ADVANCES IN ETHANOL PURIFICATION:

ALTERNATIVES

AND

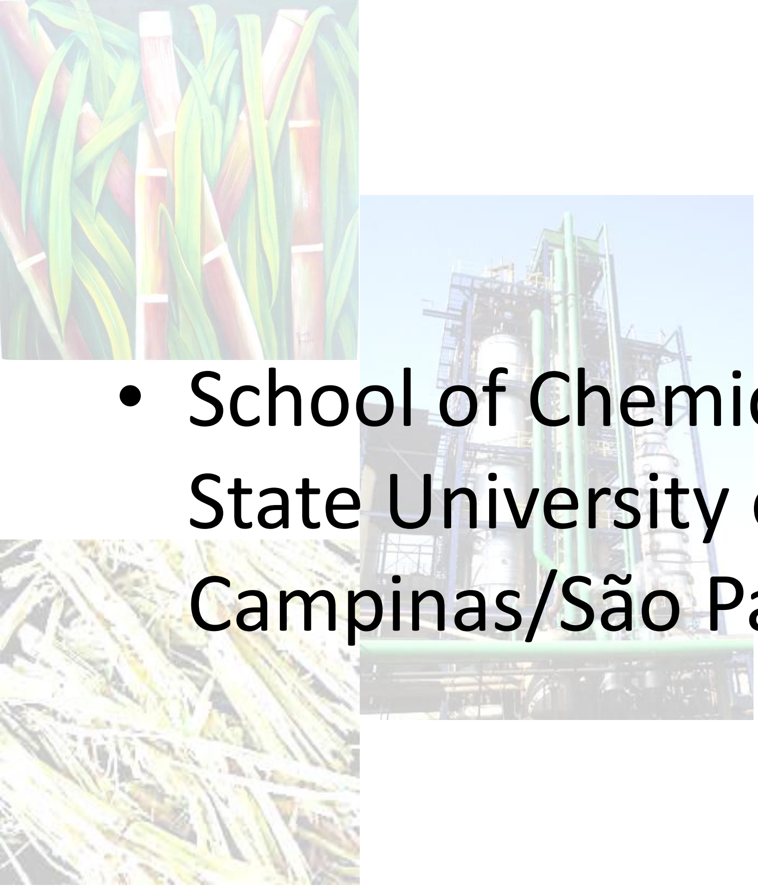
PERSPECTIVES

Sugarcane Processing and Engineering

BIOEN WORKSHOP ON PROCESSES FOR ETHANOL PRODUCTION

Professor Maria Regina Wolf Maciel, 10/09/2009

UNICAMP



- School of Chemical Engineering
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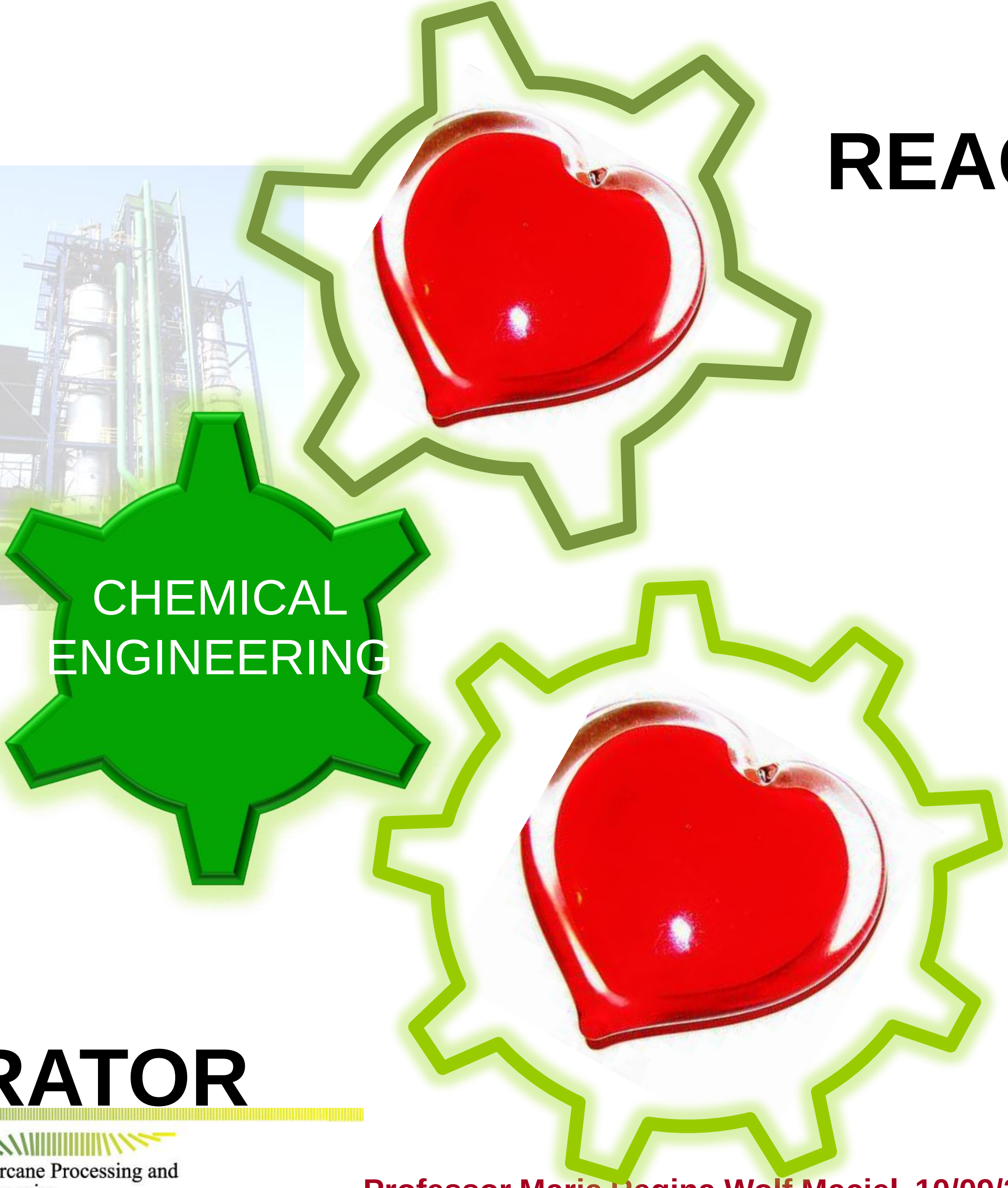
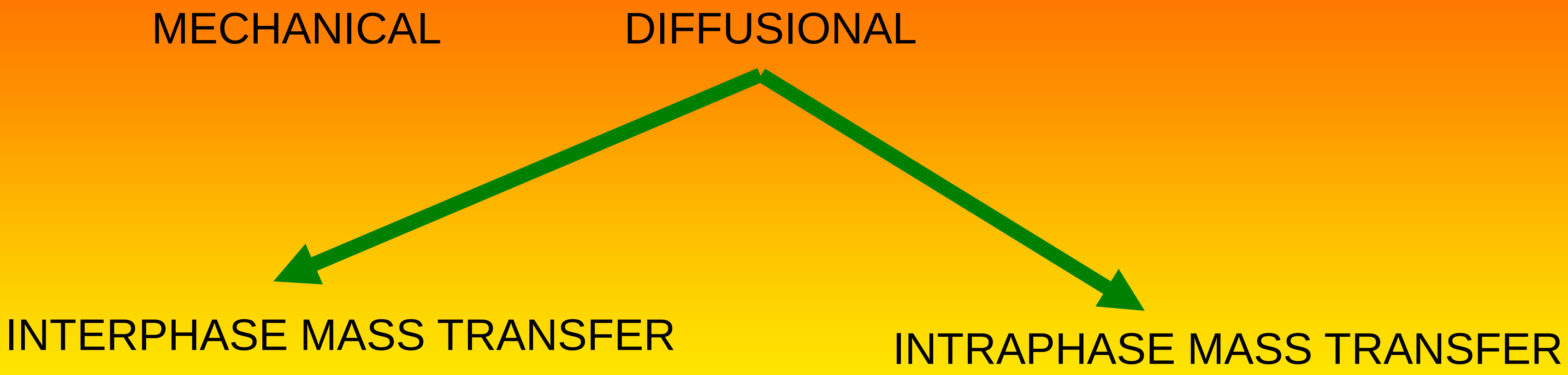


REACTOR

CHEMICAL ENGINEERING

SEPARATOR



MECHANICAL

DIFFUSIONAL

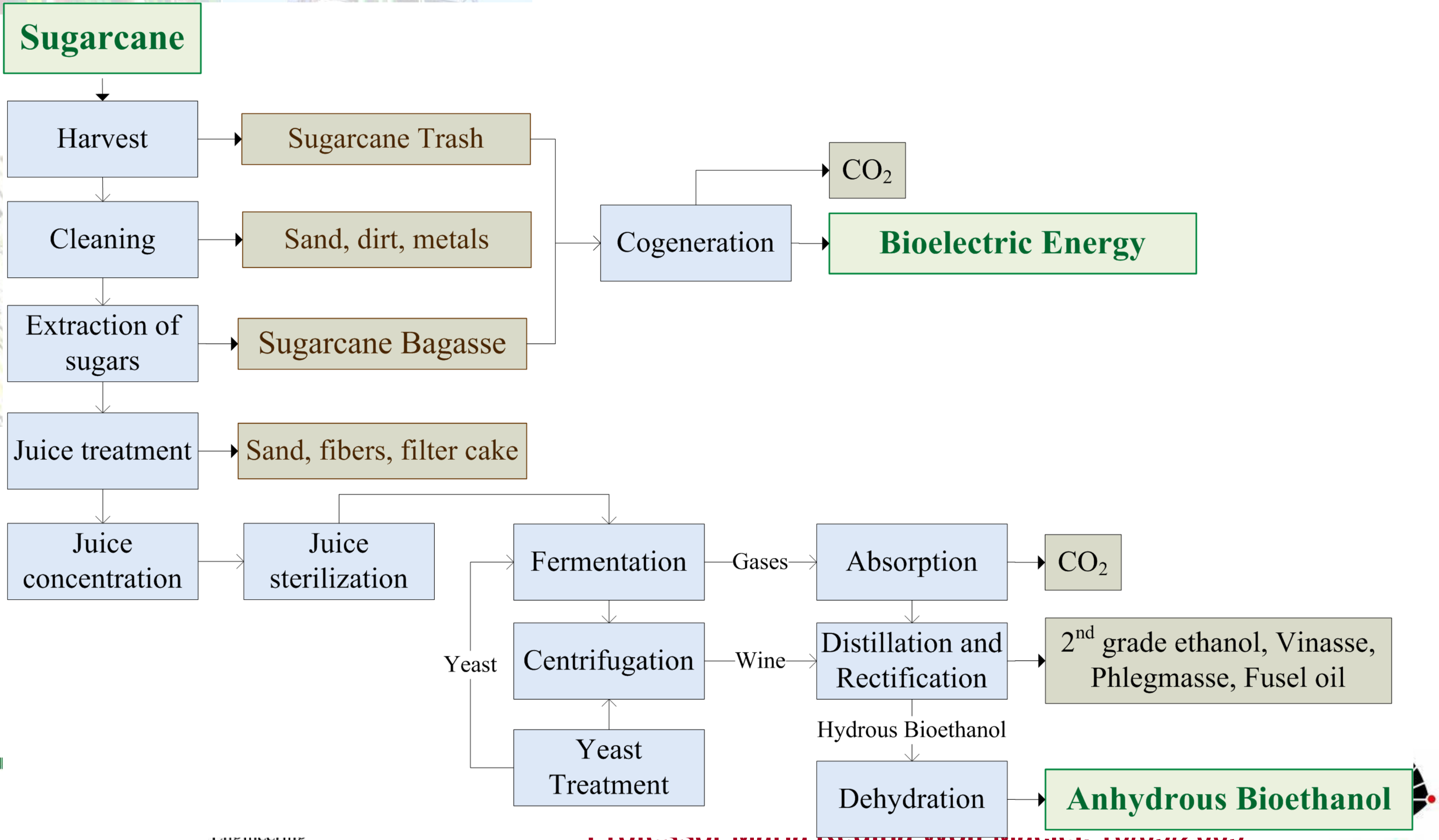
INTERPHASE MASS TRANSFER

INTRAPHASE MASS TRANSFER

REAL

- ~~EQUILIBRIUM PROCESS~~
- NON EQUILIBRIUM APPROACH

Block flow diagram – conventional bioethanol production process



Sugarcane

Harvest

Sugarcane Trash

Cleaning

Sand, dirt, metals

Extraction of sugars

Sugarcane Bagasse

Juice treatment

Sand, fibers, filter cake

Cogeneration

CO_2

Bioelectric Energy

Juice concentration

Juice sterilization

Fermentation

Gases

Absorption

CO_2

Yeast

Centrifugation

Wine

Distillation and Rectification

2nd grade ethanol, Vinasse, Phlegmasse, Fusel oil

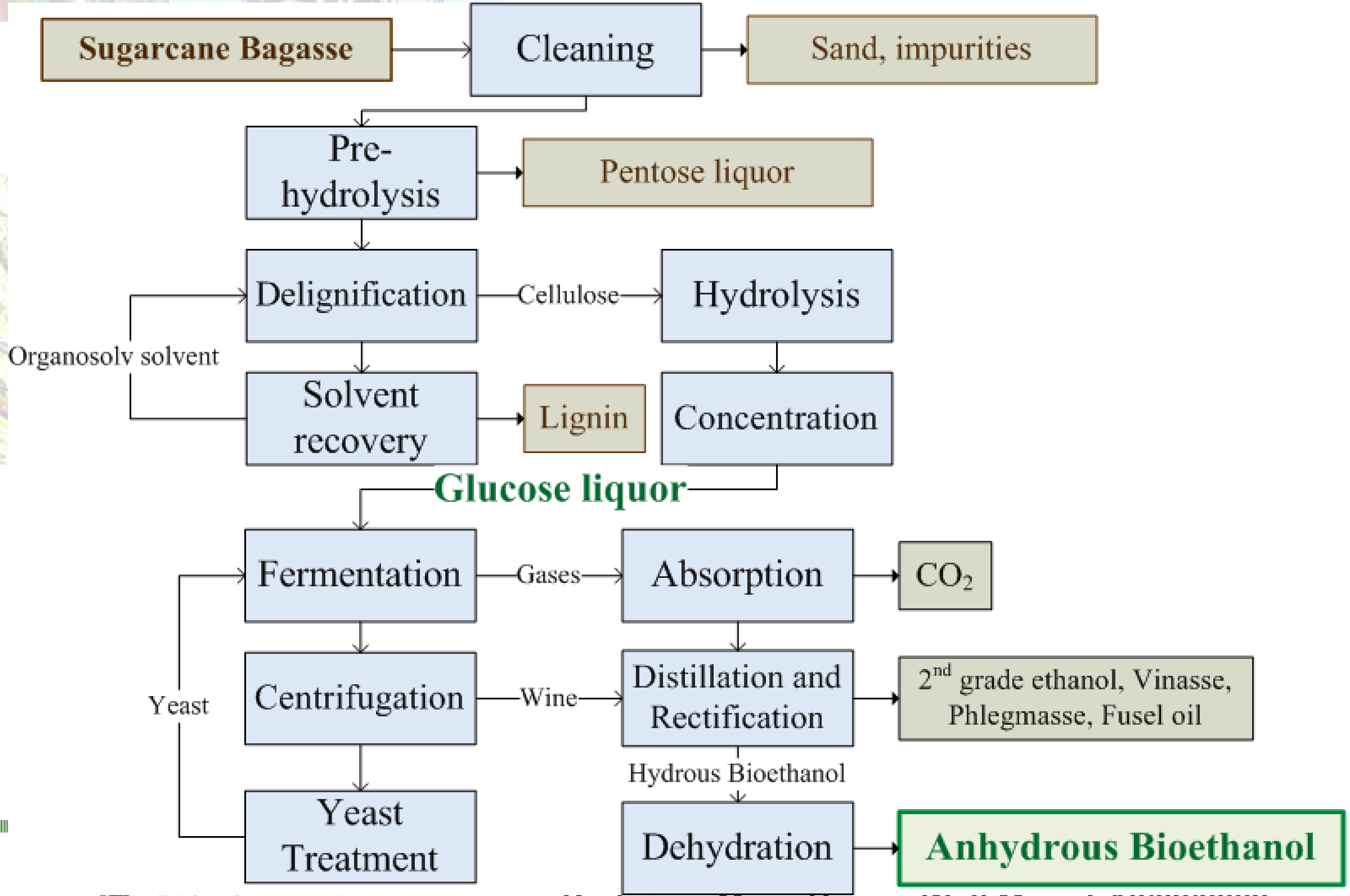
Yeast Treatment

Hydrous Bioethanol

Dehydration

Anhydrous Bioethanol

Block flow diagram –bioethanol production process from bagasse


Sugarcane Bagasse

Cleaning

Sand, impurities

Pre-hydrolysis

Pentose liquor

Delignification

Cellulose

Hydrolysis

Organosolv solvent

Solvent recovery

Lignin

Concentration

Glucose liquor

Fermentation

Gases

Absorption

CO_2

Yeast

Centrifugation

Wine

Distillation and Rectification

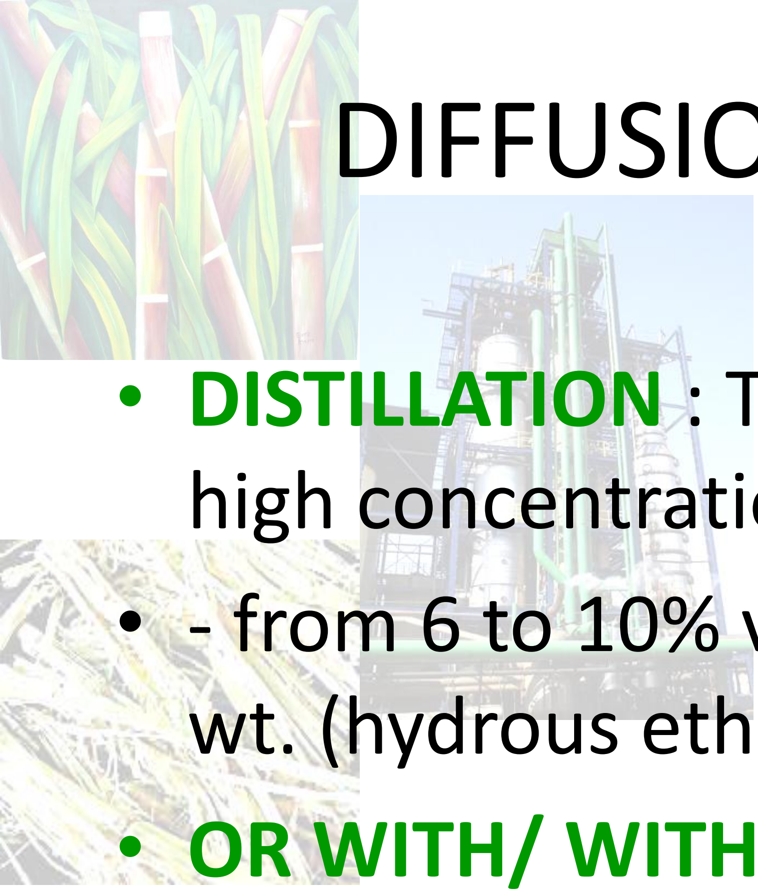
2nd grade ethanol, Vinasse, Phlegmasse, Fusel oil

Hydrous Bioethanol

Yeast Treatment

Dehydration

Anhydrous Bioethanol



DIFFUSIONAL SEPARATION

- **DISTILLATION** : To concentrate the wine to high concentration
- - from 6 to 10% vol. ethanol up to 92.6 – 93.8 wt. (hydrous ethanol)
- **OR WITH/ WITHOUT OTHER MORE COMPLEX PROCESSES - AZEOTROPE**

to 99.3 or higher (anhydrous ethanol)

Wine composition on conventional and integrated production process

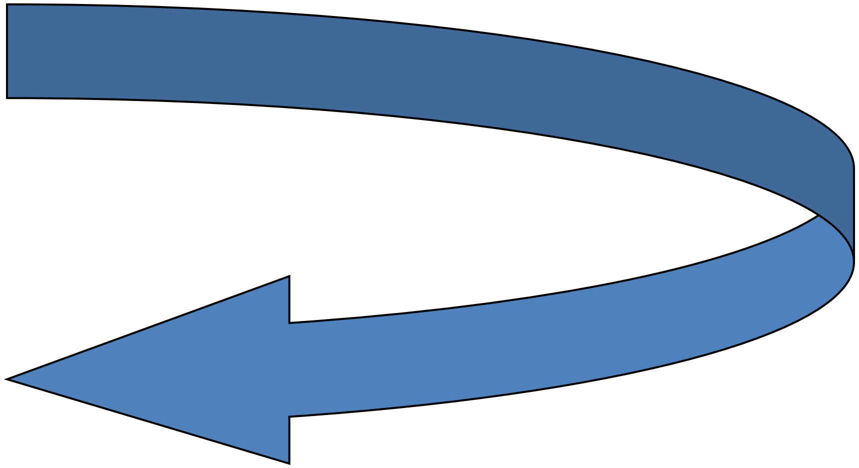
Component	Composition (wt%)	
	Conventional	Integrated (70 % bagasse)
Water	79.181	79.127
Glucose	0.607	0.607
Impurities	2.824	2.418
Ethanol	10.064	9.922
CO_2	0.129	0.122
Acetic Acid	0.005	0.173
Succinic Acid	0.001	0.040
Yeast	7.181	7.317
H_2SO_4	0.008	0.033
Pentose	-	0.130
Furfural	-	0.075
HMF	-	0.036

WINE

- HAS SEVERAL OTHER COMPONENTS (CONTAMINANTS) BEYOND WATER AND ETHANOL
- ALCOHOLS: METHANOL, PROPANOL, ISOPROPANOL, BUTANOL, ISOBUTANOL, AMYL, ISOAMYL
- ALDEHYDES: ACETALDEHYDE,

BUTYRALDEHYDE, CROTONALDEHYDE

- **ORGANIC ACIDS**: acetic; propionic
- **KETONES:** acetone
- **ESTERS:** ethyl acetate ; ethyl butyrate
- **ETHERS**: acetal

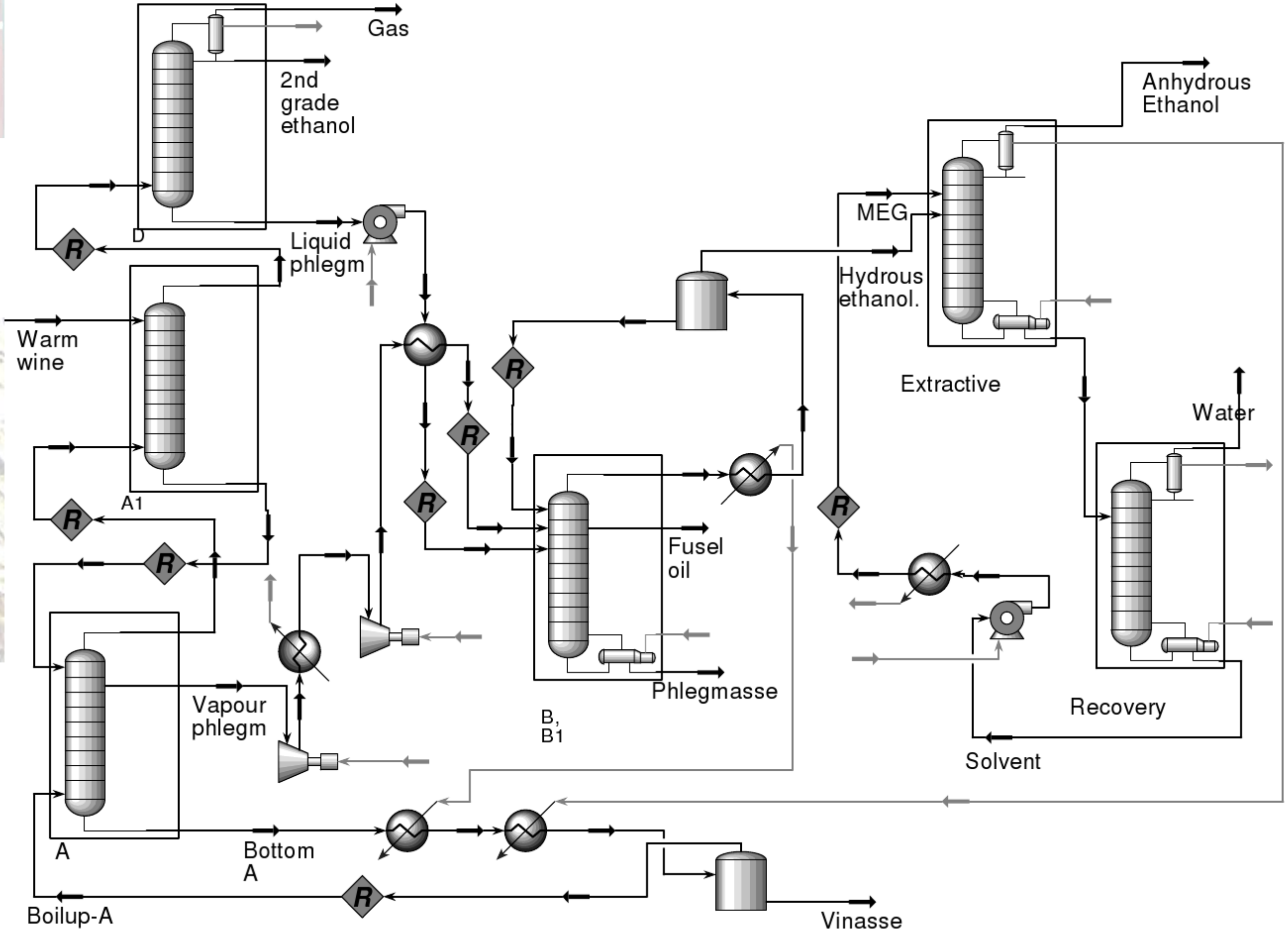


- QUALITY CRITERIA

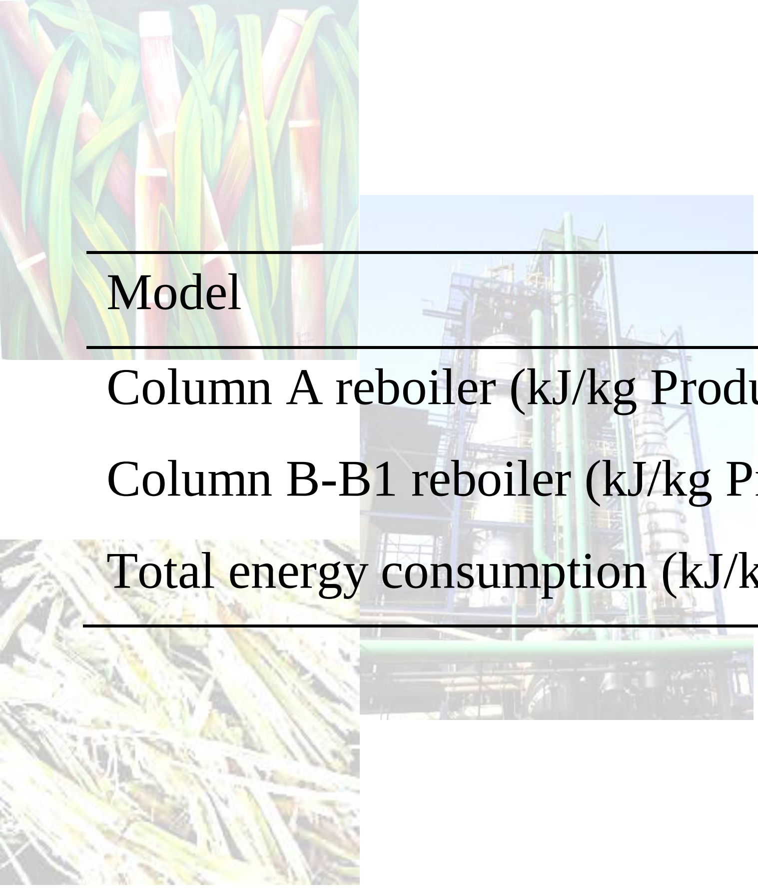
- PROBLEMS IN THE DISTILLATION PROCESS

DIFFERENT COMPONENTS

DILUTION


Gas
2nd grade ethanol
D
Liquid phlegm
Warm wine
A1
Vapour phlegm
A
Bottom A
Boilup-A
B, B1
Fusel oil
Phlegmasse
Vinasse
MEG
Hydrous ethanol.
Anhydrous Ethanol
Extractive
Water
Recovery
Solvent
R

