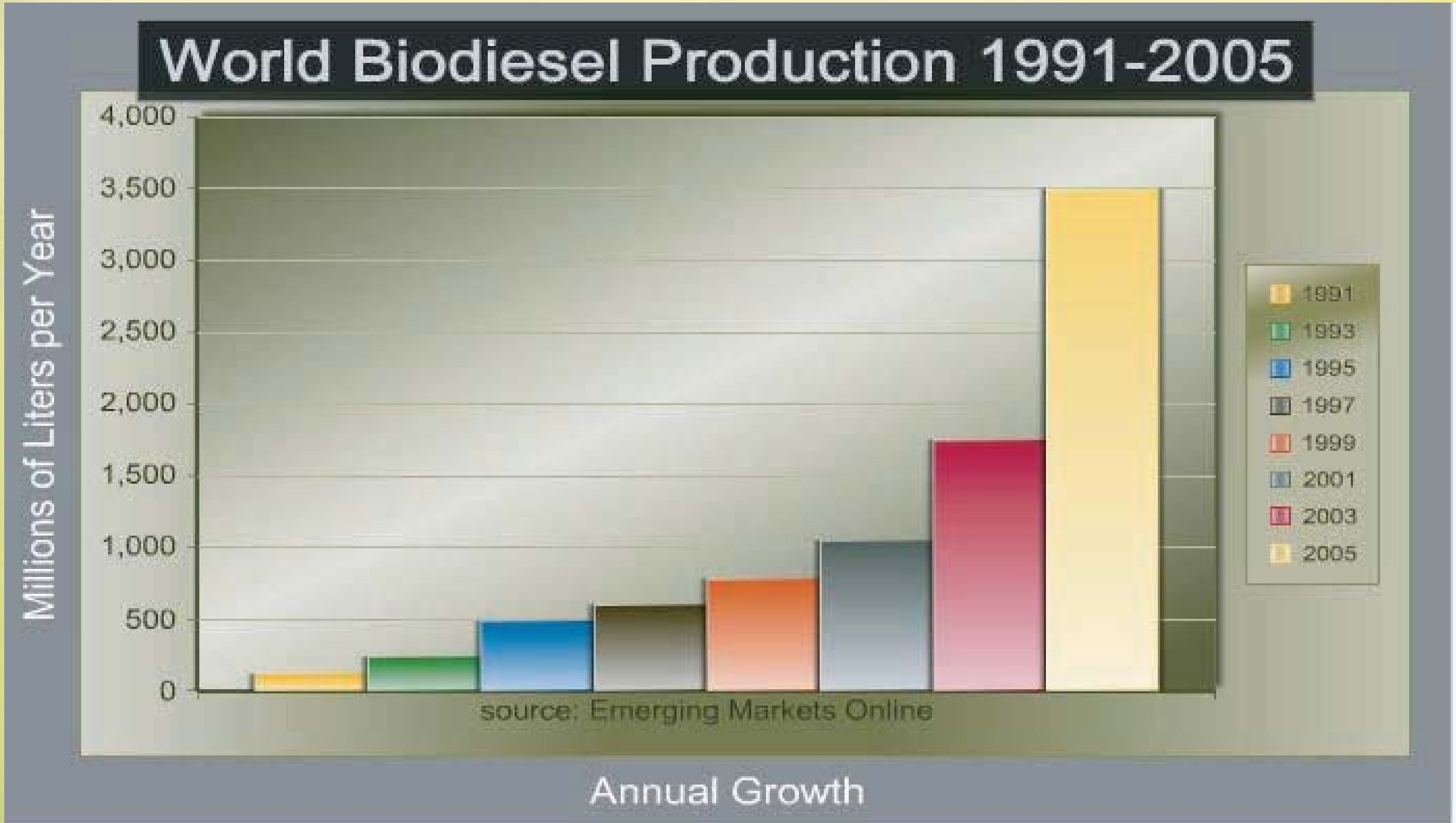