EXAMPLE FOR SIMPLE COLUMNS



Model	EQ	EQ70	NEQ
Column A reboiler (kJ/kg Product)	4503	4712	4723
Column B-B1 reboiler (kJ/kg Product)	1150	2252	2259
Total energy consumption (kJ/kg Product)	5653	6964	6982

EQ: equilibrium stage model (efficiency of 100%)

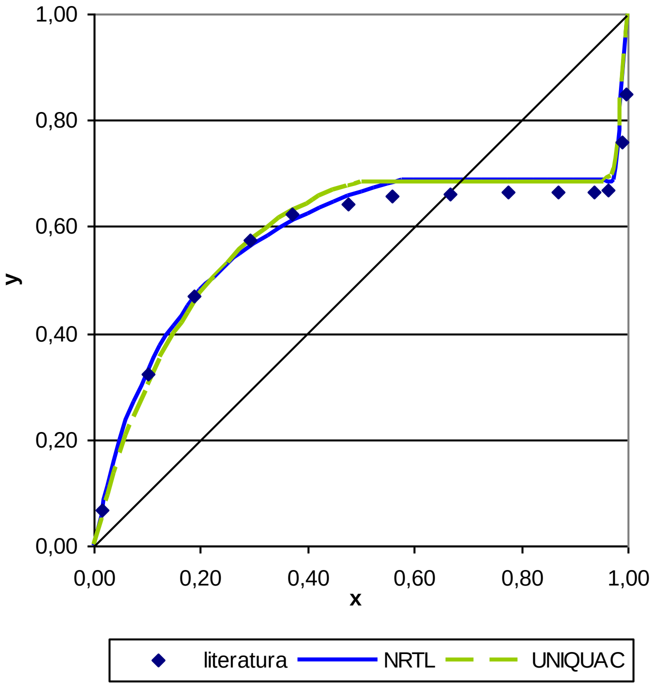
EQ70: equilibrium stage model with efficiency of 70%

NEQ: nonequilibrium stage model

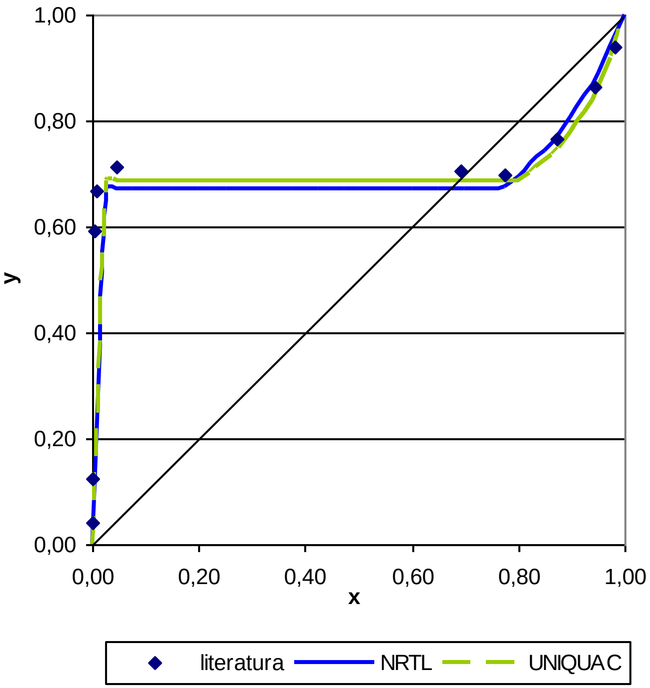
COLUMN A LARGER ENERGY BECAUSE LARGER FLOW RATES

LOWER NST ALSO

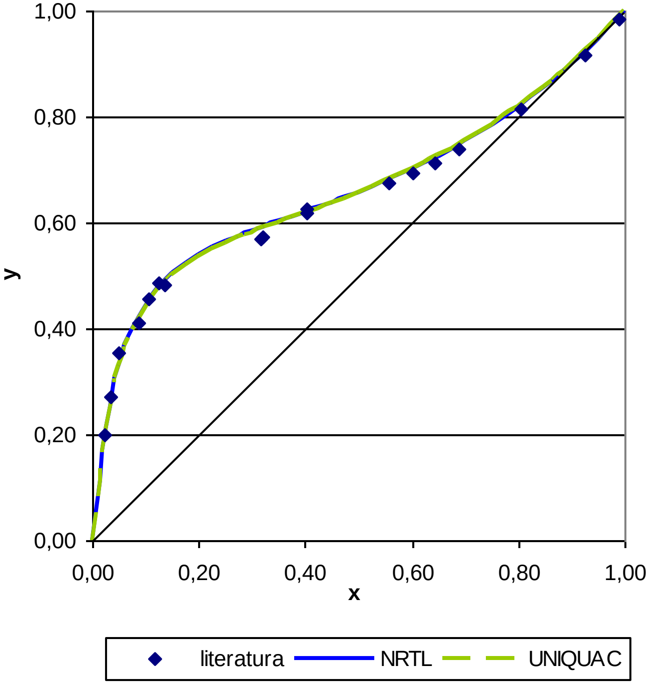
Water/Isobuthanol



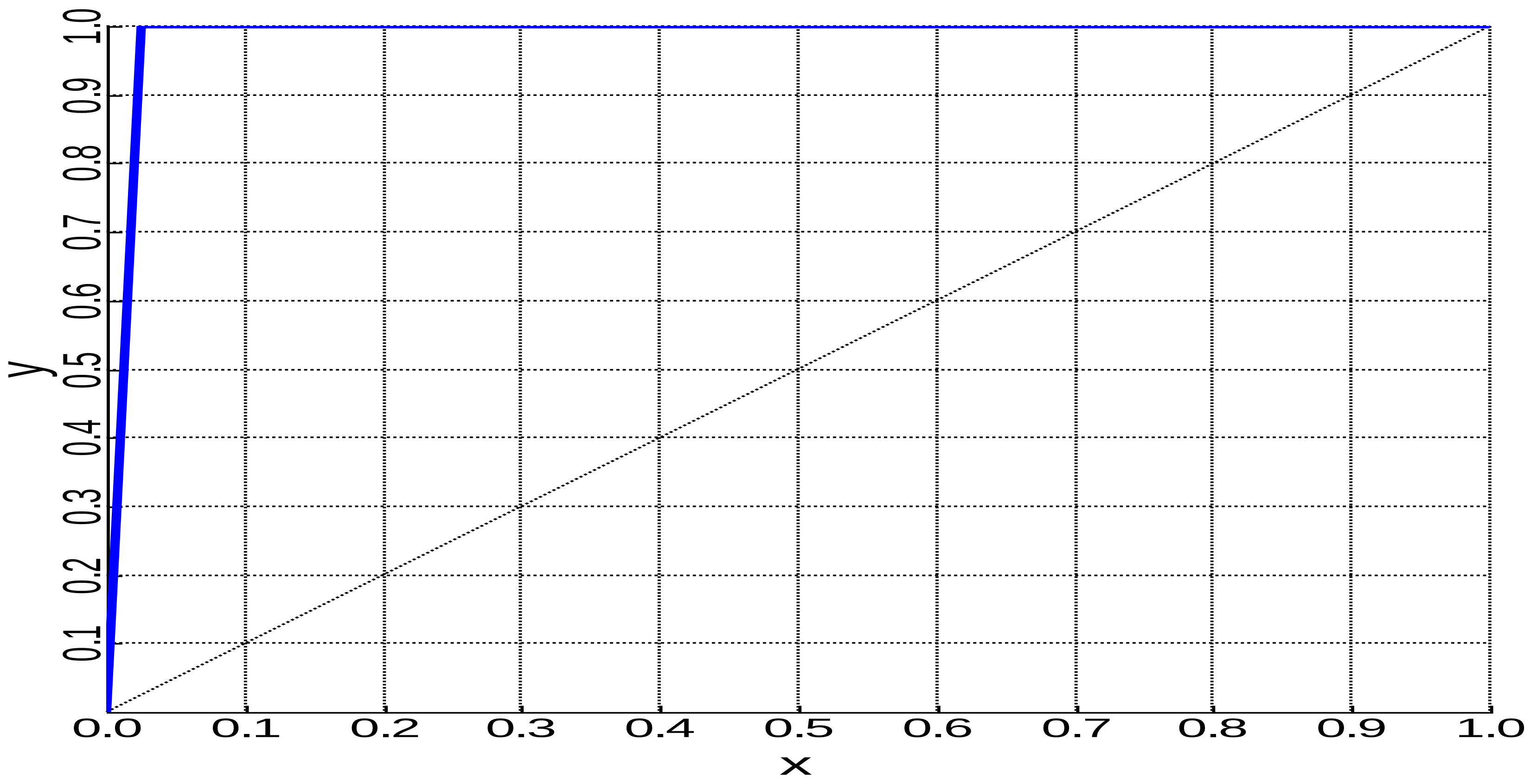
Ethyl Acetate/Water



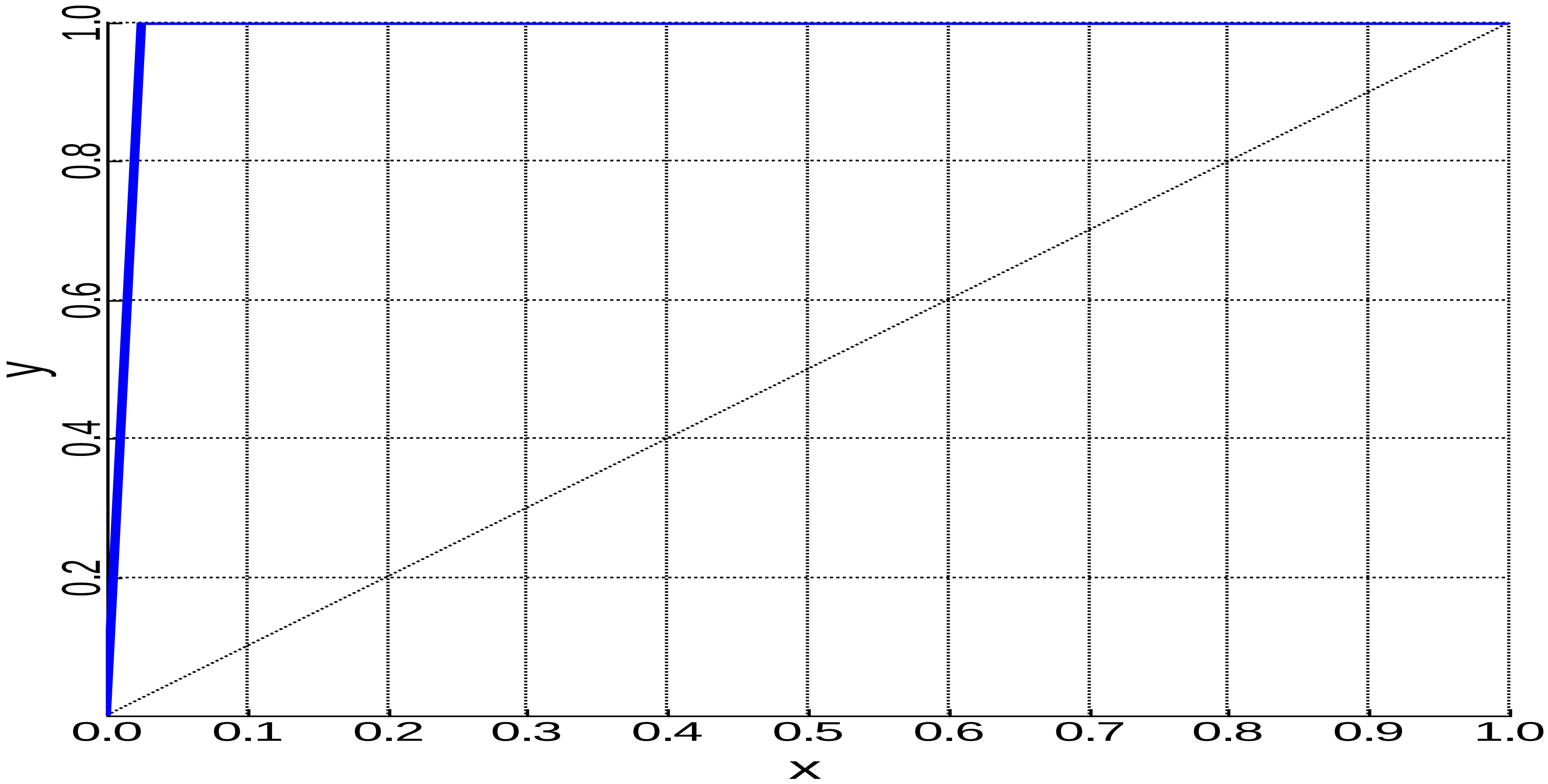
Ethanol/Water



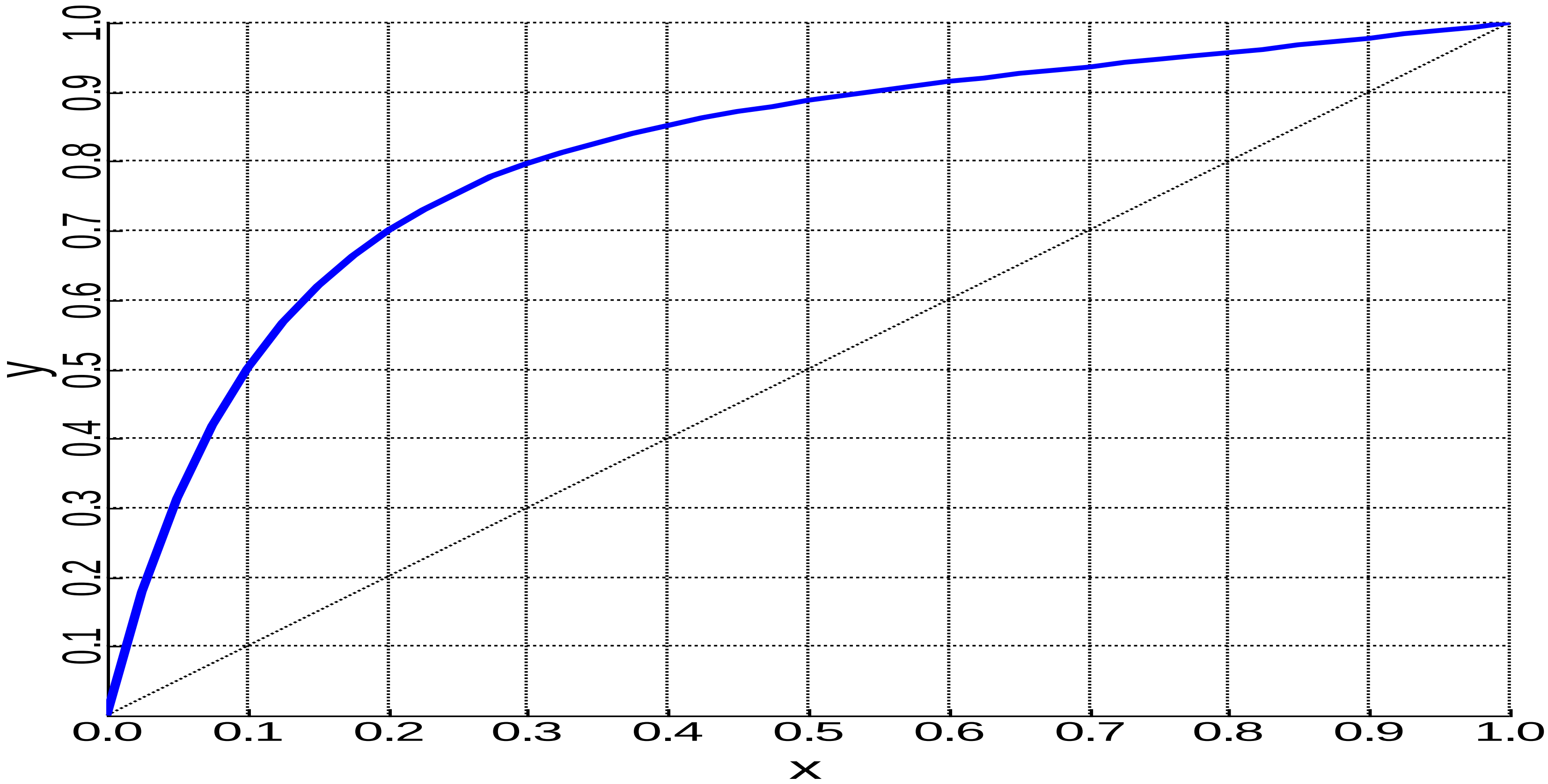
Acetaldehyde/Glucose



Acetaldehyde/Sucrose



Ethyl Acetate/Isoamilic alcohol



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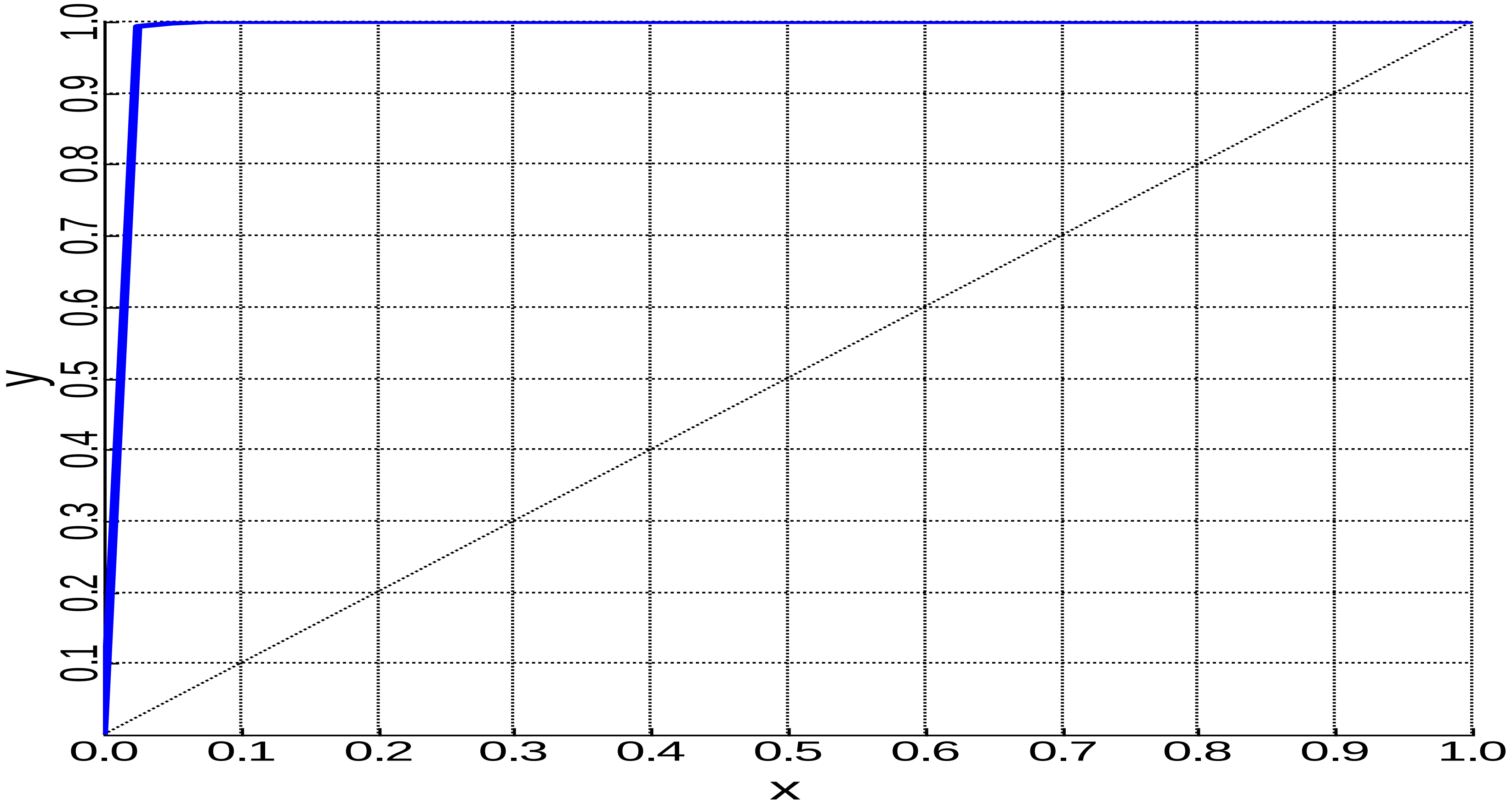
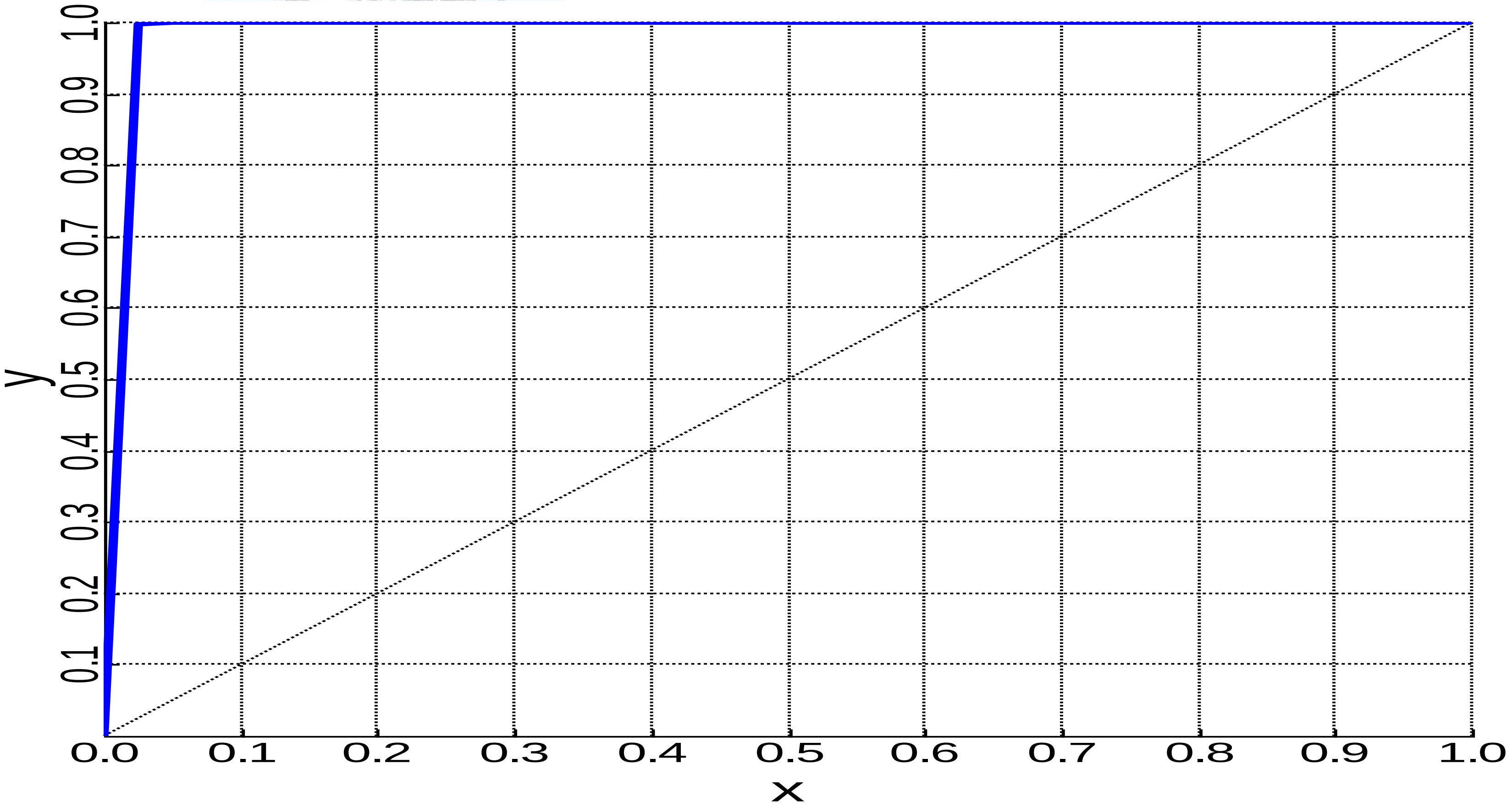
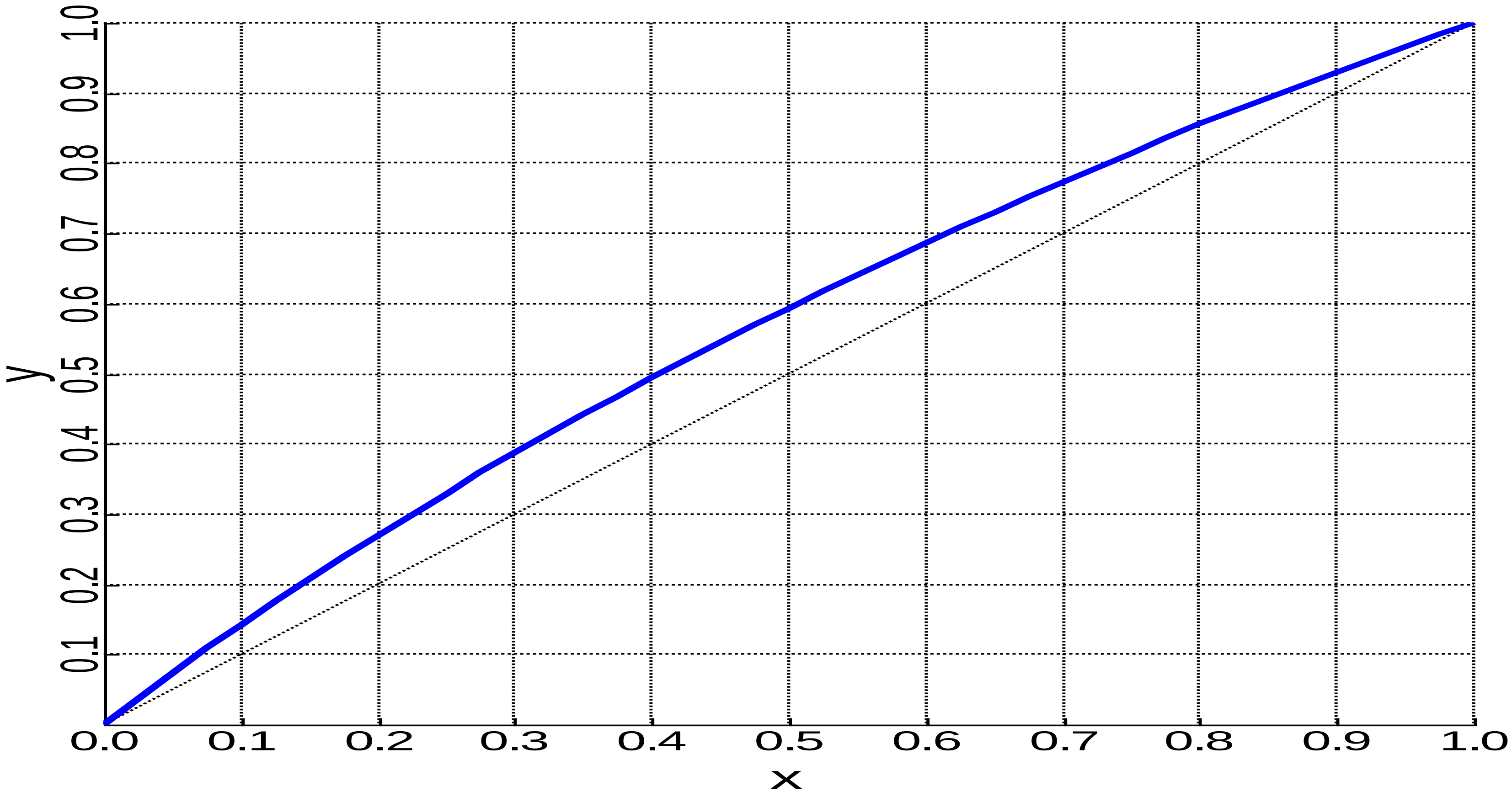
Ethyl acetato/glicerol



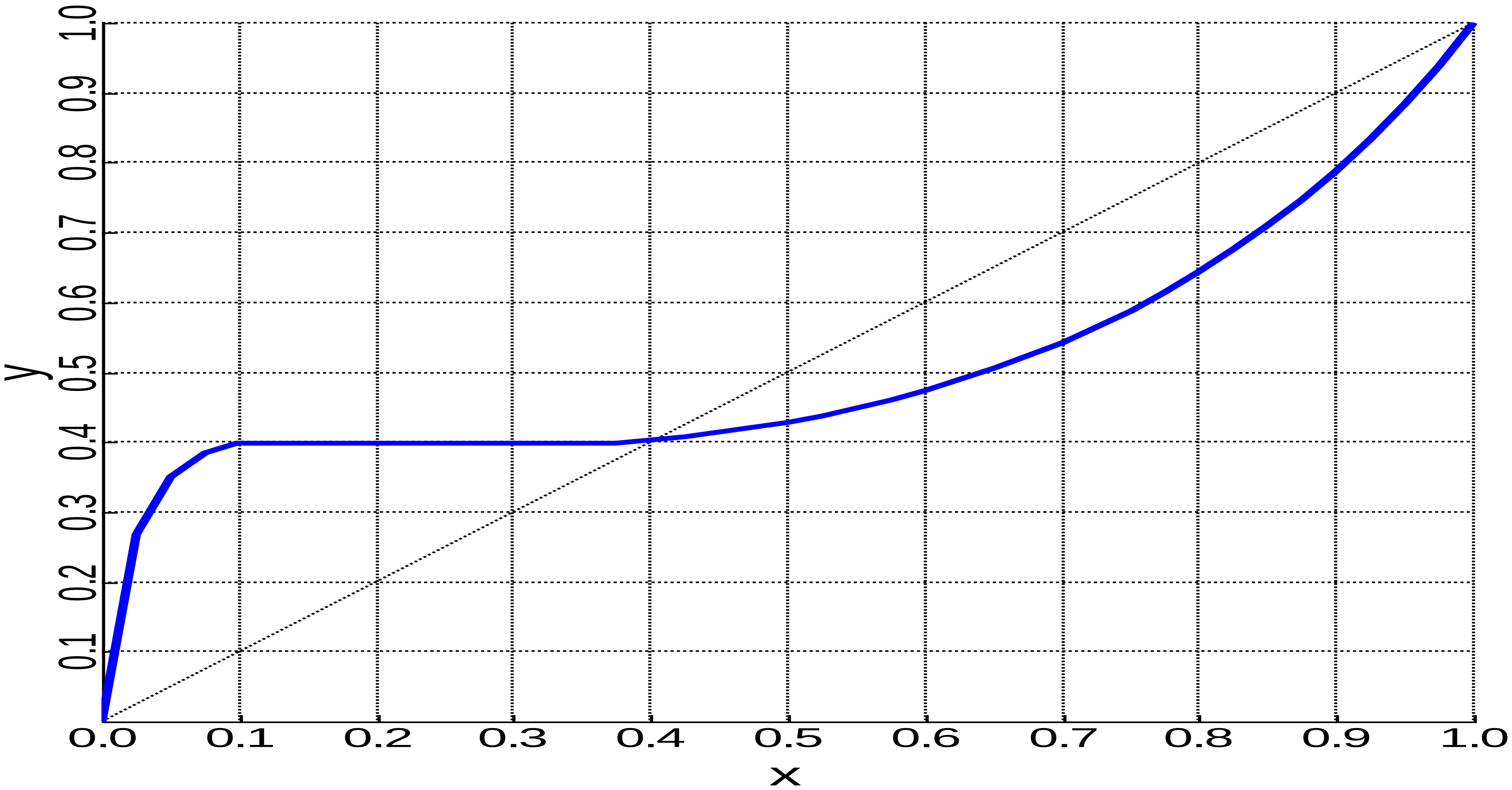
Ethanol/Sucrose



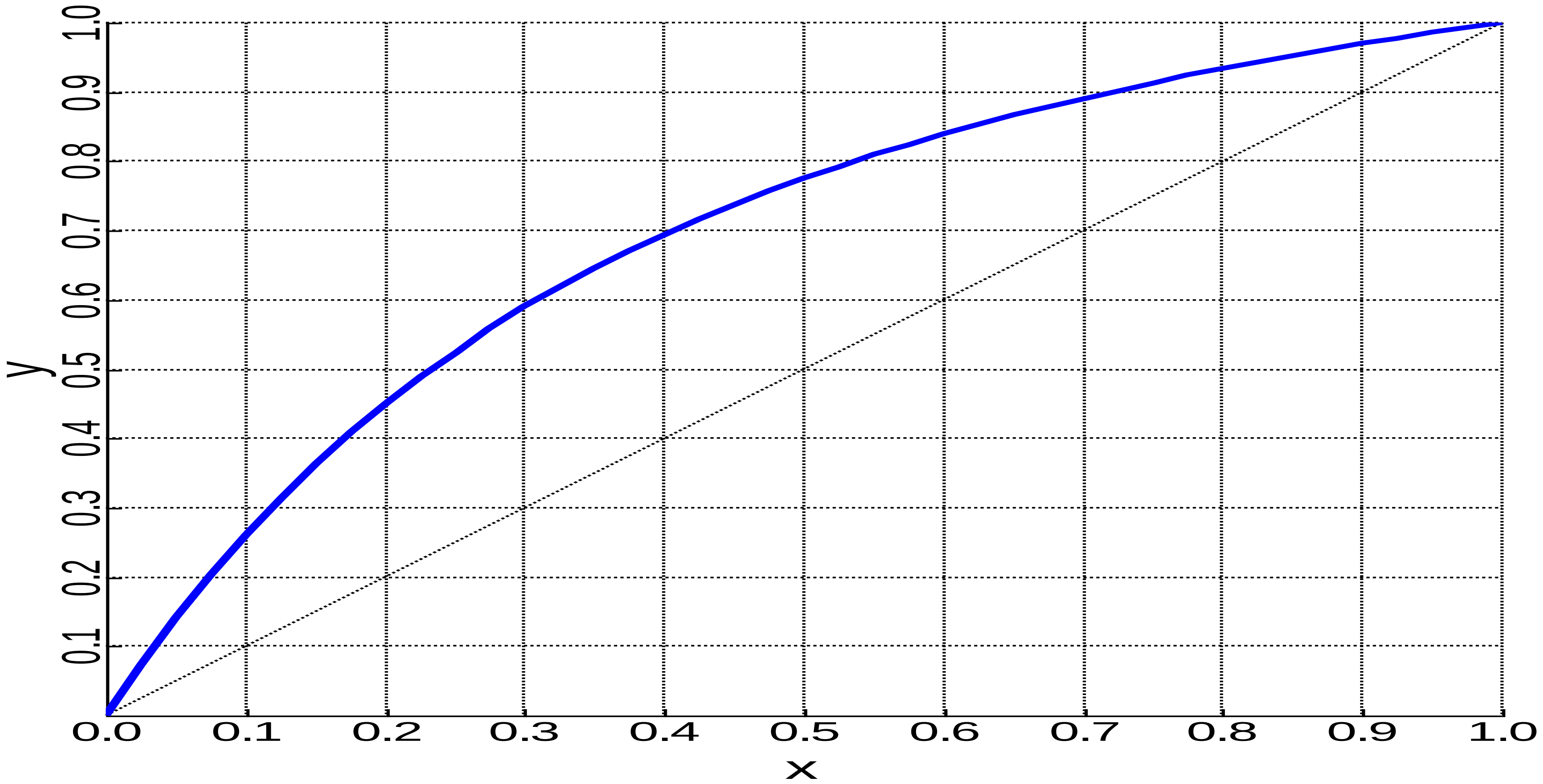
Propanol/Isobuthanol



Propanol/Water

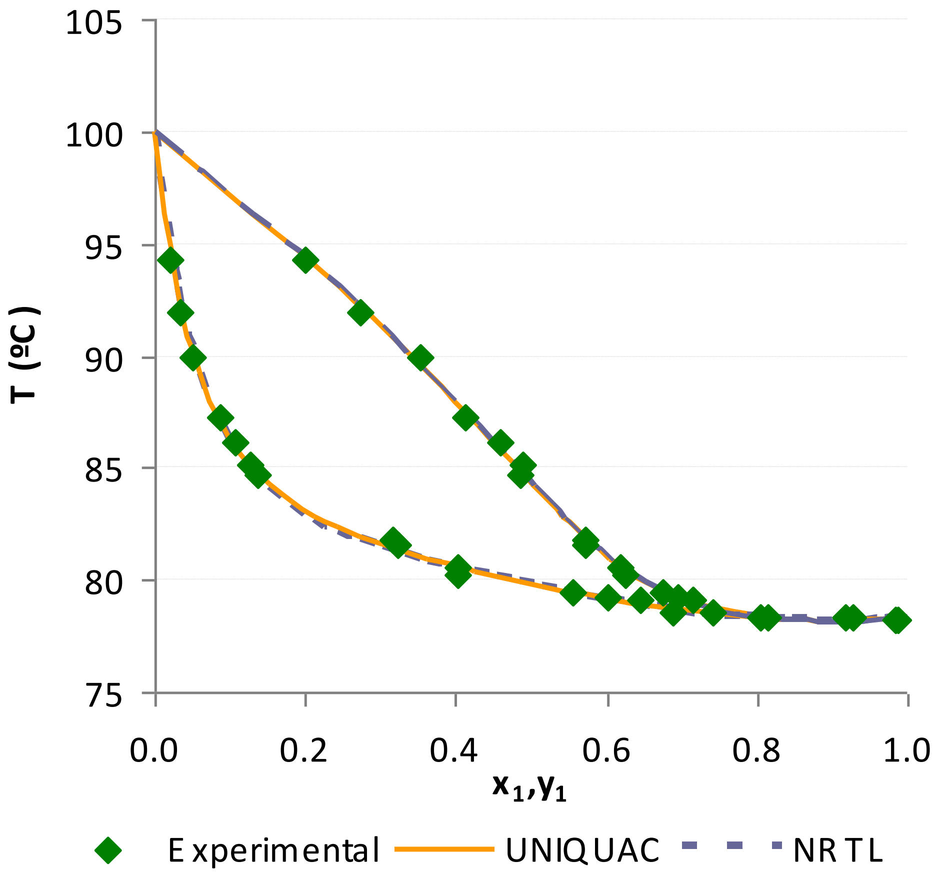


Propanol/Isoamylic alcohol

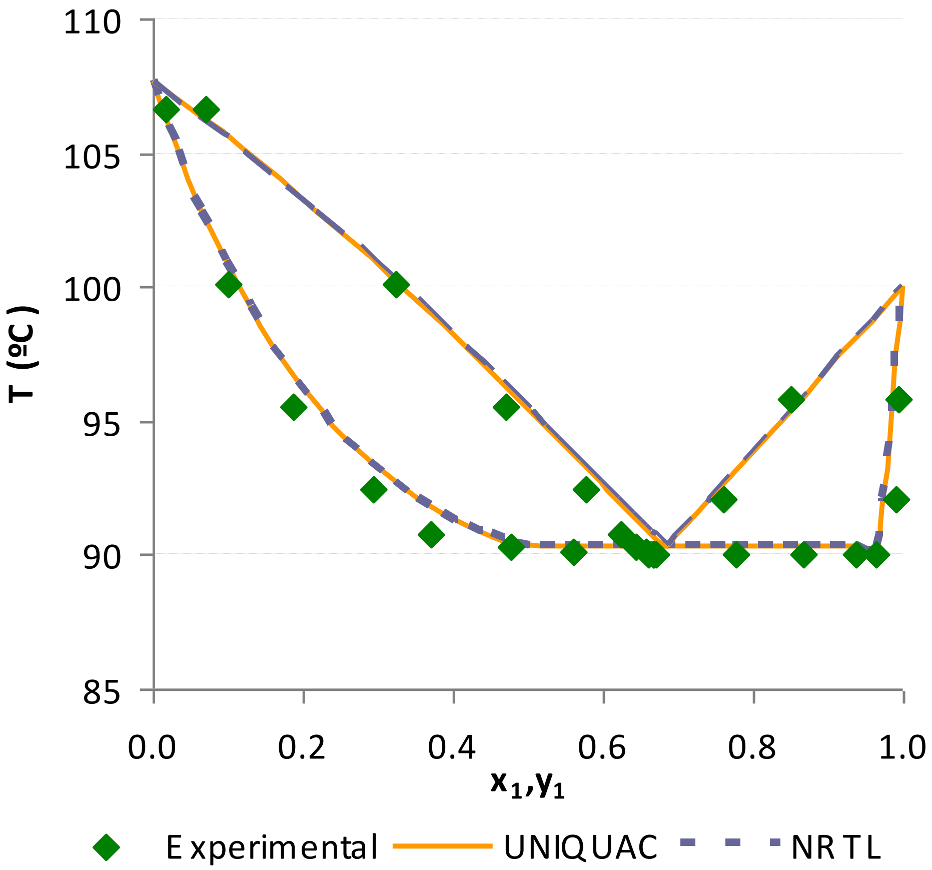


Both models represent properly

Ethanol (1) / Water (2): P=101.3 kPa

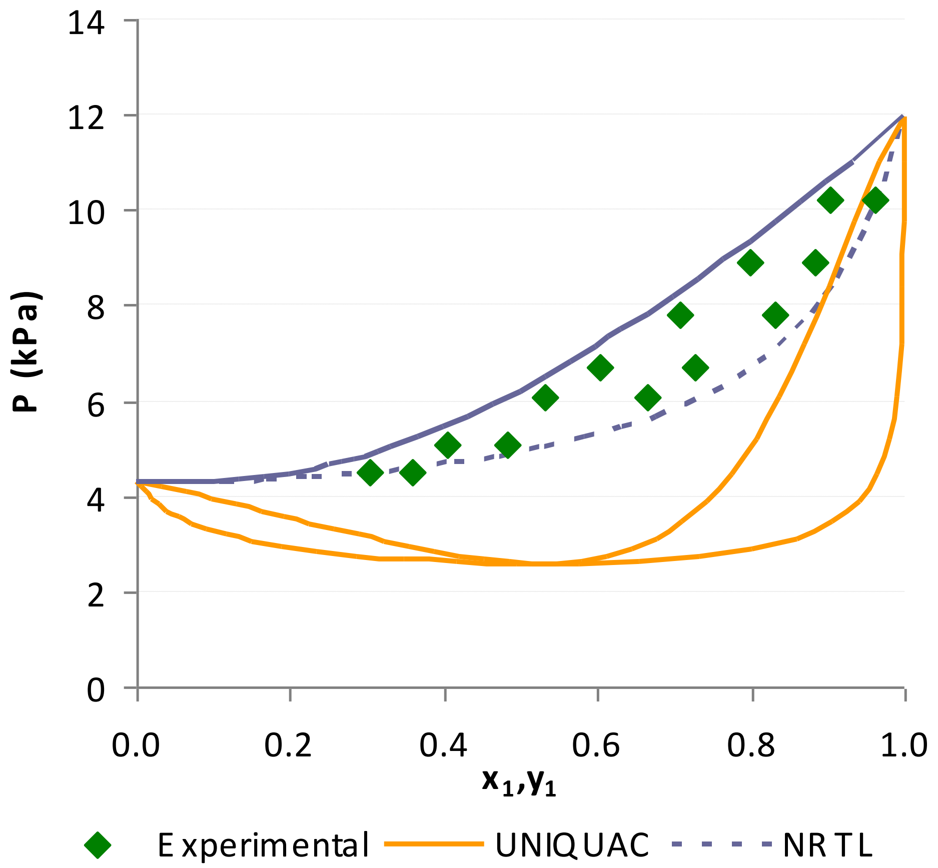


Water (1) / Isobutanol (2): P=101.3 kPa

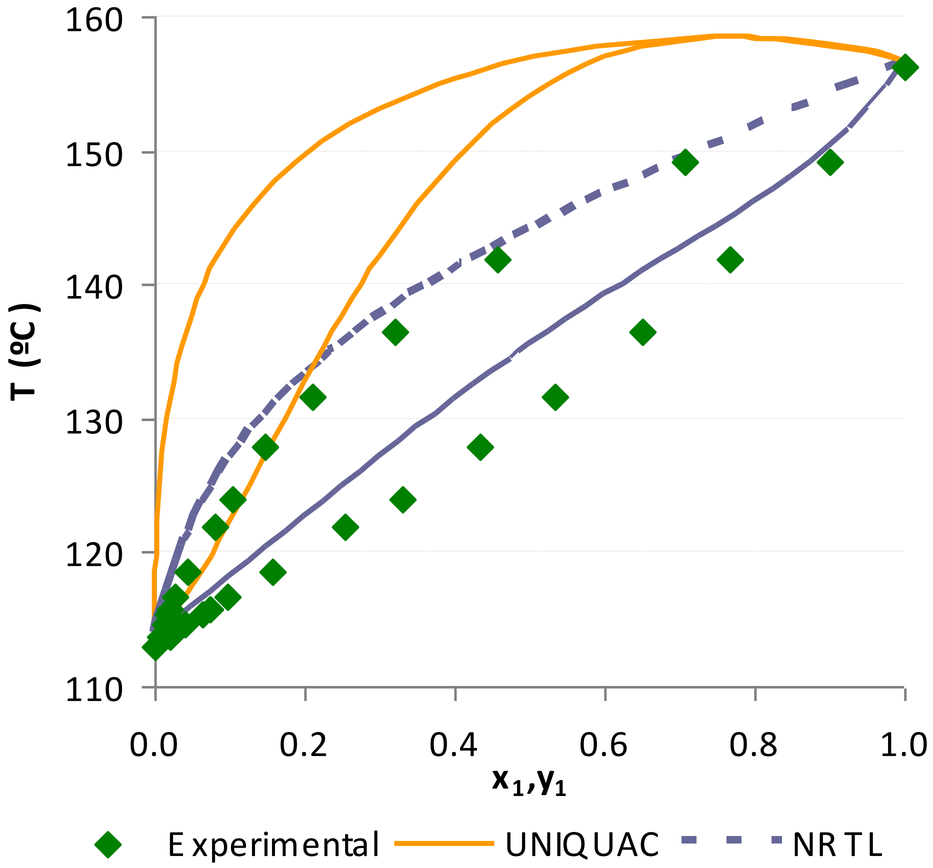


One of the models represent properly - NRTL

Acetic acid (1) / Amyl alcohol (2): T=60 ºC



Furfural (1) / Acetic acid (2): P=90 kPa



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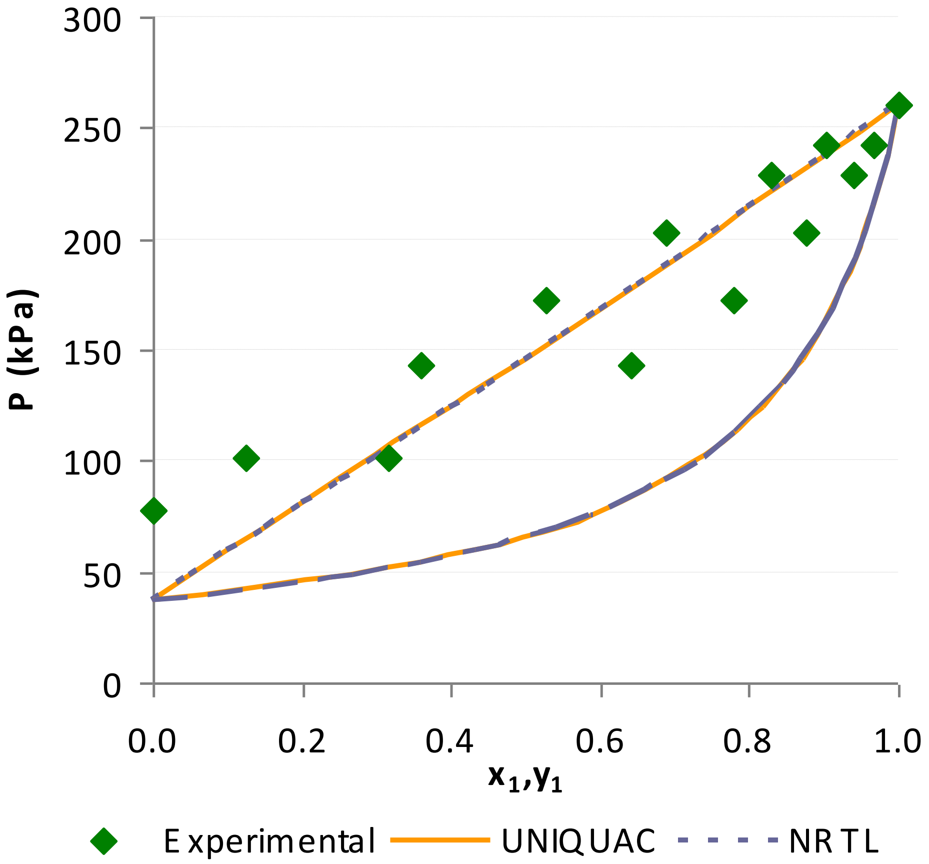
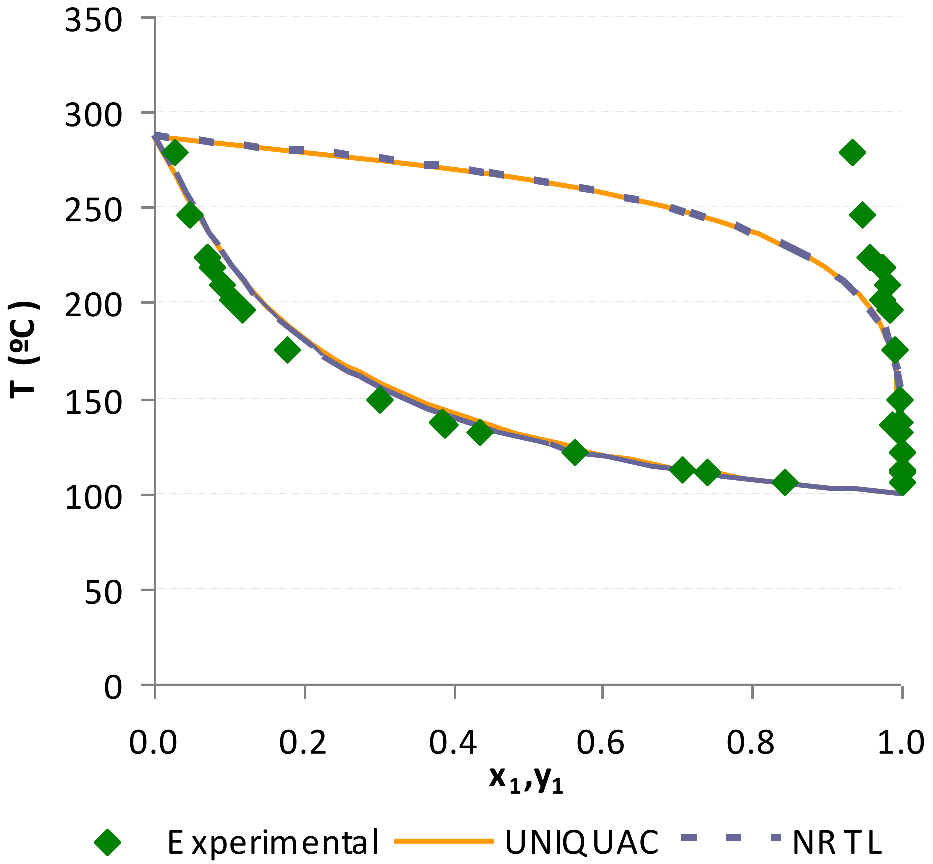
None of the models represent properly