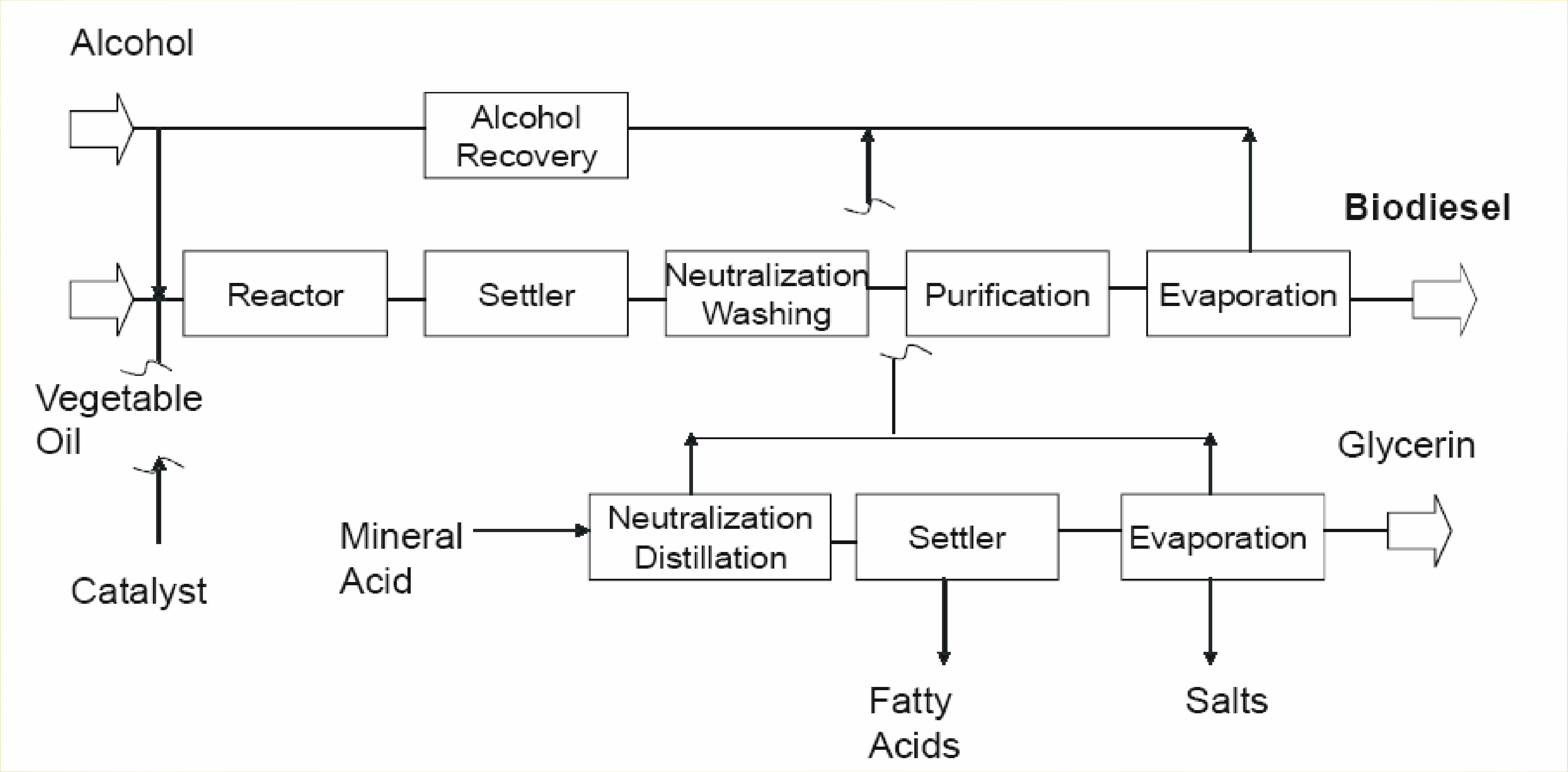