Acetaldehyde (1) / Ethyl Acetate (2) : T=50 °C



Water (1) / Glycerol (2): P=101.3 kPa



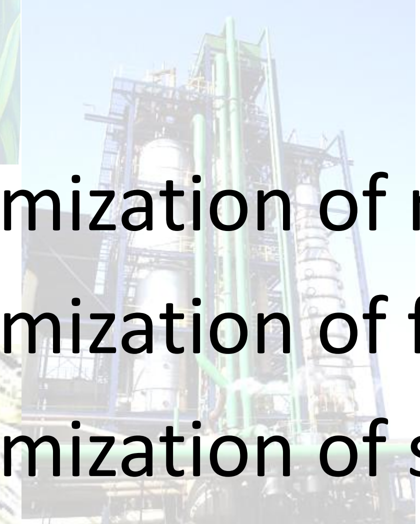
IMPROVING TECHNOLOGY

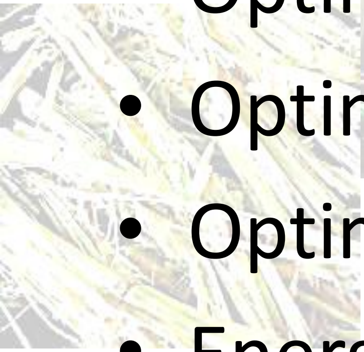
- TECHNOLOGY
- OTHER APPLICATIONS OF ETHANOL
- OPTIMIZATION
- WASTE MINIMIZATION

SEPARATION ENGINEERING

- Commercial Simulator: Data Bank
- Simulation Strategy for Desired Ethanol
- Simulation Strategy for Convergency
- Simulation Strategy for Dealing with all components
- Simulation Strategy for Sizing the Columns and the number of Units

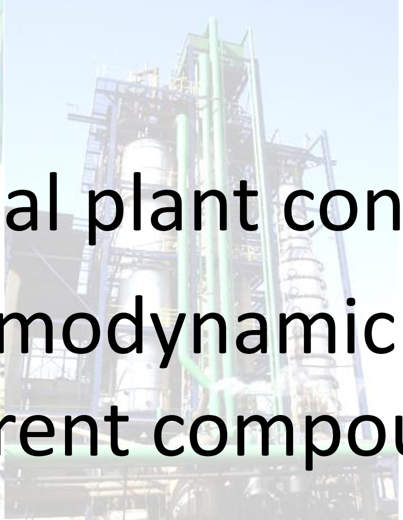
SEPARATION ENGINEERING

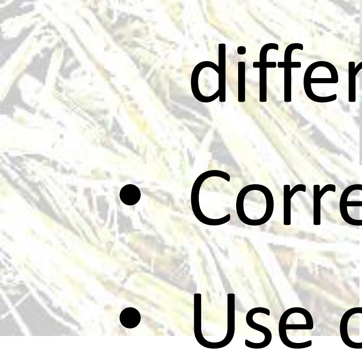




- Optimization of number of stages
- Optimization of feed positions
- Optimization of side streams
- Optimization of energy duties
- Energetic integration and optimization
- Waste minimization to air and to liquid
- New configurations of columns

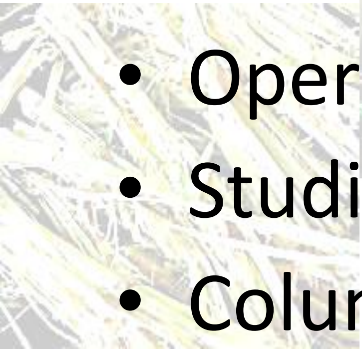
SEPARATION ENGINEERING





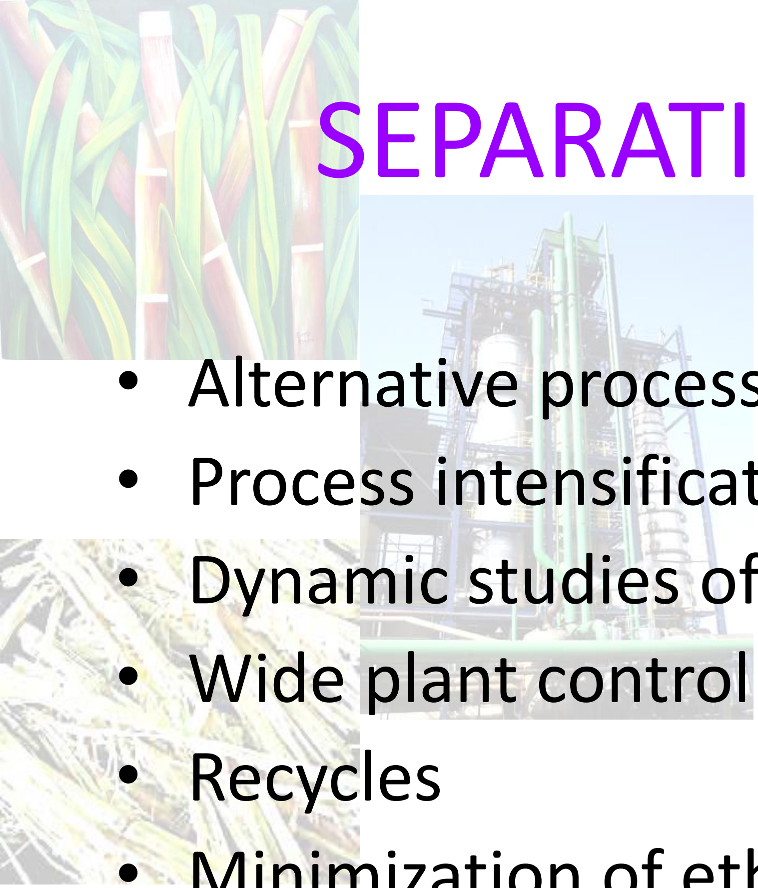
- Virtual plant configuration
- Thermodynamic models for dealing with different compounds and concentrations
- Corrections from equilibrium
- Use of nonequilibrium stage models
- New configurations in terms of operating conditions
- Hybrid processes

SEPARATION ENGINEERING



- Solvents
- Simulation and control
- Operator training
- Studies of equilibrium conditions
- Column internals
- Column flexibility analyses
- Studies of intermediate volatility components

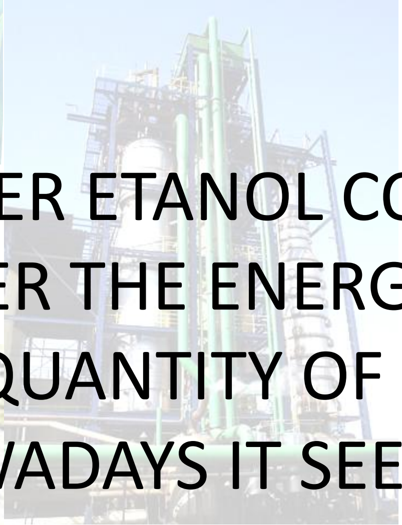
SEPARATION ENGINEERING



- Alternative process flowsheeting
- Process intensification
- Dynamic studies of the whole process
- Wide plant control
- Recycles
- Minimization of ethanol losses
- Initial alcohol concentration in the whole process
- Column retrofit
- MEE

SEPARATION ENGINEERING

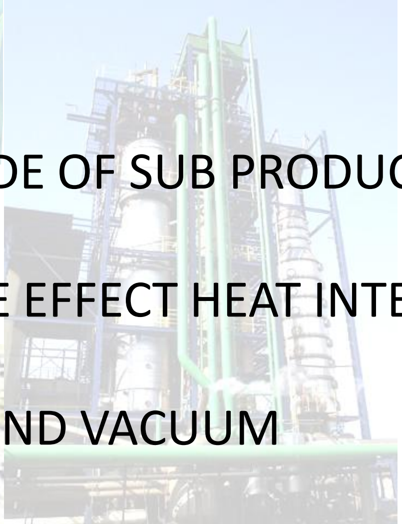
- BIOREFINERY INTEGRATION USING PINCH TECHNOLOGY

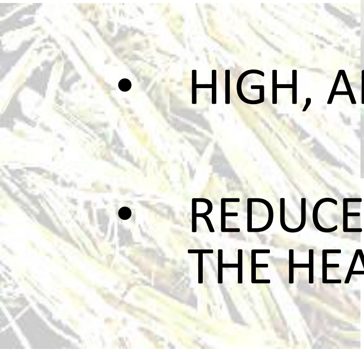


SOME RELEVANT ASPECTS

- HIGHER ETANOL CONCENTRATION IN THE WINE, LOWER THE ENERGY CONSUMPTION AND LOWER THE QUANTITY OF VINASSE AND PHLEGMASS (NOWADAYS IT SEEMS TO HAVE WINE WITH 11 TO 12 ^{0}GL)

- NST INCREASED IN ONE TOWER CAN REDUCE ABOUT 8% THE ENERGY CONSUMPTION (HYDROUS ETHANOL)





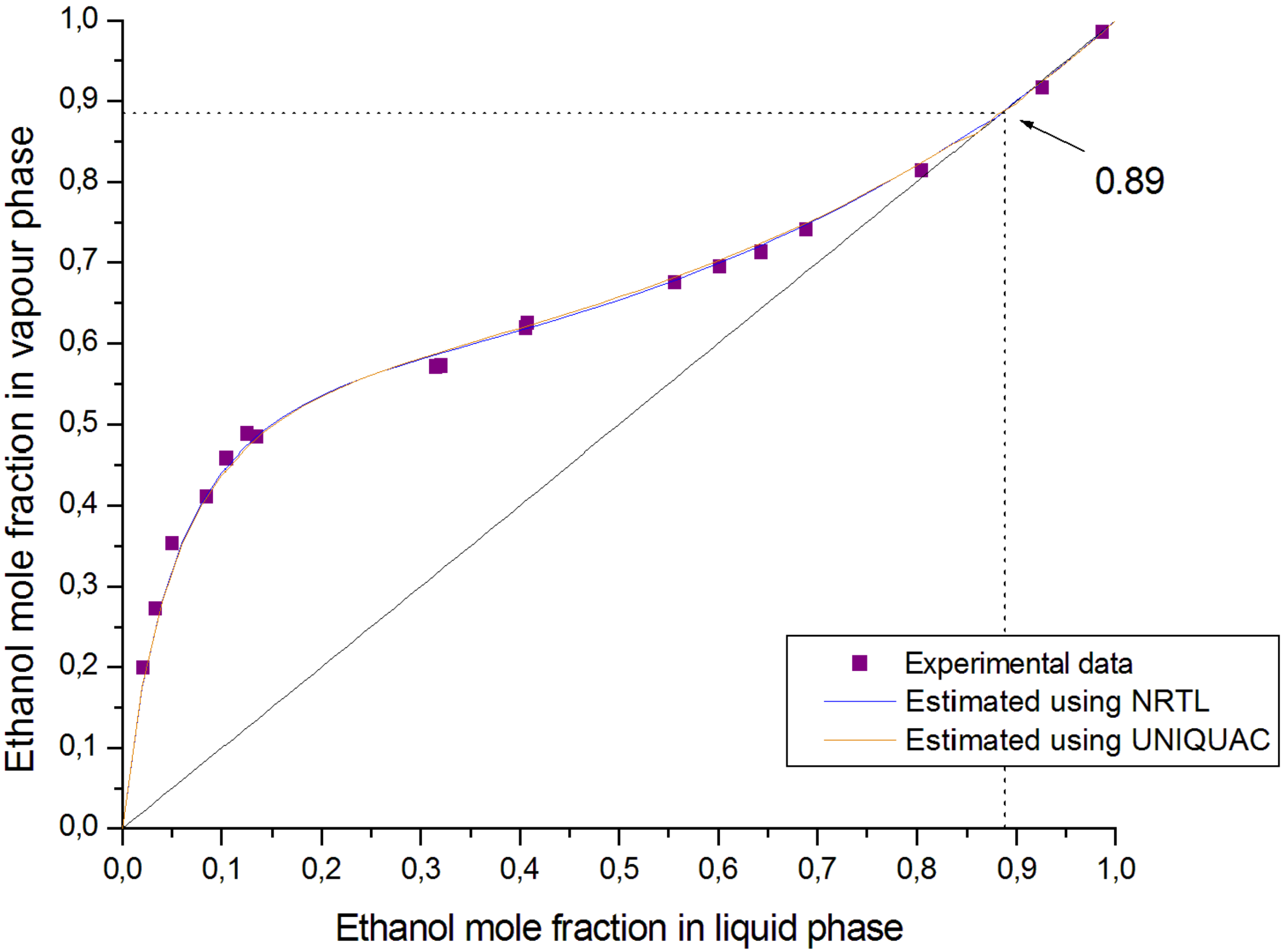
- UPGRADE OF SUB PRODUCTS SUCH AS SUPERIOR ALCOHOLS
- DOUBLE EFFECT HEAT INTEGRATION
- HIGH, AND VACUUM
- REDUCES VAPOR CONSUMPTION, HOWEVER INCREASES THE PRESSURE OF THE HEATING VAPOR, INCREASES DIAMETER
- CONDENSER OF THE VACUUM COLUMN MUST WORK WITH SUITABLE COOLING (MEG + WATER), APPEARS
- INCRUSTATIONS IN THE HIGH PRESSURE COLUMN

- Lignin separation- distillation column (Organosolv process) at 5 bar (example) or multiple effect evaporator????? It depends on the pre-treatment and hydrolysis
- HMF separation
- FURFURAL

Simulation components – hypothetical

- Since not all components present in bioethanol production are available at HYSYS/UNISIM/ASPEN database, some hypothetic components were created to represent:
  - Conventional process components: sugarcane bagasse (cellulose, hemicellulose and lignin), dirt, impurities (salts, organic acids), lime, phosphoric acid, yeast
  - Hydrolysis components: pentose and HMF

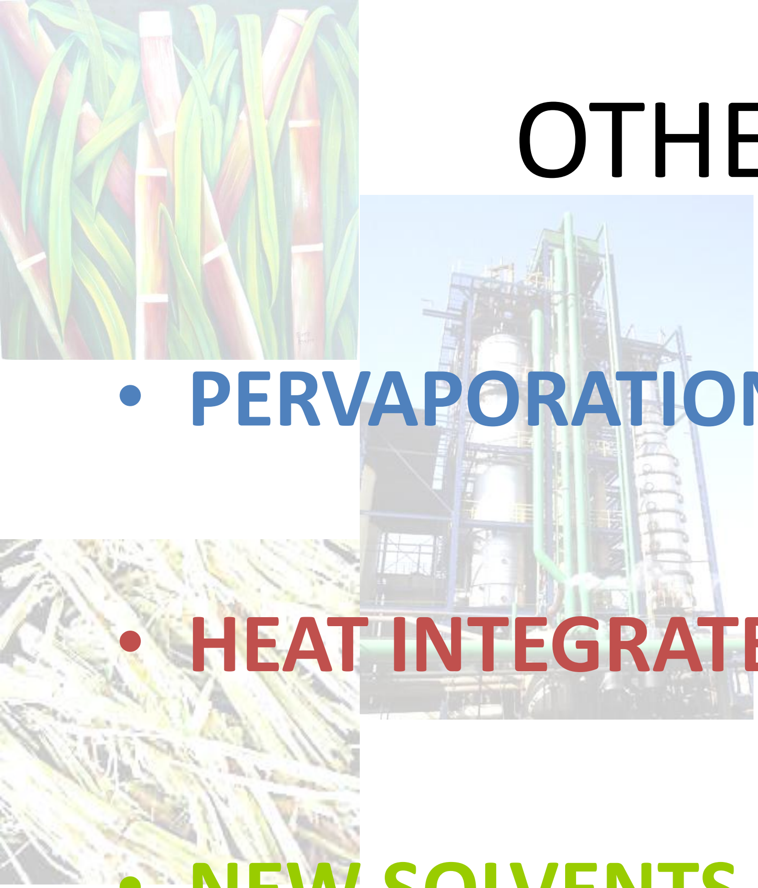
Ethanol dehydration



PRINCIPAL METHODS FOR DEHYDRATING ETHANOL IN INDUSTRY TODAY

- AZEOTROPIC DISTILLATION WITH CYCLOHEXANE
- EXTRACTIVE DISTILLATION WITH MONOETHYLENE GLICOL (MEG)
- ADSORPTION IN MOLECULAR SIEVES

OTHER BECOMING

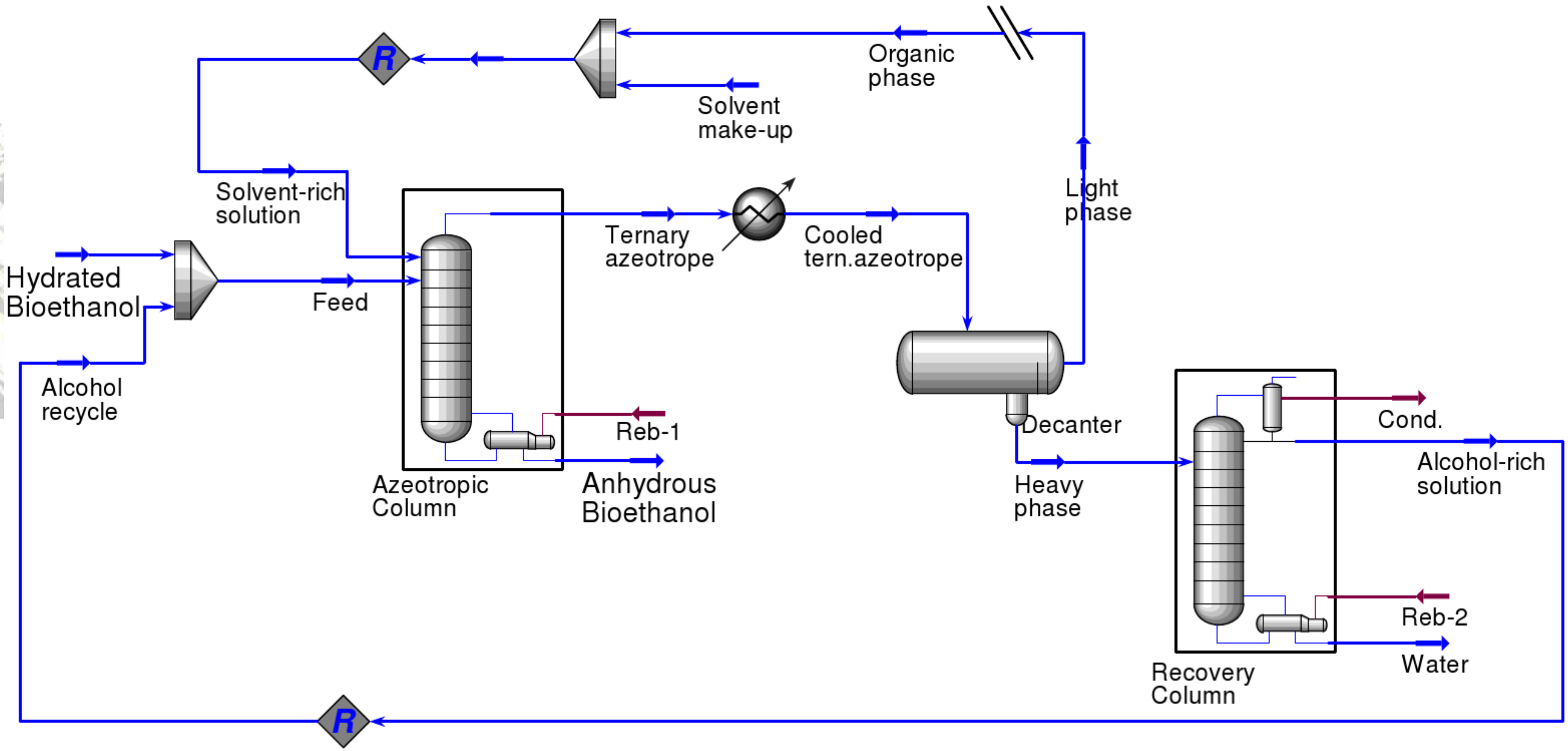


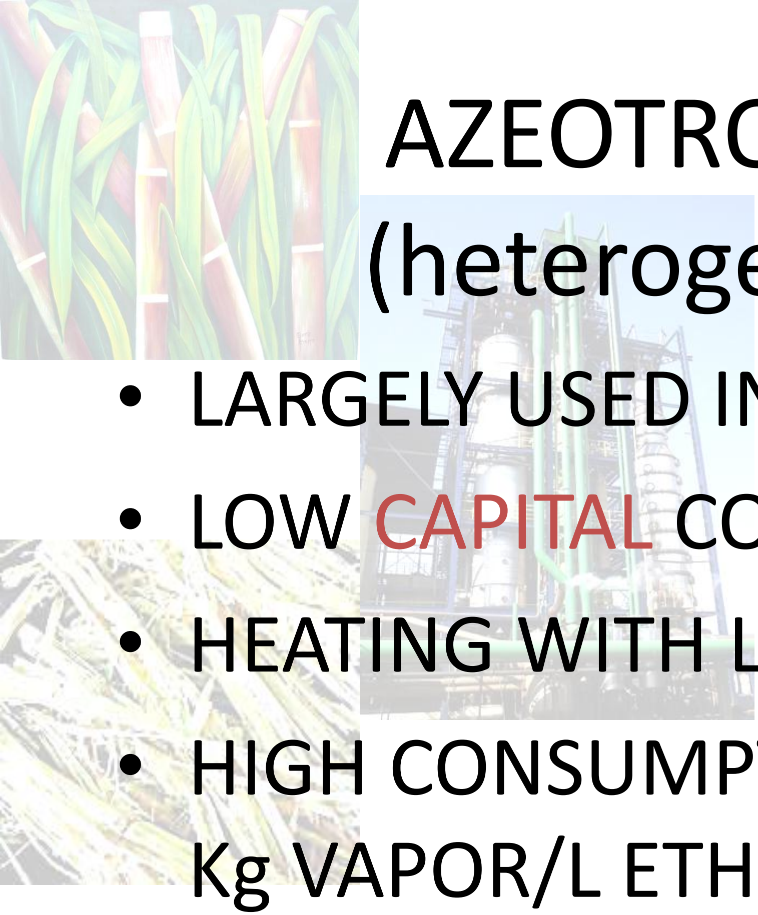
- PERVAPORATION
- HEAT INTEGRATED PROCESS
- NEW SOLVENTS
- NEW COLUMN CONFIGURATION