Source: Emerging Markets Online, ITU Turkey

Block Diagram of Biodiesel Process



Source: SRI Report, Biodiesel via Esterifip-H process

Background

- About 3% of the triglyceride feed entering biodiesel process is lost as fatty acid.
- This fatty acid can be converted to biodiesel (FAME) using strong acid cation resin as a catalyst for increased FAME yield.

Typical Feed Composition

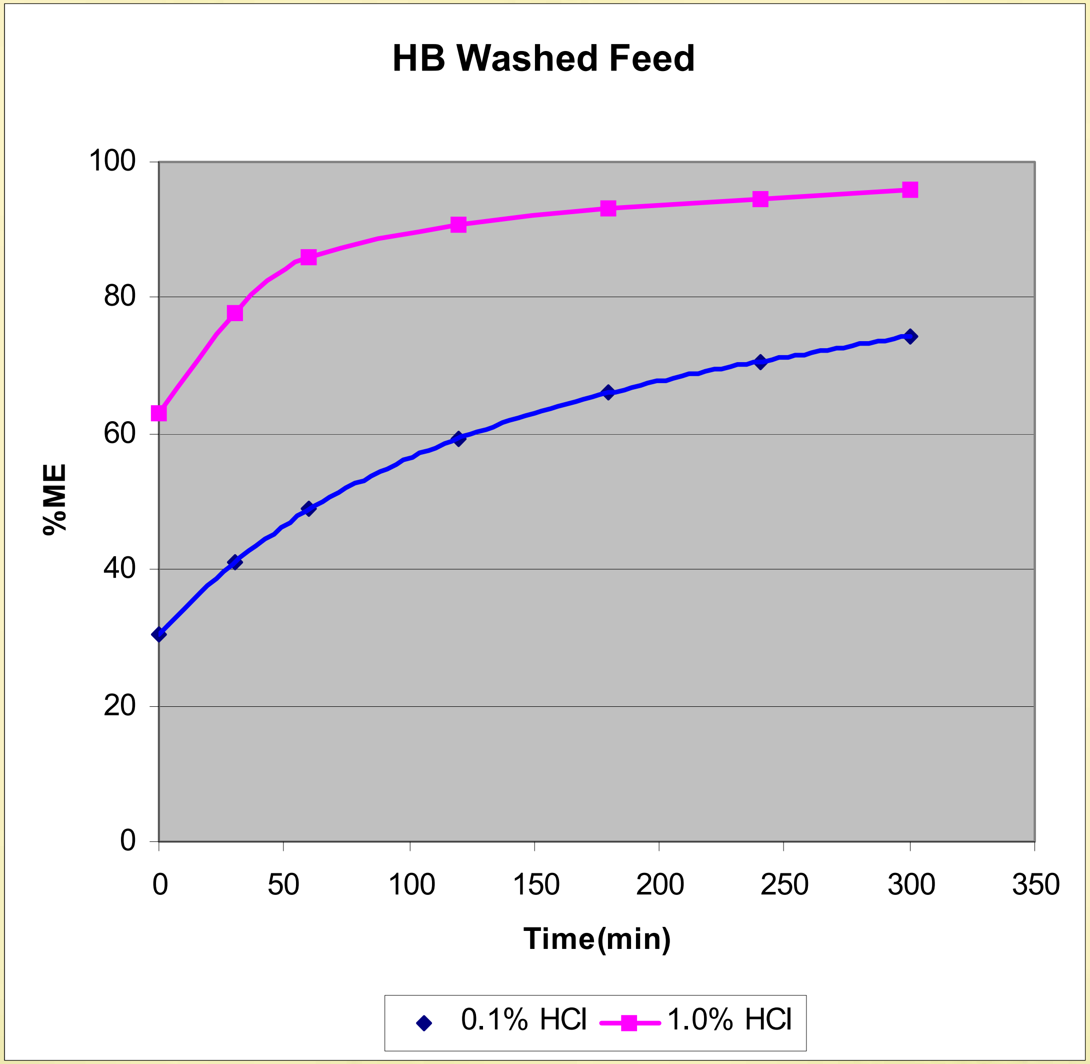
Free Fatty Acids:	72.1%
Triglycerides:	0.09%
Diglycerides:	0.07%
Monoglycerides:	1.56%
FAME:	22.02%
Glycerol:	0.31%
KF Water:	0.19%