Ethanol dehydration processes

- Two different processes can be analyzed:
  - **Extractive distillation**: both conventional and alternative configuration
  - **Azeotropic distillation**
- Solvent evaluation:
  - Extractive distillation: monoethyleneglycol (MEG) and glycerin
  - Azeotropic distillation: cyclohexane and n-heptane

Azeotropic distillation





AZEOTROPIC DISTILLATION (heterogeneous distillation)

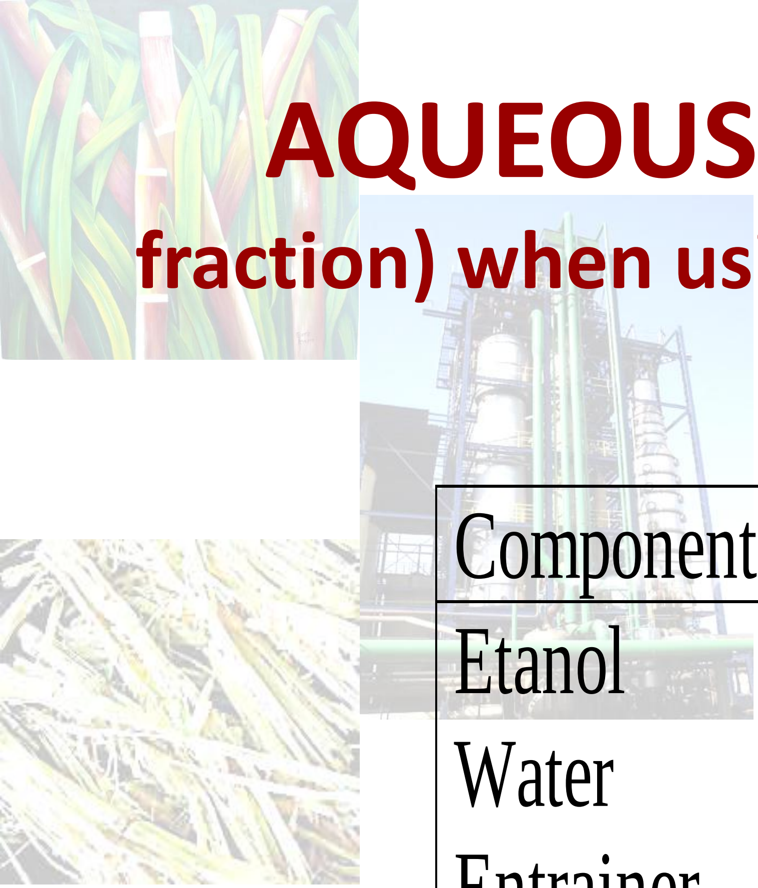
- LARGELY USED IN INDUSTRIES
- LOW CAPITAL COSTS
- HEATING WITH LOW PRESSURE STEAM
- HIGH CONSUMPTION OF VAPOR (1.5 TO 1.6 Kg VAPOR/L ETHANOL)
- LOSSES OF ENTRAINER IN THE ANHYDROUS ETHANOL STREAM

- DOUBLE EFFECT HEAT INTEGRATION SEEMS TO BE A GOOD ALTERNATIVE, BUT IT IS NECESSARY HIGH PRESSURE STEAM

ORGANIC PHASE composition (mole fraction) when using benzene and cyclohexane

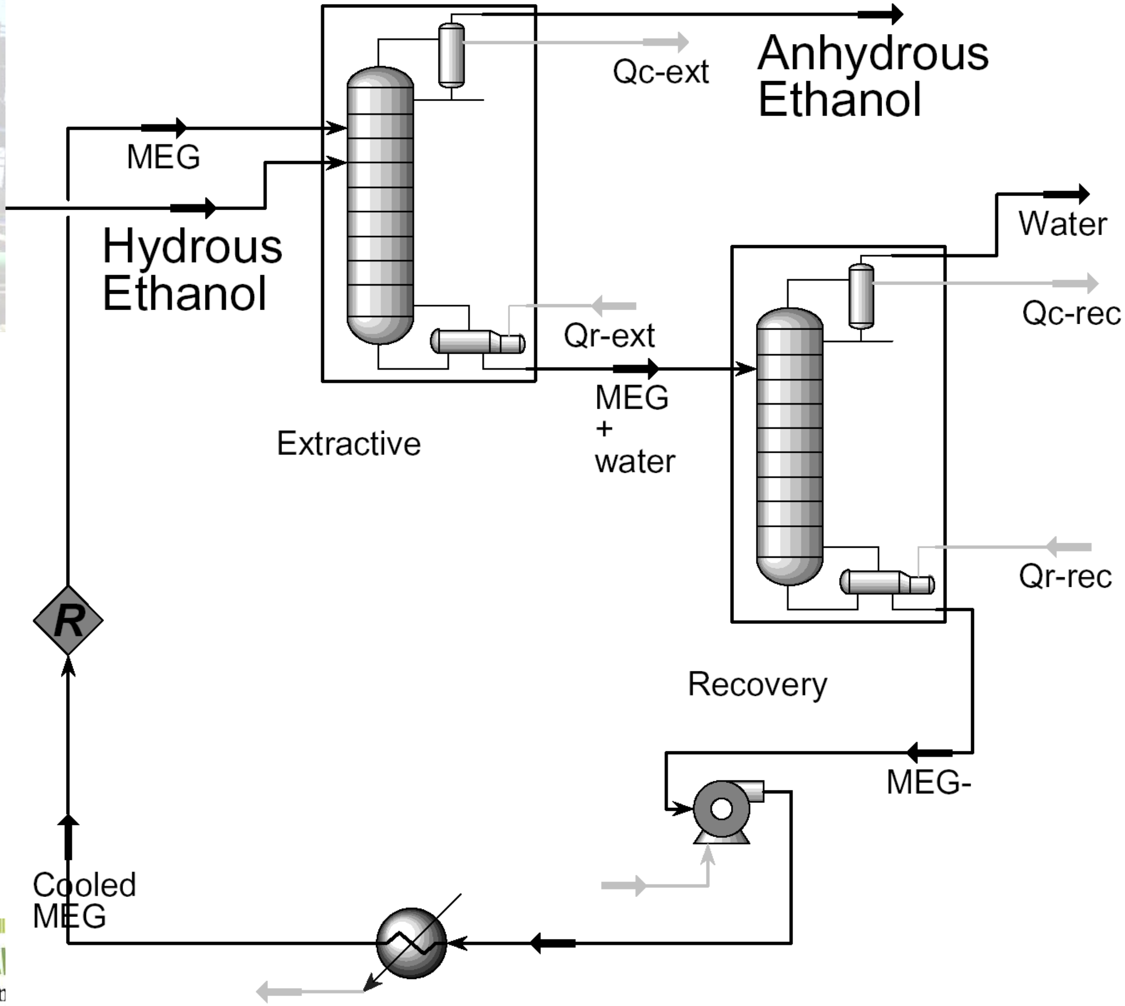
Component	Benzene	Cyclohexane
Ethanol	0.3358	0.0768
Water	0.0517	0.0015
Entrainer	0.6126	0.9217

AQUEOUS PHASE composition (mole fraction) when using benzene and cyclohexane



Component	Benzene	Cyclohexane
Etanol	0.4834	0.6766
Water	0.4773	0.2122
Entrainer	0.0394	0.1112

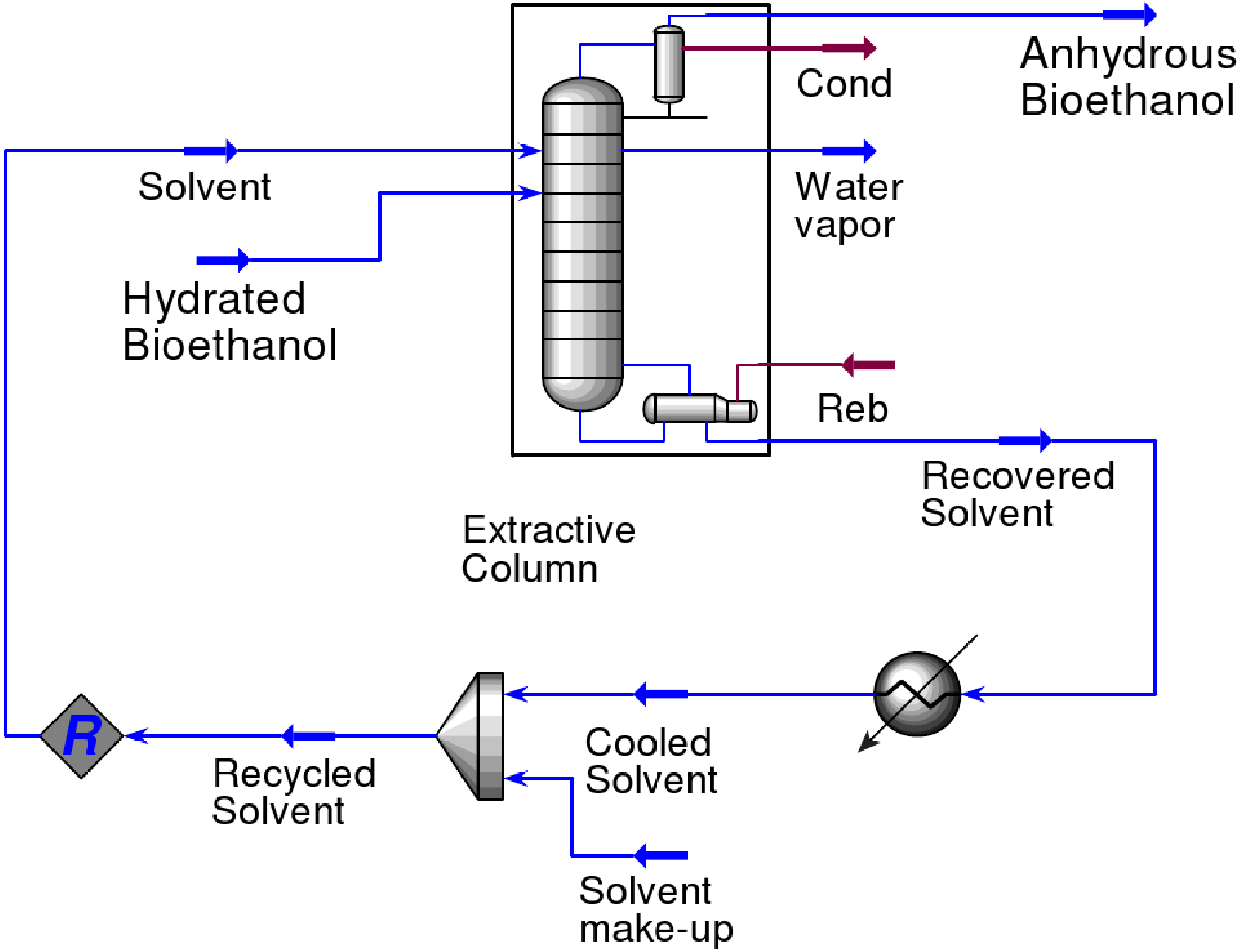
Extractive distillation with MEG – conventional configuration



- IT MAY BE POSSIBLE TO DUPLICATE THE PRODUCTION USING THE CONFIGURATION OF AZEOTROPIC TO EXTRACTIVE DISTILLATION.

- SMALLER DIAMETER WITH MEG
- LOWER SENSITIVITY TO FEED CONCENTRATION USING MEG
- DISADVANTAGE OF MEG:HIGH PRESSURE VAPOR.

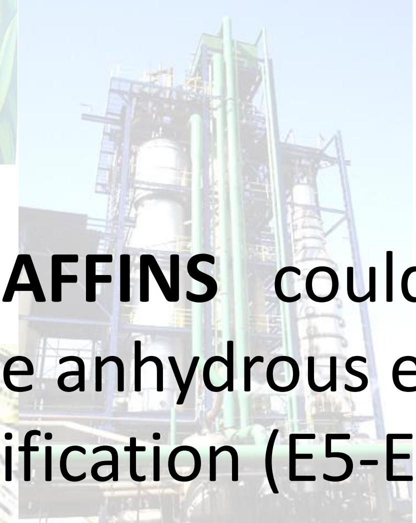
Extractive distillation – alternative configuration



Comparison between extractive and azeotropic distillation

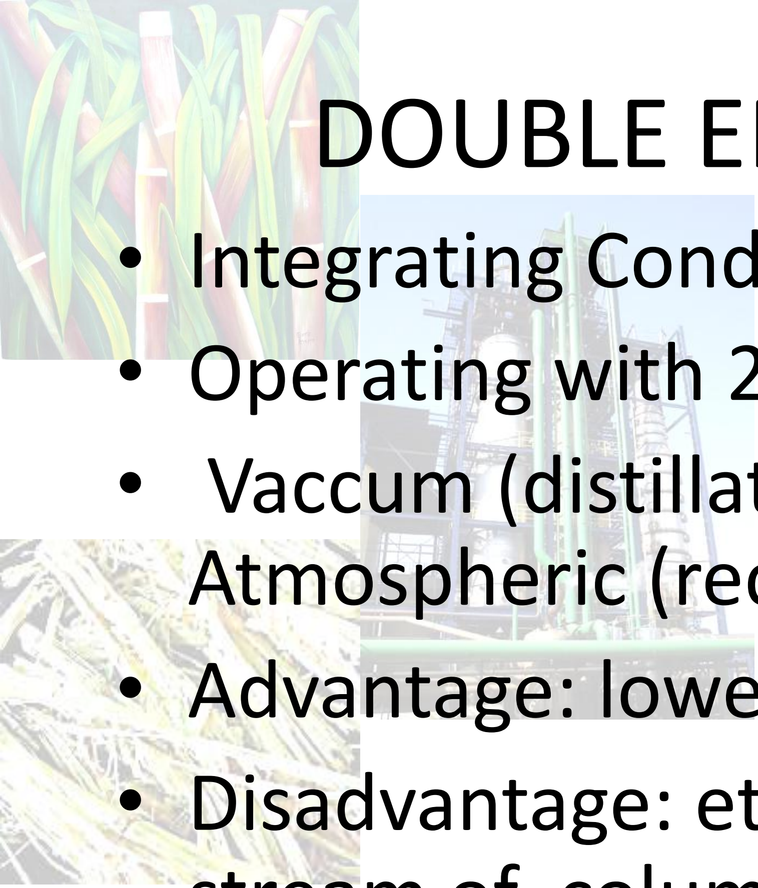
Parameter	Extractive Distillation				Azeotropic Distillation	
	Conventional		Alternative		Ciclo-hexane	n-Heptane
	MEG	Glyc.	MEG	Glyc.		
Vapor consumption (kg/L anydr ethanol)	0.43	0.47	0.41	0.56	8.0	6.1
Saturated steam pressure (bar)	6	10 / 65	6	65	2.5	2.5
Ethanol losses (%)	10^{-5}	10^{-5}	$9x10^{-5}$	$6x10^{-5}$	0.017	0.017
Solvent losses (%)	0.01	0.01	0.49	0.02	0.001	0.008
Solvent in anhydrous ethanol (wt%)	No contamination with solvent				0.017	0.04

AZEOTROPIC DISTILLATION



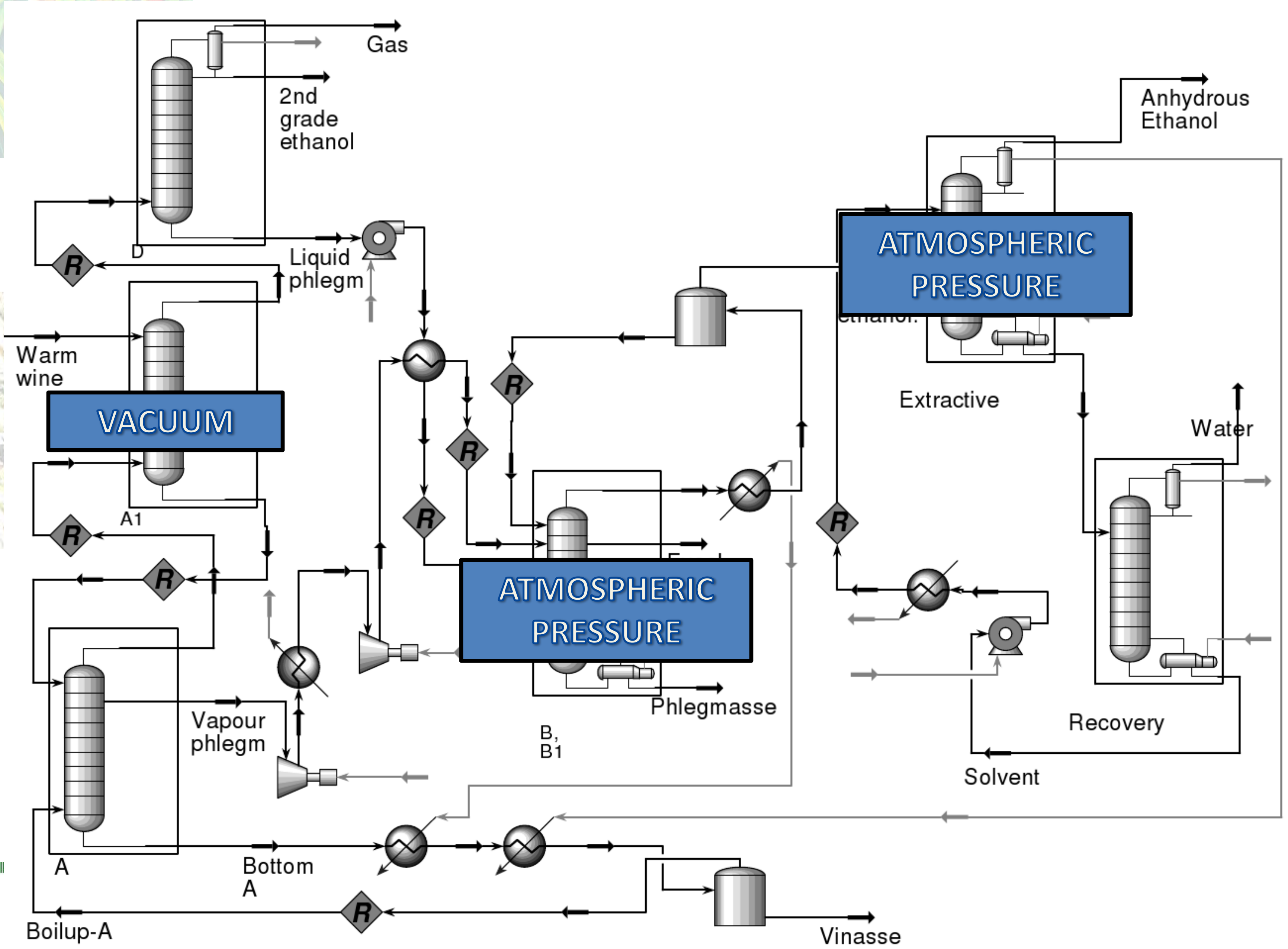
- **PARAFFINS** could be used taken into account drag in the anhydrous ethanol contributing to the fuel specification (E5-E25)
- **For large plants the vapor consumption can be overcome using multiple effect column arrangements (diferent pressures) , increasing some times NST**

DOUBLE EFFECT DISTILLATION

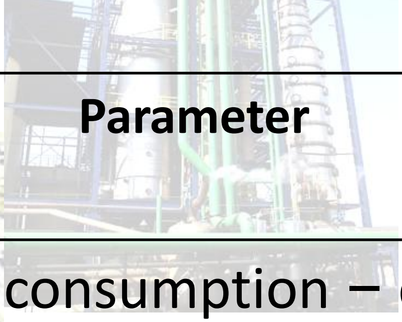


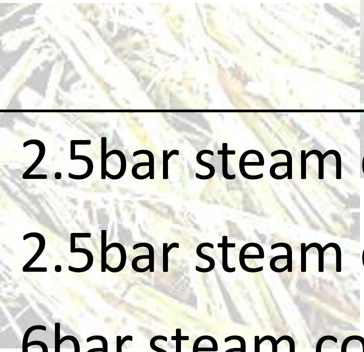
- Integrating Condenser and Reboiler
- Operating with 2 levels of pressure
- Vaccum (distillation columns A, A1 e D) e Atmospheric (rectifying B, and stripper B1)
- Advantage: lower total vapor consumption
- Disadvantage: ethanol losses at the top stream of column D in the vapor phase (necessary for discharging CO_2)

Double effect distillation



Steam consumption on column reboilers – conventional and double effect distillation





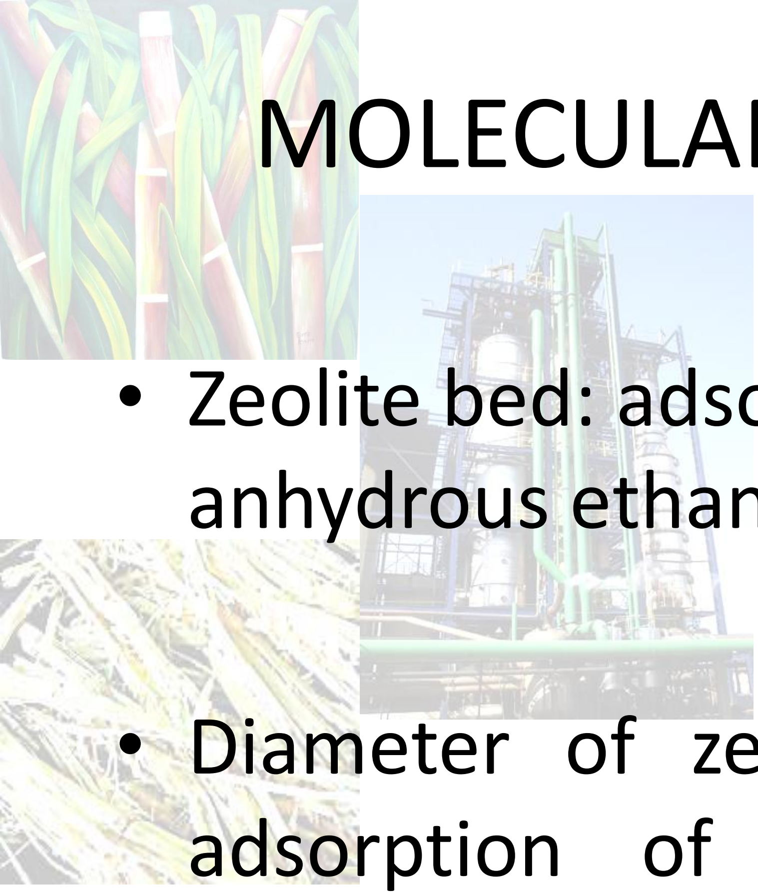
Parameter	Distillation process	
	Conventional	Double-effect
2.5bar steam consumption – column A	1.53	0.00
2.5bar steam consumption – column B	0.27	0.38
6bar steam consumption – extractive column	0.35	0.35
6bar steam consumption – recovery column	0.07	0.07
Total steam consumption	2.21	0.80

Steam consumption - [kg/L anhydrous ethanol]

- Cyclohexane in (B) – 4th **Technical** of Mélle Plants

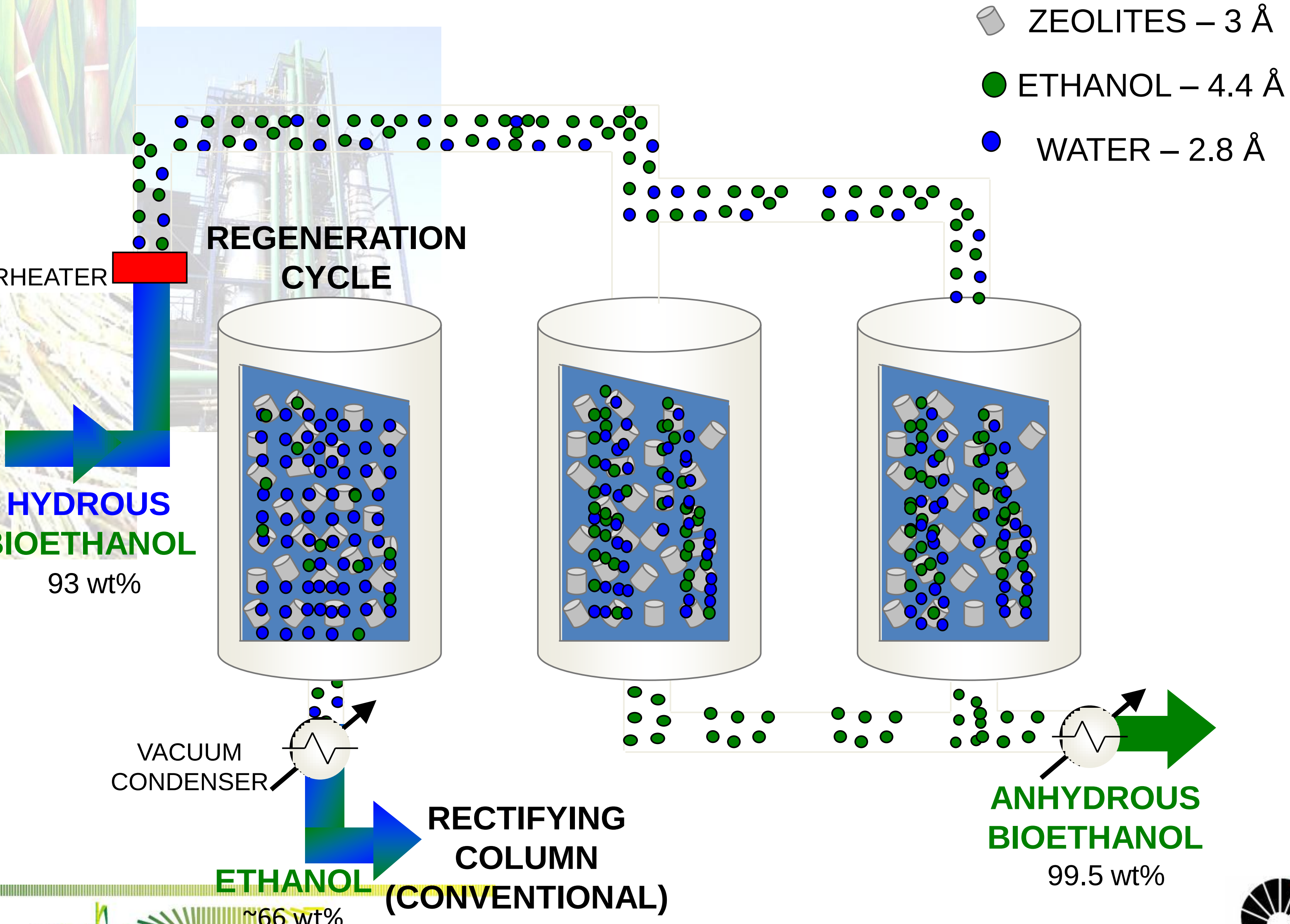
- Vapor global consumption for anhydrous ethanol can decrease from 4.2 to 2.8 kg vapor/L ethanol (Meirelles, 2006).