c

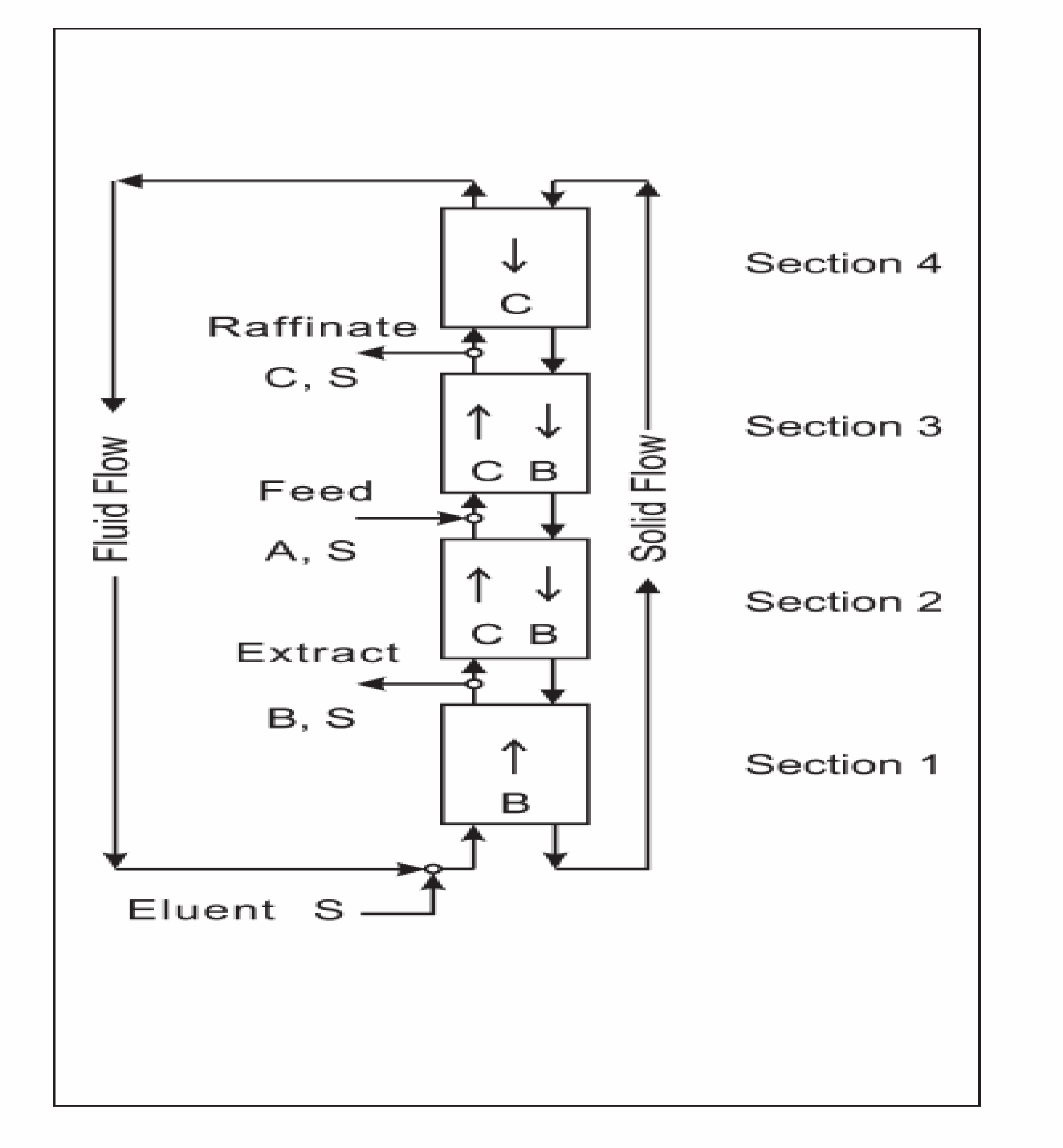
Esterification Reaction

- Fatty acid (FA) reacts with methanol to form fatty acid methyl ester (FAME)

$$FA + CH_3OH \rightleftharpoons FAME + H_2O$$


HB Washed Feed
%ME
100
80
60
40
20
0
0
50
100
150
200
250
300
350
Time(min)
0.1% HCl
1.0% HCl