MOLECULAR SIEVE ADSORPTION



- Zeolite bed: adsorb water producing anhydrous ethanol
- Diameter of zeolites: about 3 Å, allowing adsorption of water molecules (2.8 Å), separating them from ethanol (4.4 Å)

MOLECULAR SIEVES



ZEOLITES – 3 Å

● ETHANOL – 4.4 Å

● WATER – 2.8 Å

SUPERHEATER

REGENERATION CYCLE

HYDROUS BIOETHANOL
93 wt%

VACUUM CONDENSER

ETHANOL
~66 wt%

RECTIFYING COLUMN (CONVENTIONAL)

ANHYDROUS BIOETHANOL
99.5 wt%

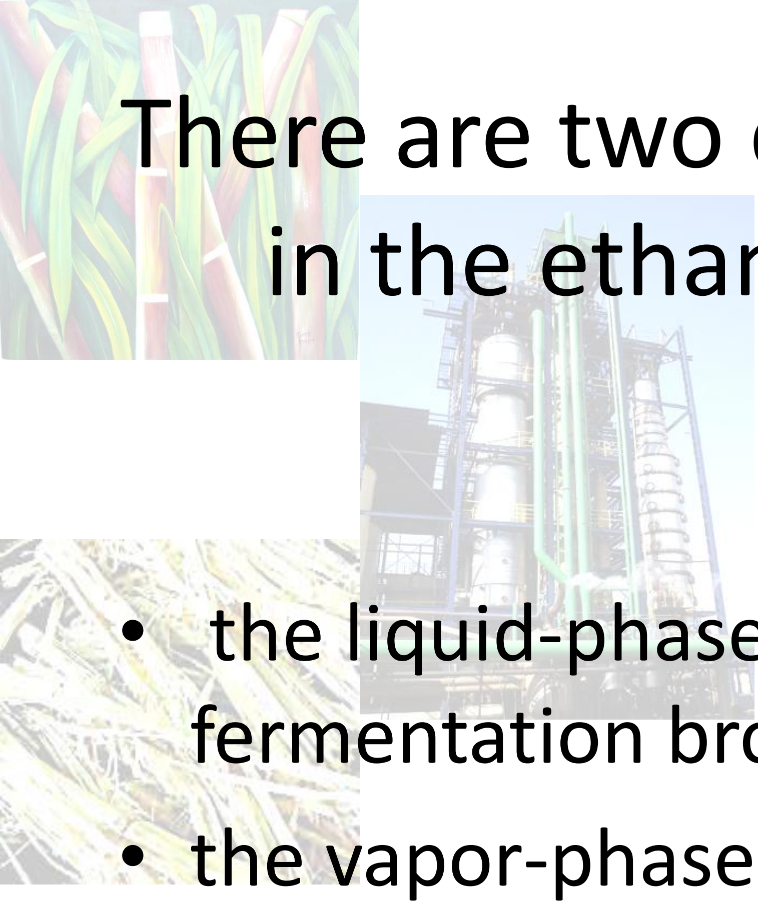
Disadvantages:

- High investment cost
- Zeolites are imported
- High vaccum for bed regeneration

- Huang et al. (2008)
- A review of separation technologies in current and future biorefineries

- SEPARATION AND PURIFICATION TECHNOLOGY

There are two categories of adsorption in the ethanol–water separation



- the liquid-phase adsorption of water from the fermentation broth
- the vapor-phase adsorption of water from the process stream out of distillation column

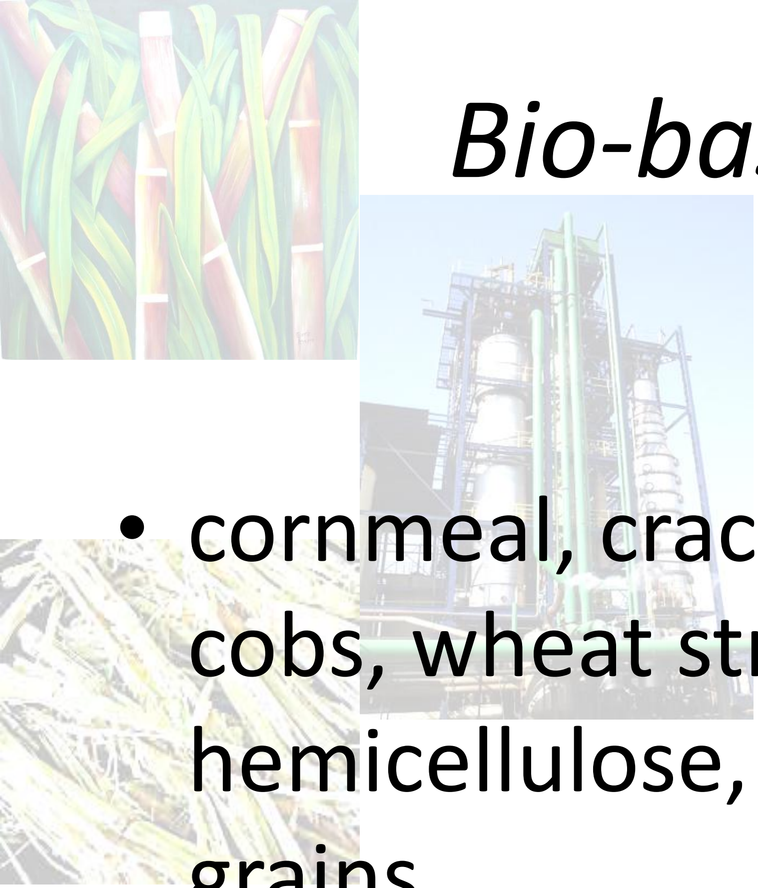
ADSORBENTS - vapor phase- adsorption of water

- Inorganic adsorbents such as molecular sieves (Zeolites 3A). Recently 4A , 5A
- lithium chloride
- silica gel
- activated alumina
- bio-based adsorbents such as corn grits

BIOADSORBENTS

- **Renewable**
- **Biodegradable**

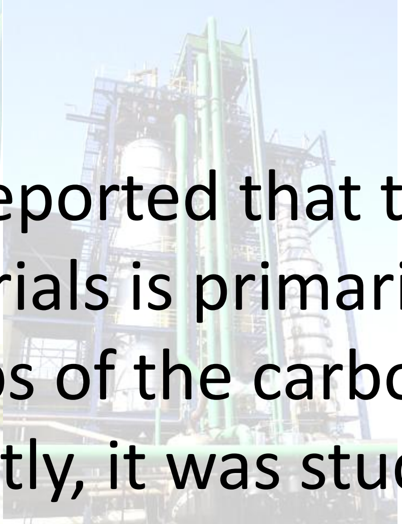
Bio-based adsorbents

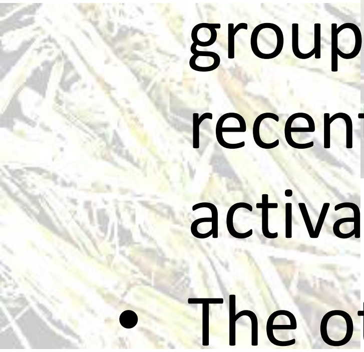


- cornmeal, cracked corn, starch, corn cobs, wheat straw, bagasse, cellulose, hemicellulose, wood chips, and other grains

- to obtain more than 99.5 wt% ethanol

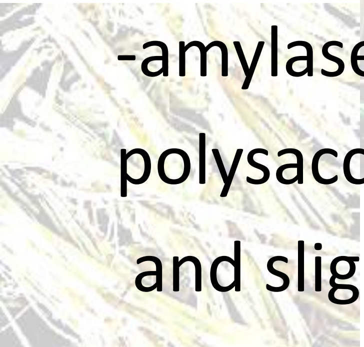
- fluidized-bed regeneration for breaking the ethanol–water azeotrope to obtain anhydrous ethanol.





- It is reported that the adsorption on lignocellulosic materials is primarily dependent on the hydroxyl groups of the carbohydrates and the lignin. Most recently, it was studied natural corncobs, natural and activated palm stone and oak.
- The other three lignocellulose-based adsorbents (bleached wood pulp, oak sawdust, and kenaf core) have also been explored in a thermal swing adsorption column.

Liquid-phase adsorption of water



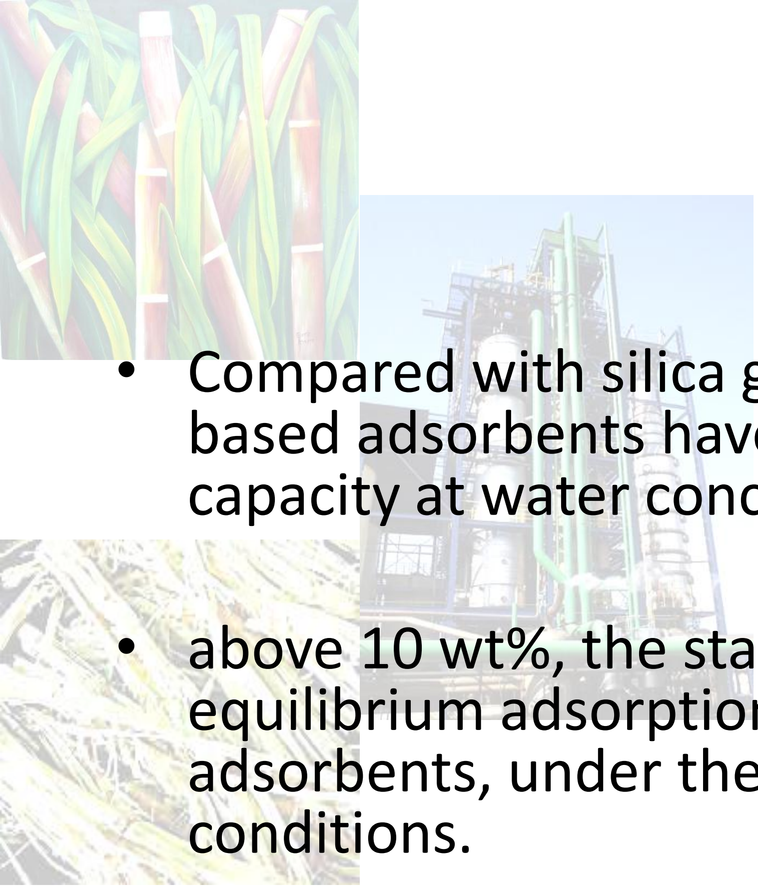
Recently, several combinations of starch-based and cellulosic materials, including white corn grits,

-amylase-modified yellow corn grits,

polysaccharide-based synthesized adsorbent,

and slightly gelled polysaccharide-based

synthesized adsorbent, have also been tested and screened for liquid-phase adsorption of water.



- Compared with silica gel and molecular sieves, these starch-based adsorbents have lower nonequilibrium adsorption capacity at water concentration below 10 wt%.

- above 10 wt%, the starch-based adsorbents have similar non-equilibrium adsorption capacity to that of the inorganic adsorbents, under the same adsorption and regeneration conditions.

- Among a variety of bio-based adsorbents, corn grits are reported as the only bio-based adsorbents which have been successfully applied in industry

Advantages and disadvantages of adsorption

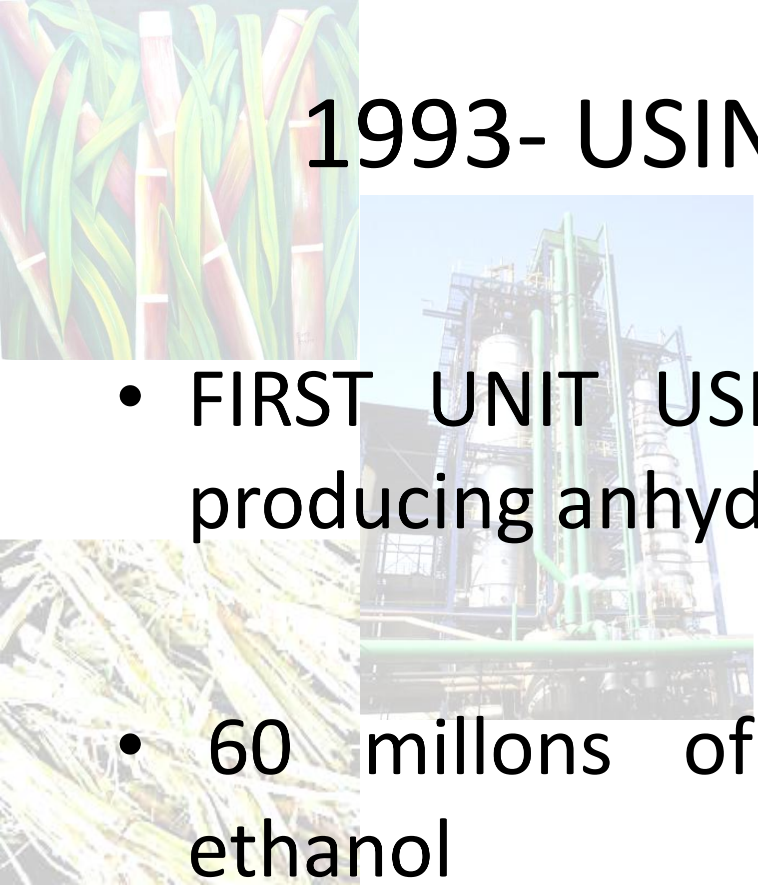
- The vapor phase adsorption consumes lower energy than distillation

- Zeolite molecular sieves are highly selective, but water is very strongly adsorbed and high temperatures and/or low pressures are required to regenerate them .

` Bio-based adsorbents have lower separation capacity than molecular sieves, but their regeneration temperature is much lower than molecular sieves.

- Molecular sieves are more expensive than bio-based adsorbents. In some cases of using bio-based adsorbents for removal of water, the saturated adsorbents can be used directly as feedstock, and simply fresh adsorbents are used without regeneration step.

1993- USINA DA PEDRA PLANT

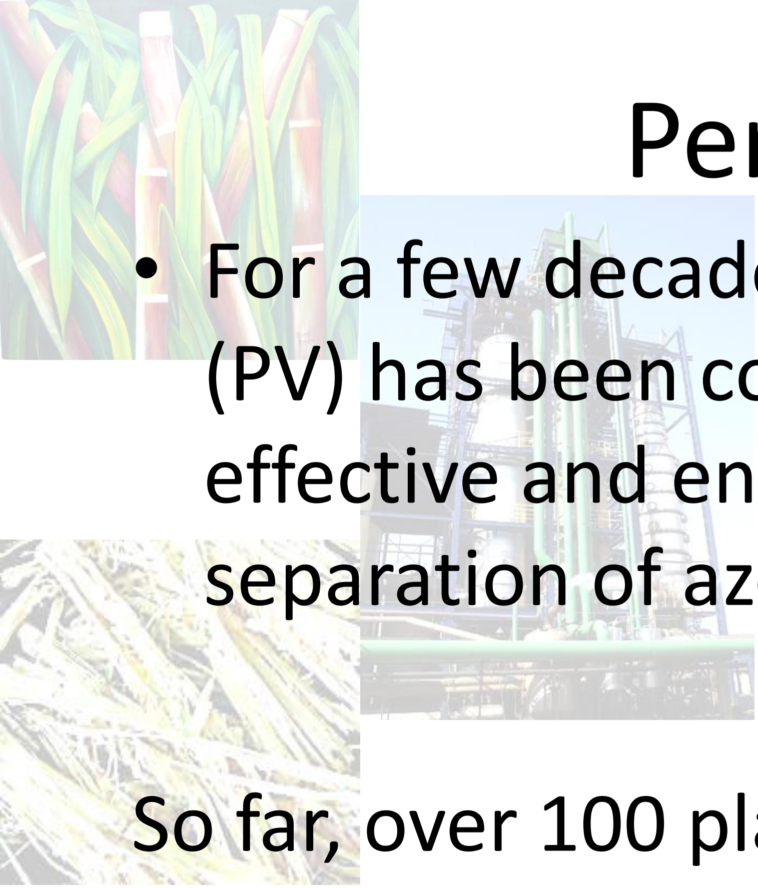


- FIRST UNIT USING MOLECULAR SIEVES for producing anhydrous ethanol in Brazil
- 60 millons of galons/year of anhydrous ethanol

PERVAPORATION

- **Is the most efficient in terms of energy consumption**
- **alcohol with high purity**
- **This is a new technology (demonstration)**
- **More studies are necessary**

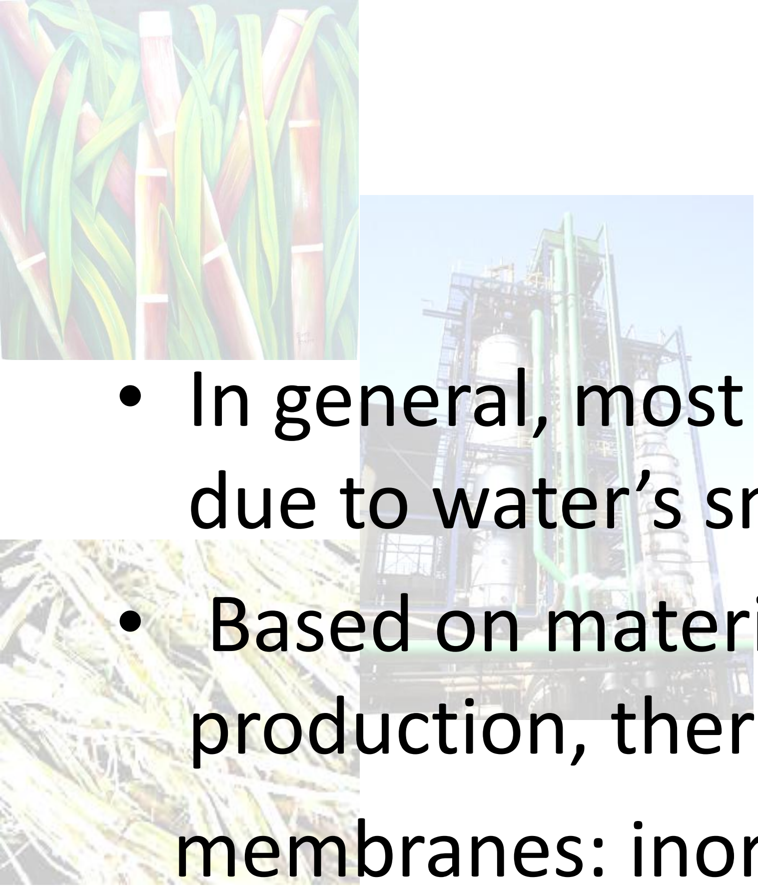
Pervaporation



- For a few decades, membrane pervaporation (PV) has been considered as one of the most effective and energy-saving process for separation of azeotropic mixtures.

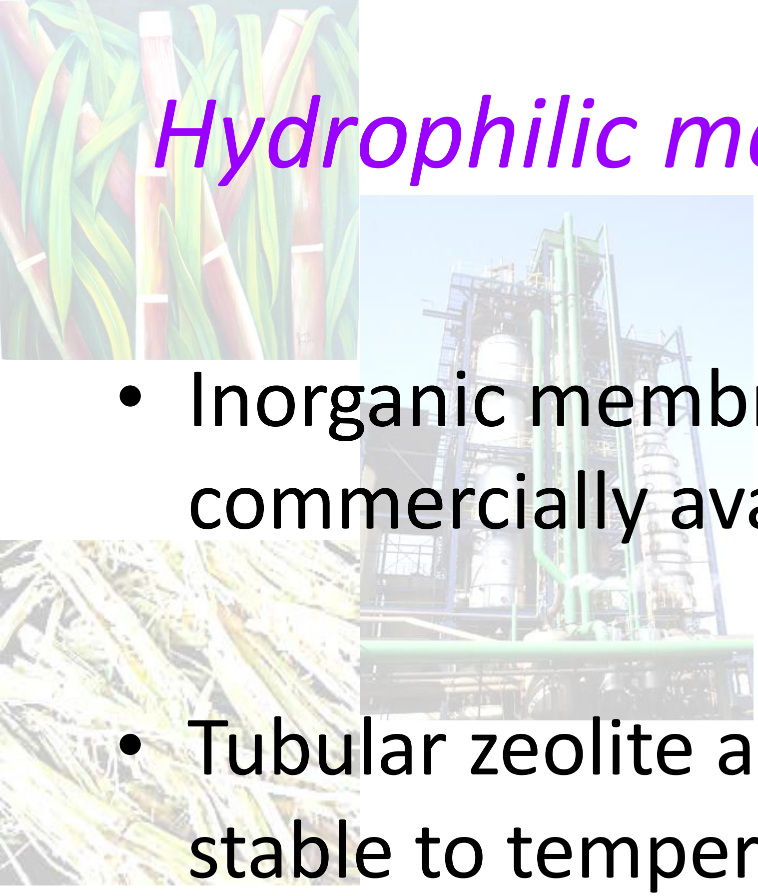
So far, over 100 plants in the world use PV technique for alcohol dehydration

- Membranes can be either hydrophilic or hydrophobic.



- In general, most membranes are hydrophilic due to water’s smaller molecular size
- Based on materials used for membrane production, there are three categories of membranes: inorganic, polymeric and composite membrane.

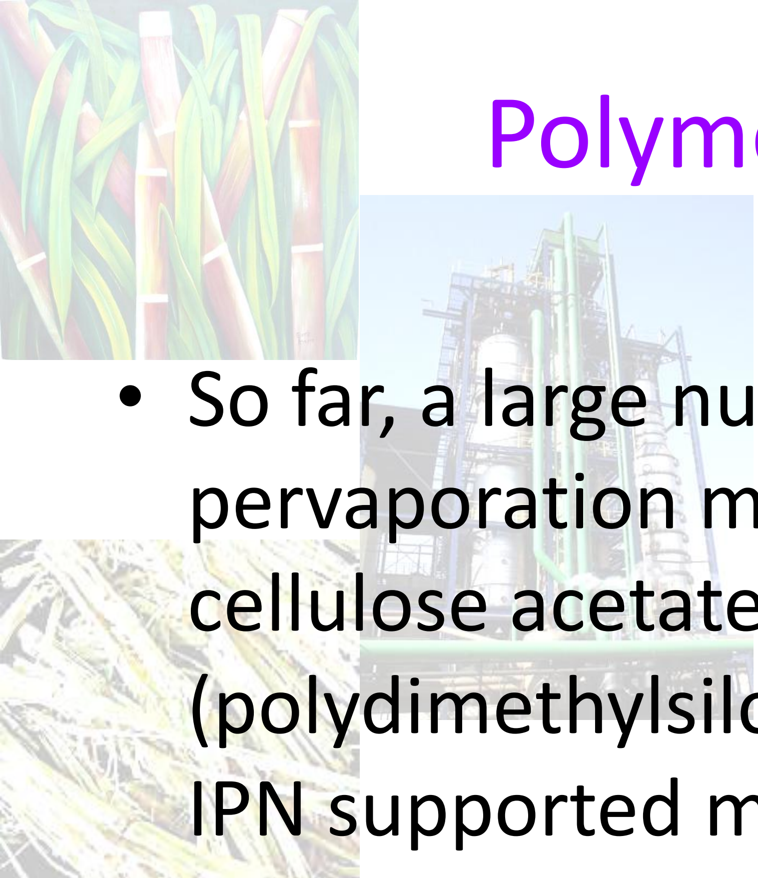
Hydrophilic membrane for removal of water



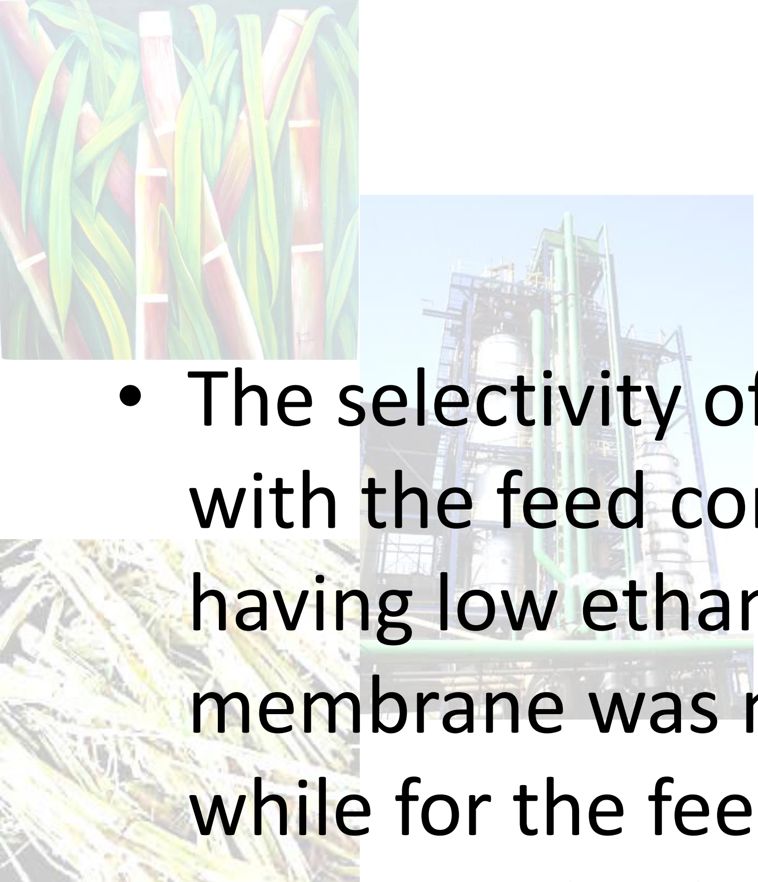
- Inorganic membrane:have recently become commercially available.

- Tubular zeolite and silica membranes are still stable to temperatures of above 300 ◦C and feed pressures of above 100 bar.

Polymeric membrane.

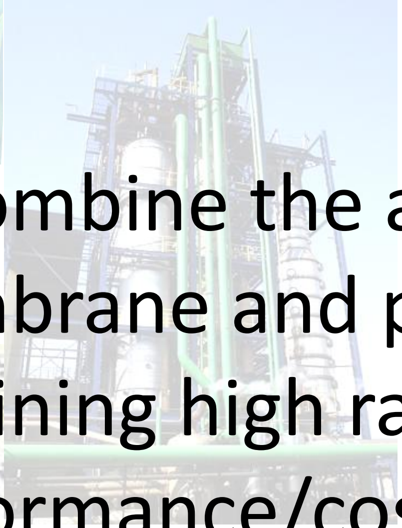


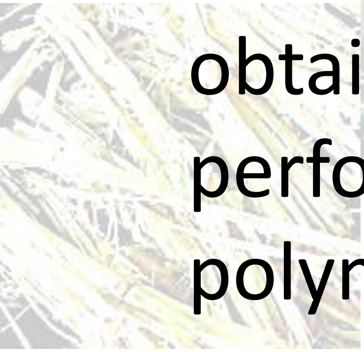
- So far, a large number of polymeric pervaporation membranes, for example cellulose acetate butyrate membrane , PDMS (polydimethylsiloxane) membrane , PDMS-PS IPN supported membranes, and aromatic polyetherimide membranes have been investigated.



- The selectivity of PDMS-PS membranes varied with the feed composition. For the feed having low ethanol concentration, the membrane was more selective for ethanol, while for the feed with high ethanol concentration it was more selective for water.

Composite or mixed membrane.





- To combine the advantages of inorganic membrane and polymeric membrane for obtaining high ratio of membrane performance/cost, recently, various inorganic-polymer or polymer–polymer composite membranes have been studied for pervaporation separation of ethanol/water mixtures.

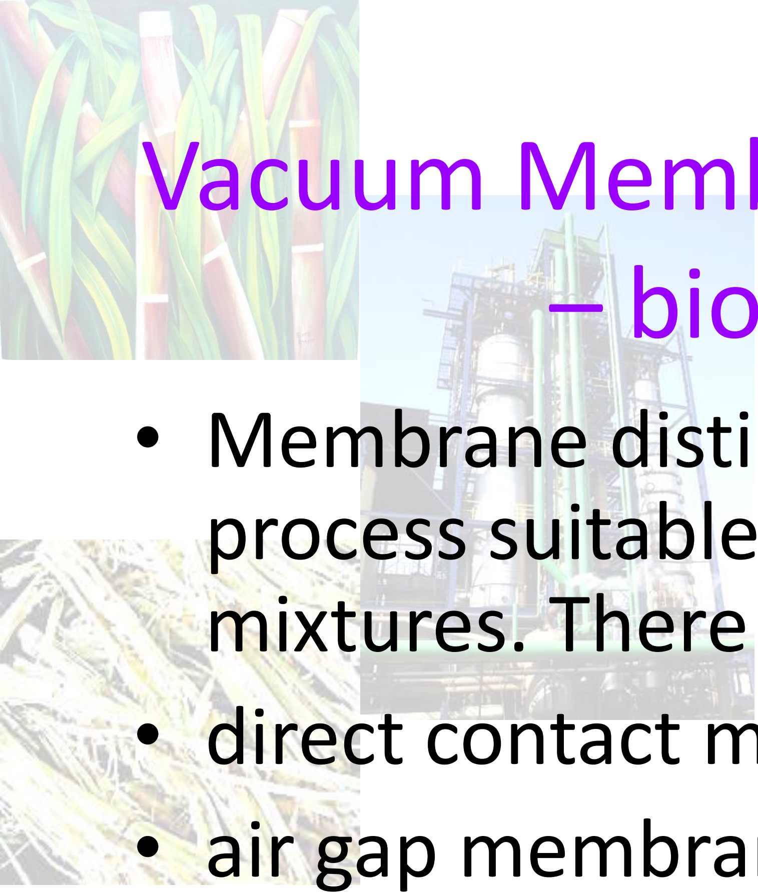
Membrane pervaporation-bioreactor hybrid

- Fermentation broth generally contains inhibiting substances including ethanol product, flavors phenolics, and other chemicals.

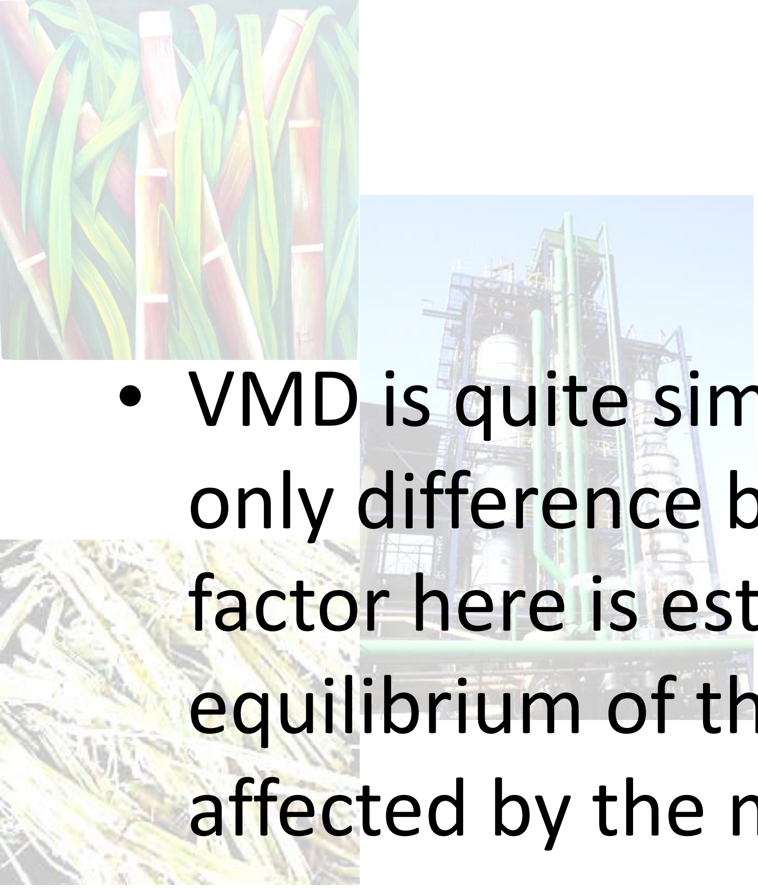
- This problem can be overcome by combining fermentation with hydrophobic membrane pervaporation for removal of the inhibitors from the fermentation broth.

- Hence, the process can be carried out continuously and the recovered organic VOCs (ethanol, acetone, butanol, 2-propanol) can be reused within other processes.

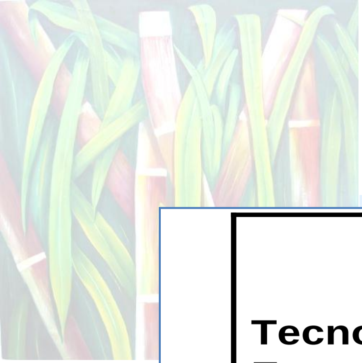
Vacuum Membrane Distillation (VMD) – bioreactor hybrid



- Membrane distillation (MD) is an appealing process suitable for separation of aqueous mixtures. There are four types of MD:
- direct contact membrane distillation (DCMD),
- air gap membrane distillation (AGMD),
- sweeping gas membrane distillation
- (SGMD)
- vacuum membrane distillation (VMD).



- VMD is quite similar to pervaporation, the only difference being that the separation factor here is established by vapor–liquid equilibrium of the feed solution which is not affected by the membrane used .



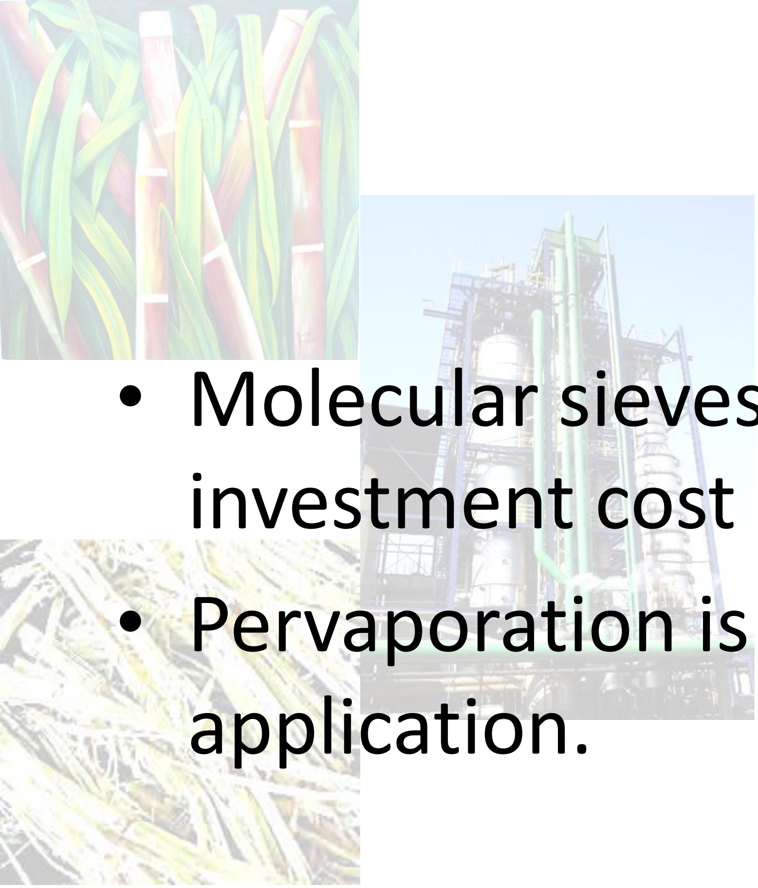
Energy consumption

Tecnologia Empregada	Consumo de vapor Kg/m³ de AEHC	Consumo de Energia Elétrica KWh/m³ de AEAC	Energia primaria total Kcal/m³ de AEAC	
Destil com cicloexano convencional	**1750**	**-**	1272,5	Vapor de escape
Destil com cicloexano otimizada	**1450**	**-**	1062,5	Vapor de escape
Destil. com cicloexano a 3 efeitos	**580**	**23**	**435,5**	**Vacuo, vapor de escape e vapor de baixa pressão**
Absorção com MEG	**750**	**15**	**572,5**	**vapor a 10 Kg/cm2, escape e vacuo**
Pervaporação	**110**	**34,5**	**124,5**	**Vapor de escape e vácuo**
Peneiras moleculares	550	19	**432,5**	**vapor a 10 Kg/cm2 e vácuo**

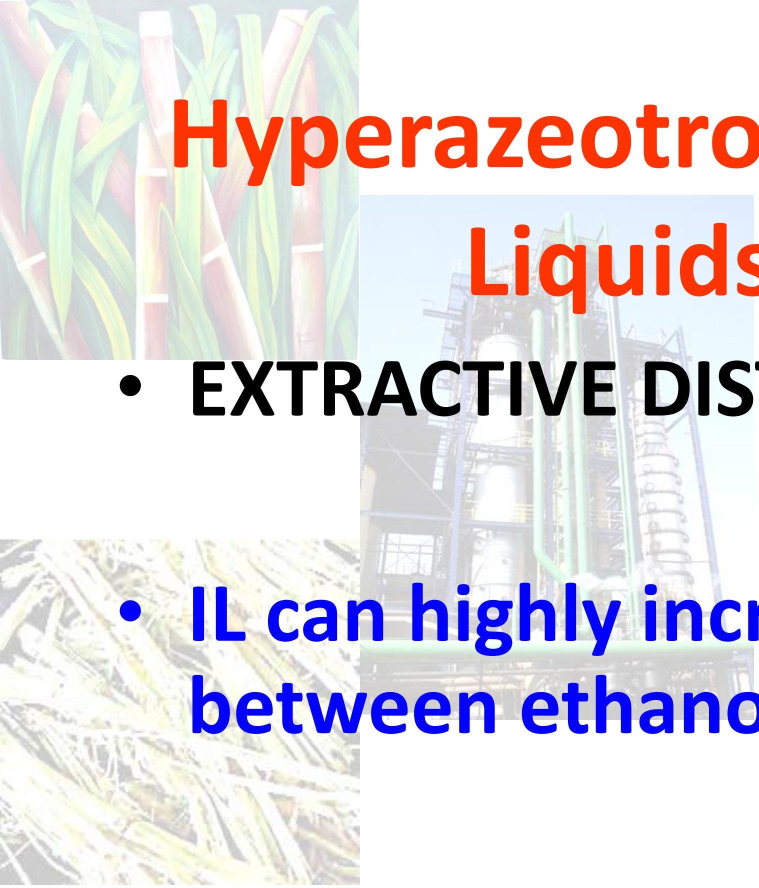
Fig 6 Comparação dos consumos energéticos para diversas tecnologias de desidratação

INFORMATION

- MULTIPLE EFFECT AZEOTROPIC DISTILLATION
- VIABLE
- LARGE DIMENSION DISTILLERIES (1000 000 liters/day)
- SIMILAR ENERGY CONSUMPTION THAN MEG AND MOLECULAR SIEVES.



- Molecular sieves present the highest investment cost and cyclohexane the lowest.
- Pervaporation is still incipient in terms of application.



Hyperazeotropic Ethanol using Ionic Liquids (IL) as Solvents

- **EXTRACTIVE DISTILLATION**

- **IL can highly increase the relative volatility between ethanol and water like salts**

- **No problem of solvent at top as can occur in azeotropic and extractive distillations**

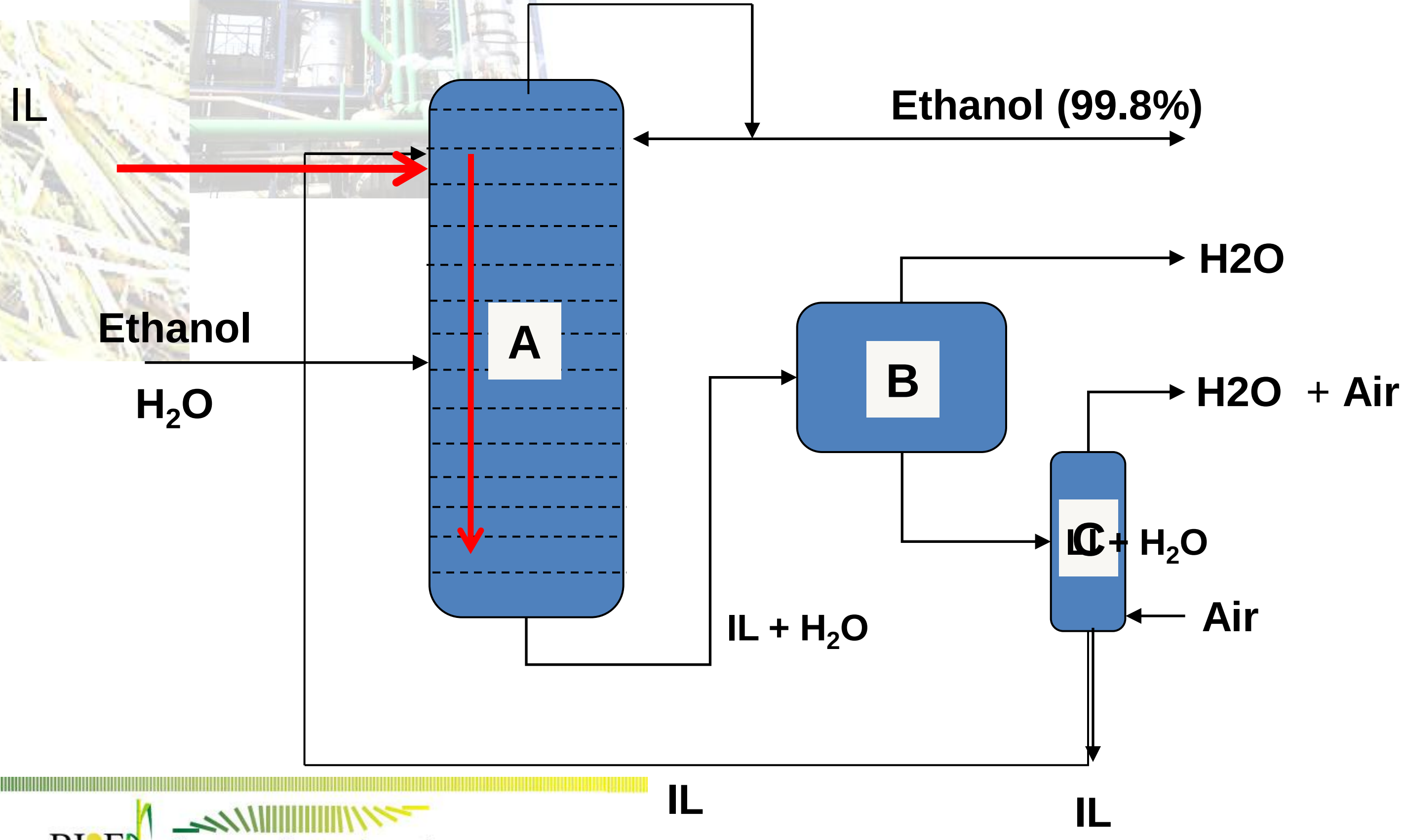
Organic Salts, Liquid at room temperature.

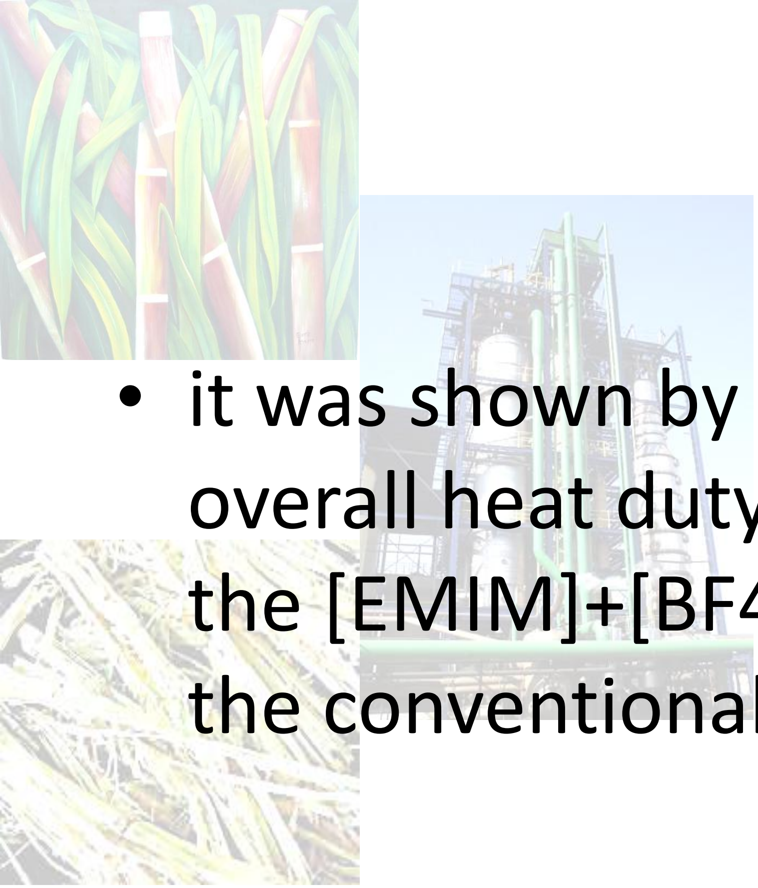
Composed by a mixture: ORGANIC CATIONS and INORGANIC ANIONS

Favorable properties such as low viscosity,

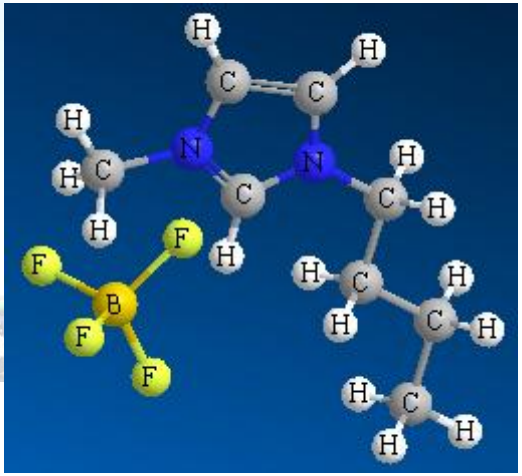
thermal stability, good solubility and lower corrosiveness than ordinary high melting salts.

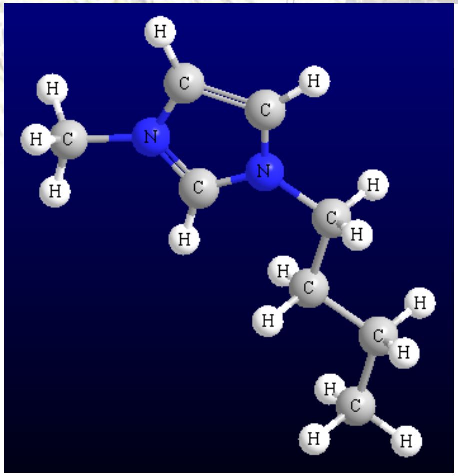
A: principal column
B: flash
C: recovery column



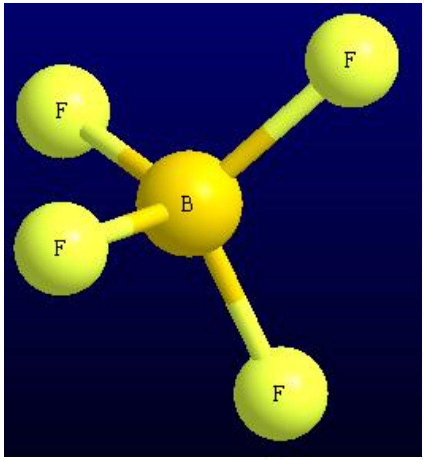


- it was shown by process simulation that the overall heat duty can be saved up to 24% for the [EMIM]+[BF4]– process as compared with the conventional ED process.