Schematic of Reactive Chromatography
(A ⇄ B + C)



Source: A new reaction-separation unit: the simulated moving bed reactor.
F. Lode, M. Mazzotti, and M. Morbidelli. Chimia 55, 883-886,2001

Optimization Variables

- Column configuration
  - How many total columns
  - How many columns in each zone
- Flow rates
  - Feed flow rate
  - Eluent flow rate
  - Product flow rate
  - Raffinate flow rate
- Step time

Mathematical Model

Adsorption/desorption zone:

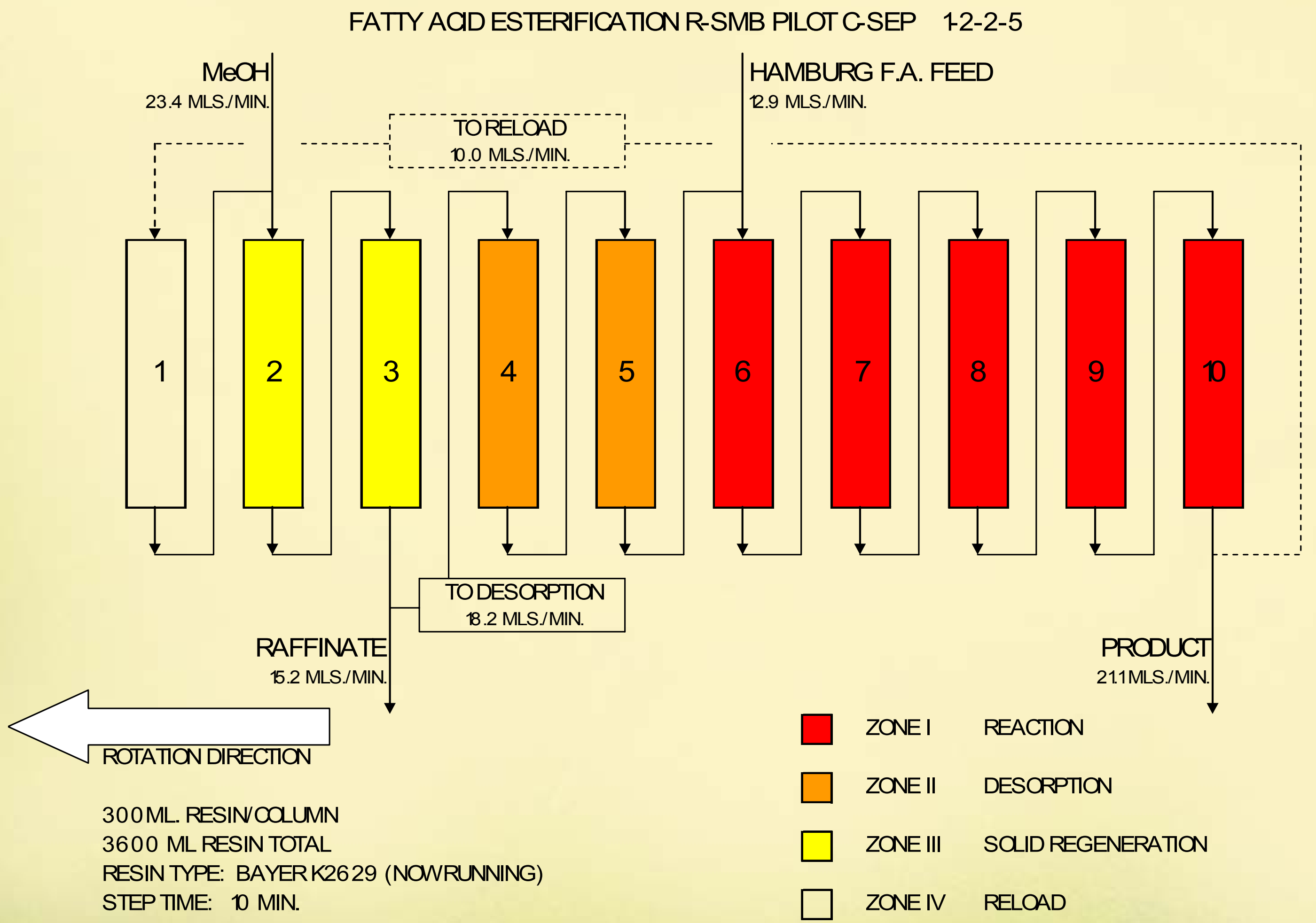
$$\frac{\partial(C_{ik})}{\partial t}+\frac{(1-\varepsilon)}{\varepsilon}\left[\frac{\partial(\overline{q}_{ik})}{\partial t}-u_s\frac{\partial(\overline{q}_{ik})}{\partial z}\right]+ + v_k\frac{\partial(C_{ik})}{\partial z}-D_a\frac{\partial^2(C_{ik})}{\partial z^2}=0$$

$$\frac{\partial(\overline{q}_{ik})}{\partial t}=u_s\frac{\partial(\overline{q}_{ik})}{\partial z}+k_{TM}(q_i^*-\overline{q}_{ik})$$

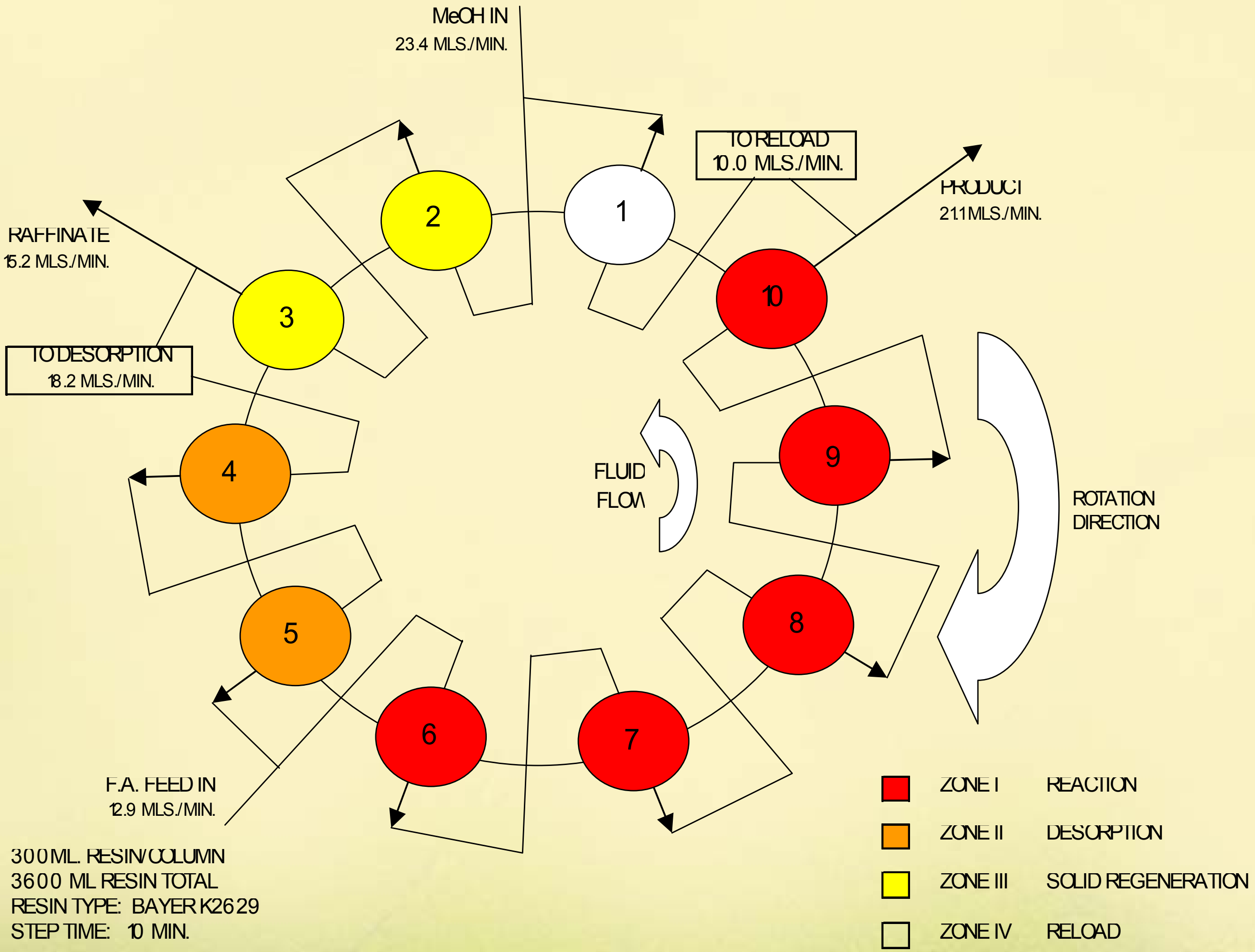
Reaction zone:

$$\frac{\partial(C_{ik})}{\partial t}+v_k\frac{\partial(C_{ik})}{\partial z}-D_a\frac{\partial^2(C_{ik})}{\partial z^2}+\frac{(1-\varepsilon_r)}{\varepsilon_r}.r_i=0$$

Reactor-Separator Column Configuration



Top View

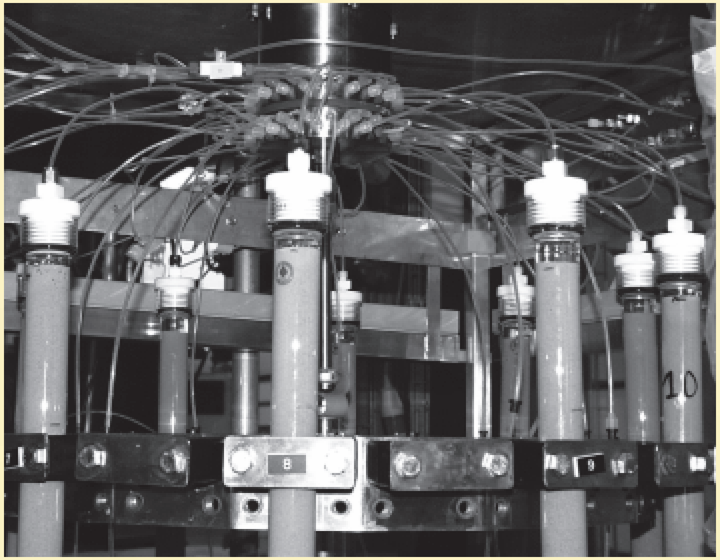


MeOH IN
23.4 MLS./MIN.
TO RELOAD
10.0 MLS./MIN.
PRODUCT
21.1 MLS./MIN.
RAFFINATE
15.2 MLS./MIN.
TO DESORPTION
18.2 MLS./MIN.
1
2
3
4
5
6
7
8
9
10
FLUID
FLOW
ROTATION
DIRECTION
F.A. FEED IN
12.9 MLS./MIN.
300 ML. RESIN/COLUMN
3600 ML RESIN TOTAL
RESIN TYPE: BAYER K2629
STEP TIME: 10 MIN.
ZONE I REACTION
ZONE II DESORPTION
ZONE III SOLID REGENERATION
ZONE IV RELOAD

Pilot Scale Simulated Moving Bed Reactor-Separator

- Rotary valve implements flow configuration
- Each column is 2.0 L
- 20 columns in the carousel

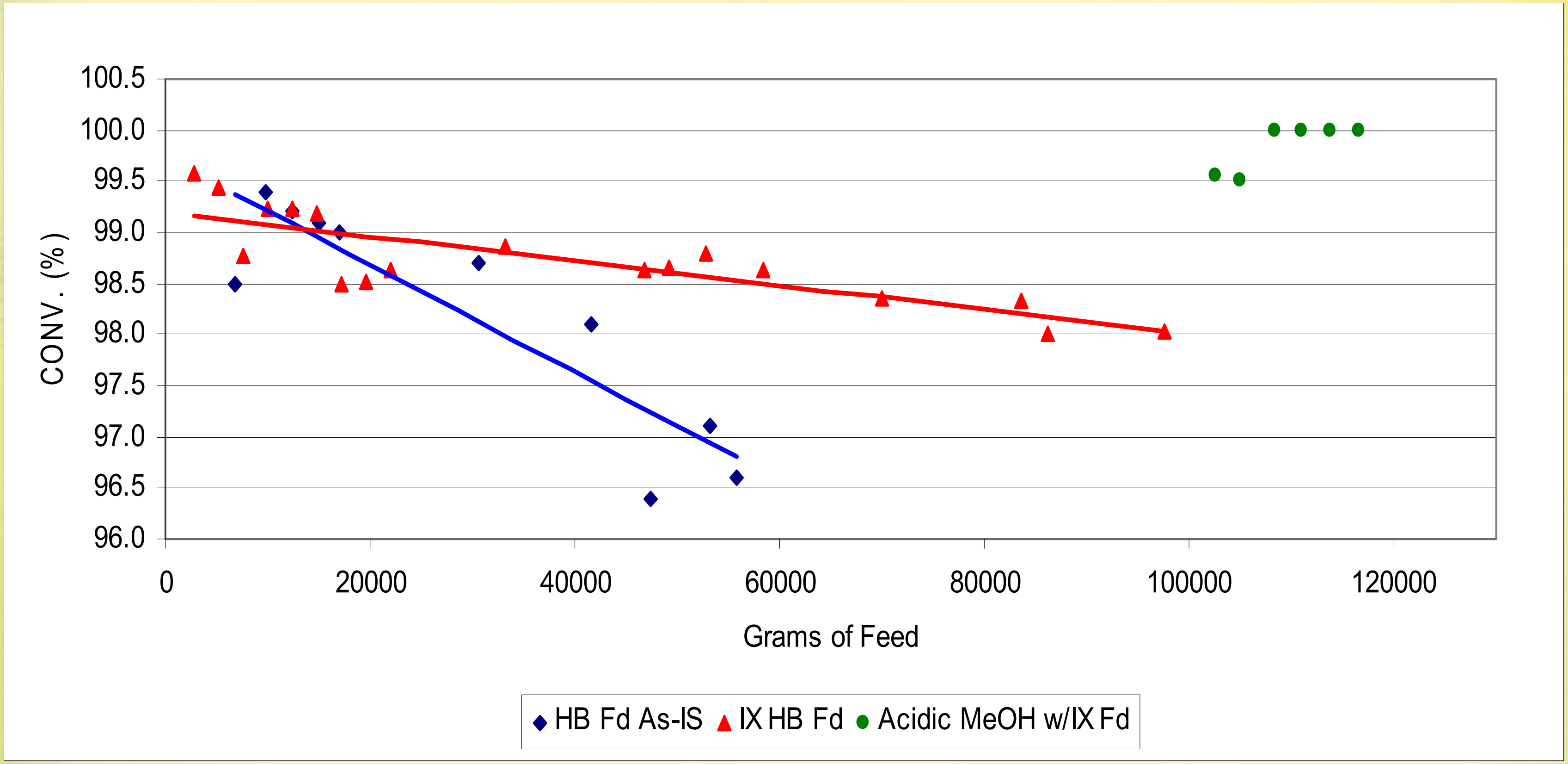
Pilot Scale Simulated Moving Bed Reactor-Separator



Summary of Results

- Conversion: 99.0-99.4%
- Composition:
  - Product
    - FAME: 45-55%
    - FA: 0.3-0.5%
  - Raffinate
    - FAME: 0.3-1.1%
    - FA: 0.01-0.04%

Catalyst Deactivation Problem



Scale up

- The interstitial fluid velocity is kept constant.
- It is possible to scale up based on the volume ratio of the plant column to the lab column. However, this might not work if the width of the wave expands significantly with higher velocity.

Conclusions

- Prevention of catalyst deactivation was critical.
- Removing cations from feed also led to about 15% higher productivity.
- Adding 0.1% HCl in the eluent (methanol) ensured high conversion.
- Reactive chromatography was demonstrated as an effective method for improving biodiesel yield.

Acknowledgement

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