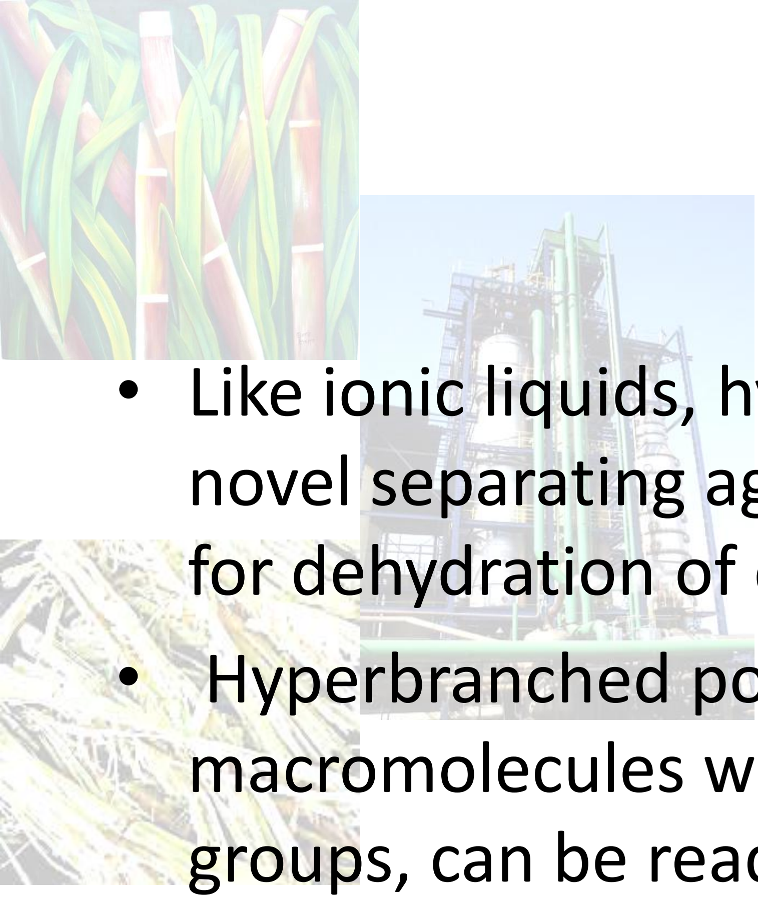


Organic cation

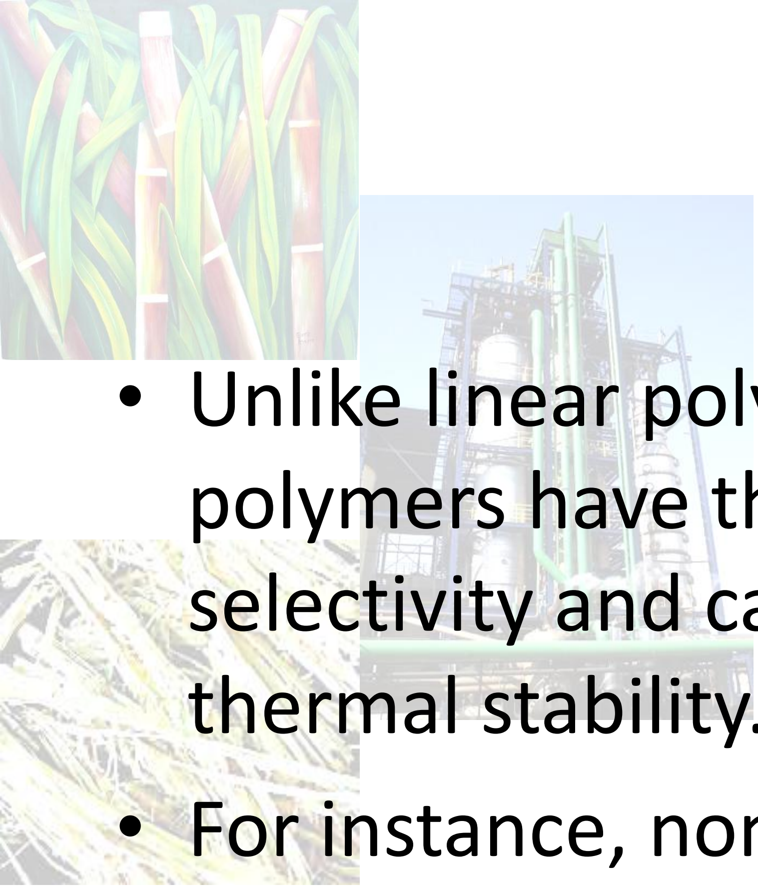


Inorganic anion

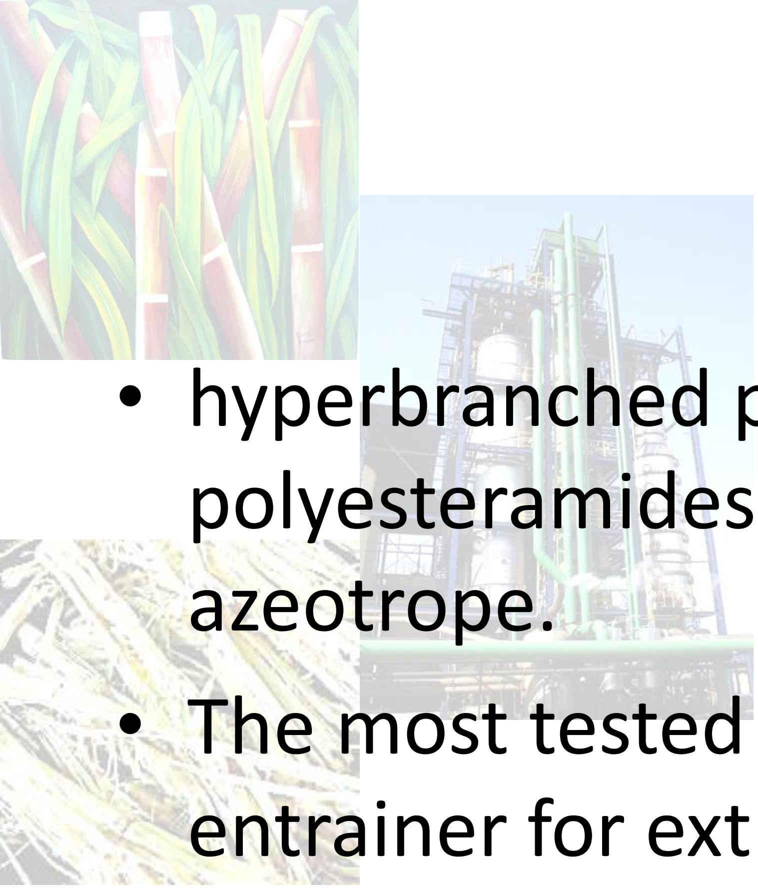
HYPERBRANCHED POLYMERS



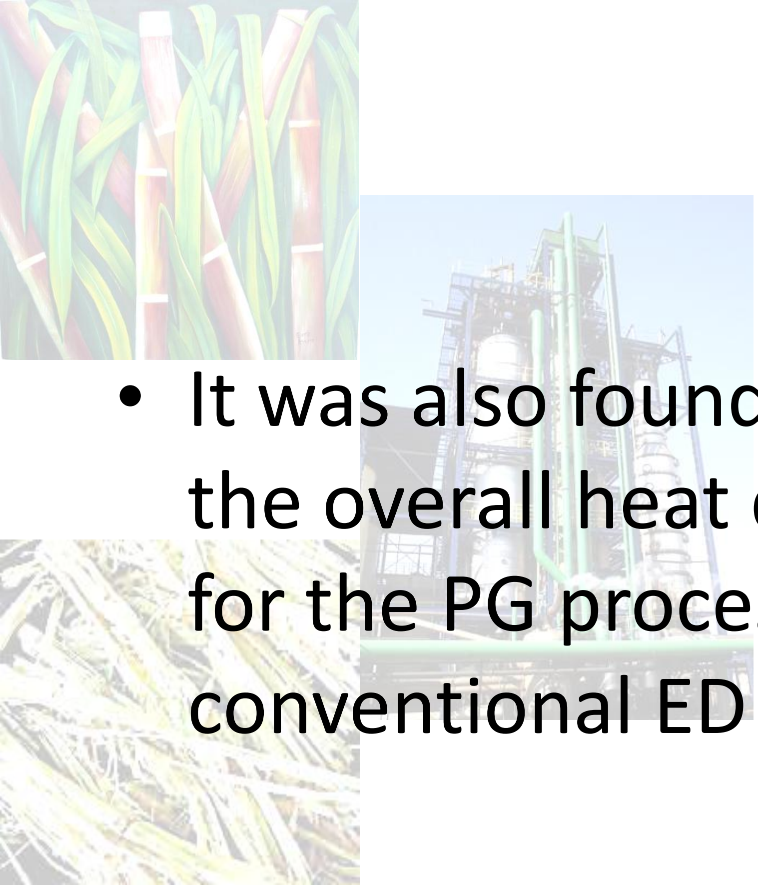
- Like ionic liquids, hyperbranched polymers are also novel separating agents used in extractive distillation for dehydration of ethanol from aqueous solutions.
- Hyperbranched polymers, the highly branched macromolecules with a large number of functional groups, can be readily manufactured by one-step reactions, representing economically favorable agents for large-scale industrial applications



- Unlike linear polymers, hyperbranched polymers have the features of remarkable selectivity and capacity, low viscosity and thermal stability.
- For instance, non-volatile polymeric entrainers such as poly(ethylene glycol) and poly(acrylic acid) for dehydrating ethanol were employed.

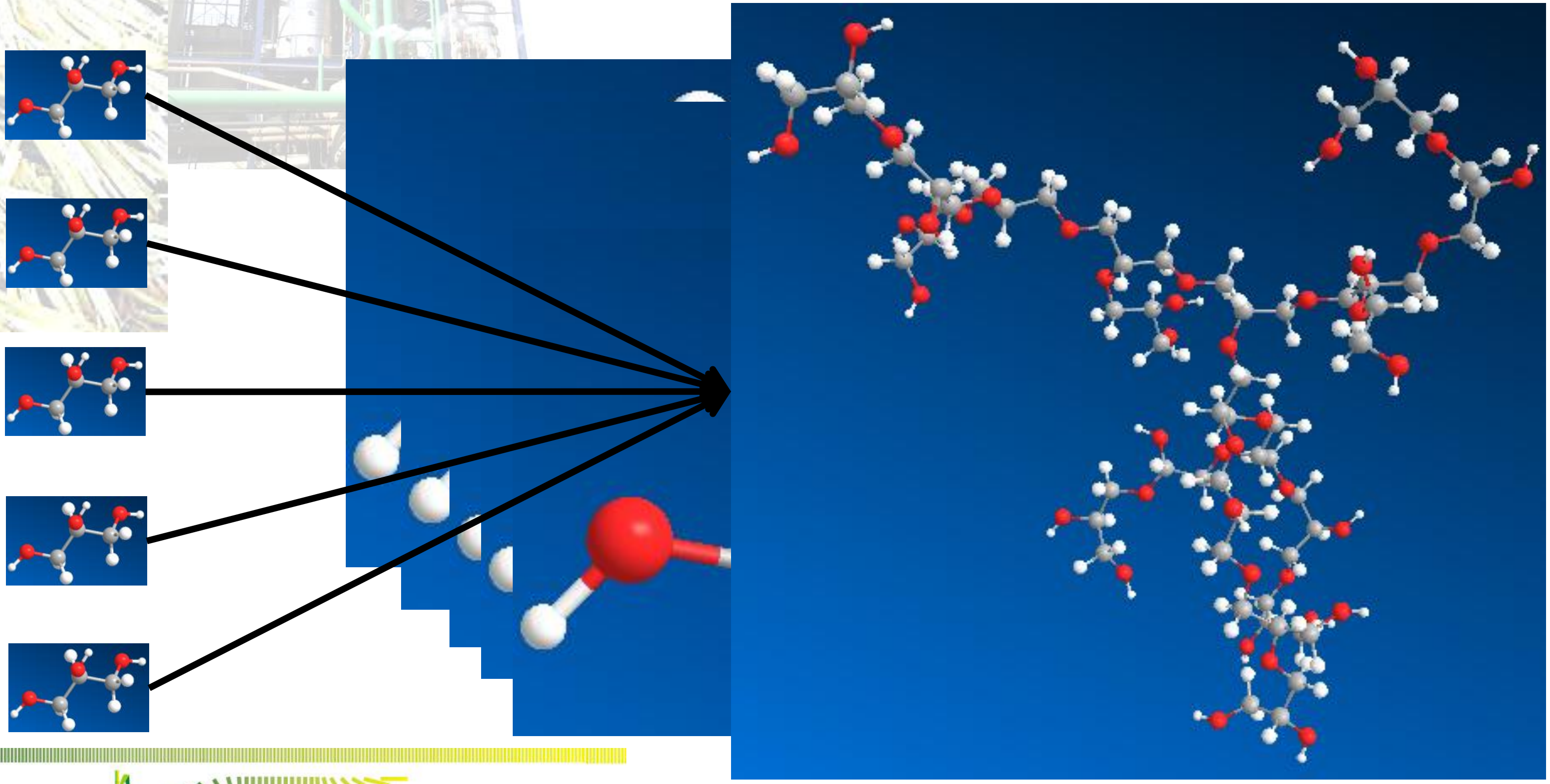


- hyperbranched polyesters and hyperbranched polyesteramides can break the ethanol–water azeotrope.
- The most tested hyperbranched polymer as entrainer for extractive distillation of the ethanol–water mixture is hyperbranched polyglycerol (PG).

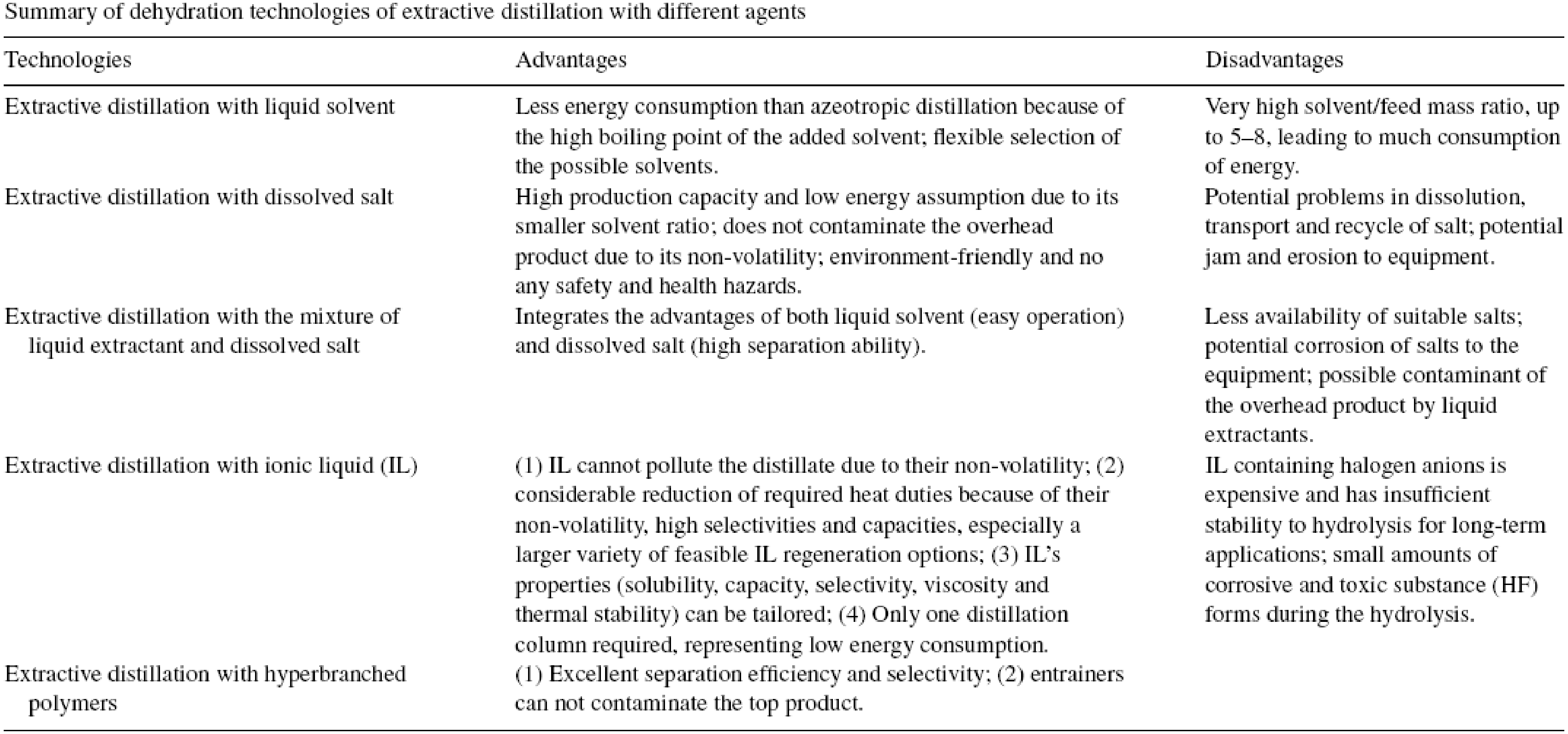


- It was also found by process simulation that the overall heat duty can be saved up to 19% for the PG process, compared to the conventional ED process

poliglycerol



Polyglicerol



Summary of dehydration technologies of extractive distillation with different agents

Technologies	Advantages	Disadvantages
Extractive distillation with liquid solvent	Less energy consumption than azeotropic distillation because of the high boiling point of the added solvent; flexible selection of the possible solvents.	Very high solvent/feed mass ratio, up to 5–8, leading to much consumption of energy.
Extractive distillation with dissolved salt	High production capacity and low energy assumption due to its smaller solvent ratio; does not contaminate the overhead product due to its non-volatility; environment-friendly and no any safety and health hazards.	Potential problems in dissolution, transport and recycle of salt; potential jam and erosion to equipment.
Extractive distillation with the mixture of liquid extractant and dissolved salt	Integrates the advantages of both liquid solvent (easy operation) and dissolved salt (high separation ability).	Less availability of suitable salts; potential corrosion of salts to the equipment; possible contaminant of the overhead product by liquid extractants.
Extractive distillation with ionic liquid (IL)	(1) IL cannot pollute the distillate due to their non-volatility; (2) considerable reduction of required heat duties because of their non-volatility, high selectivities and capacities, especially a larger variety of feasible IL regeneration options; (3) IL's properties (solubility, capacity, selectivity, viscosity and thermal stability) can be tailored; (4) Only one distillation column required, representing low energy consumption.	IL containing halogen anions is expensive and has insufficient stability to hydrolysis for long-term applications; small amounts of corrosive and toxic substance (HF) forms during the hydrolysis.
Extractive distillation with hyperbranched polymers	(1) Excellent separation efficiency and selectivity; (2) entrainers can not contaminate the top product.	

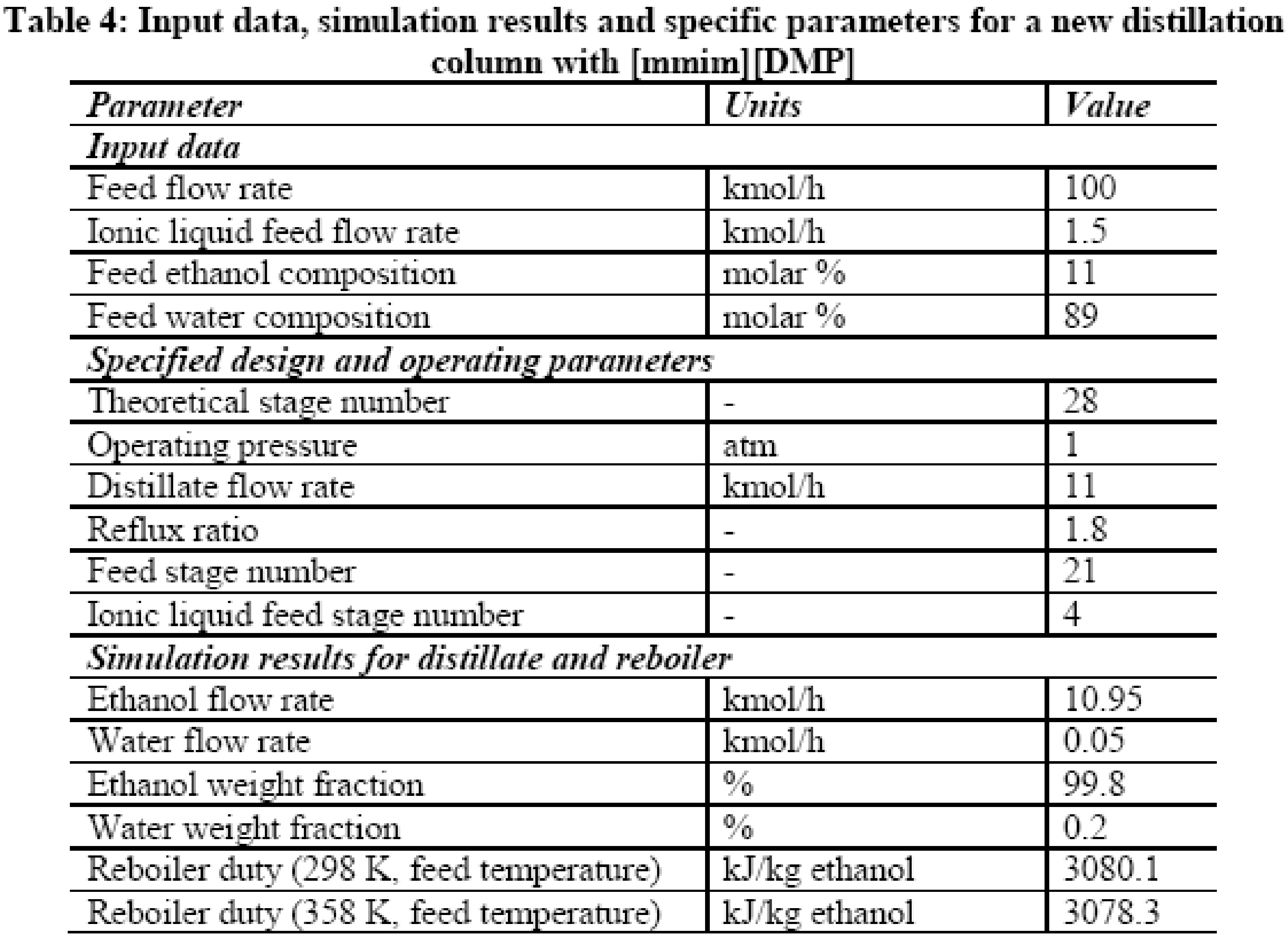
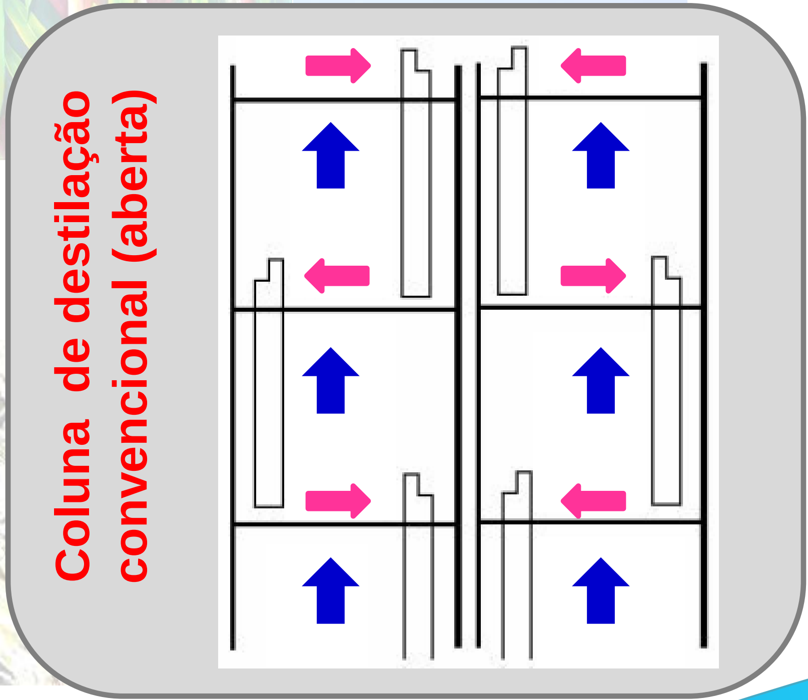
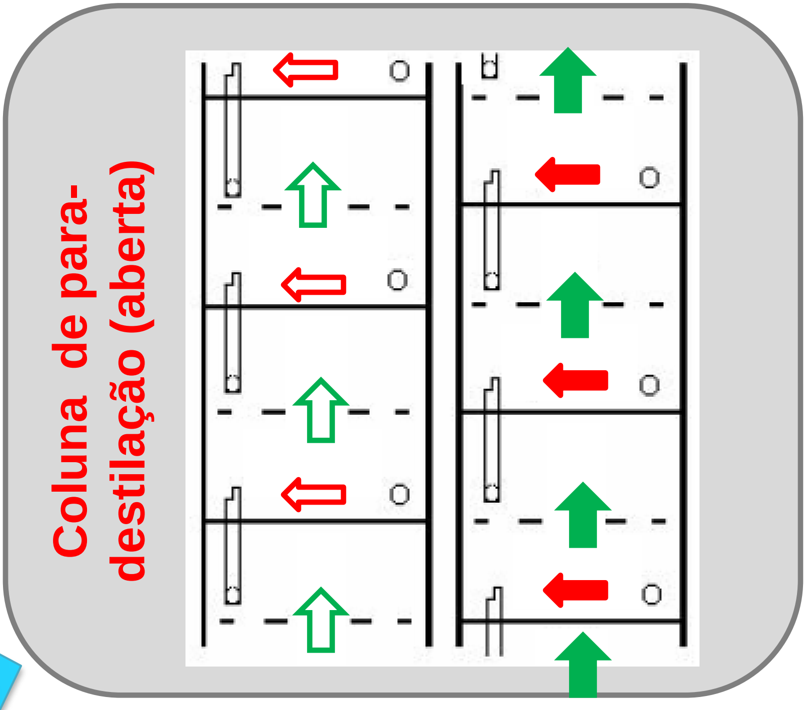


Table 4: Input data, simulation results and specific parameters for a new distillation column with [mmim][DMP]

Parameter	*Units*	*Value*
Input data		
Feed flow rate	kmol/h	100
Ionic liquid feed flow rate	kmol/h	1.5
Feed ethanol composition	molar %	11
Feed water composition	molar %	89
Specified design and operating parameters		
Theoretical stage number	-	28
Operating pressure	atm	1
Distillate flow rate	kmol/h	11
Reflux ratio	-	1.8
Feed stage number	-	21
Ionic liquid feed stage number	-	4
Simulation results for distillate and reboiler		
Ethanol flow rate	kmol/h	10.95
Water flow rate	kmol/h	0.05
Ethanol weight fraction	%	99.8
Water weight fraction	%	0.2
Reboiler duty (298 K, feed temperature)	kJ/kg ethanol	3080.1
Reboiler duty (358 K, feed temperature)	kJ/kg ethanol	3078.3

DIVIDED WALL DISTILLATION COLUMN





MORE THAN 2 PURE PRODUCTS

The wall is introduced in part of the column

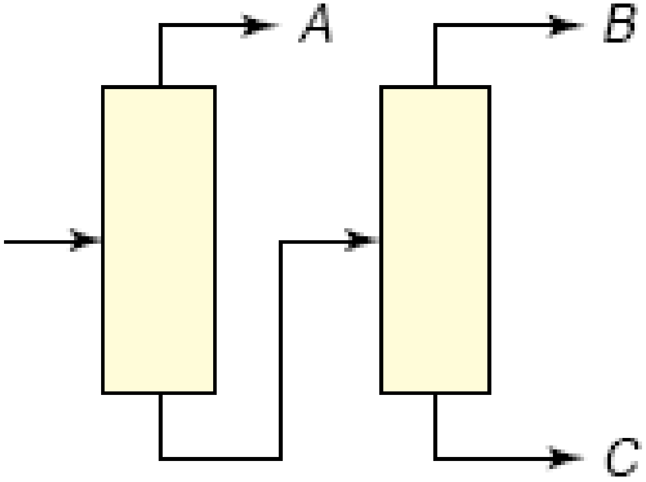
Sugarcane Processing and Engineering

BIOEN WORKSHOP ON PROCESSES FOR ETHANOL PRODUCTION

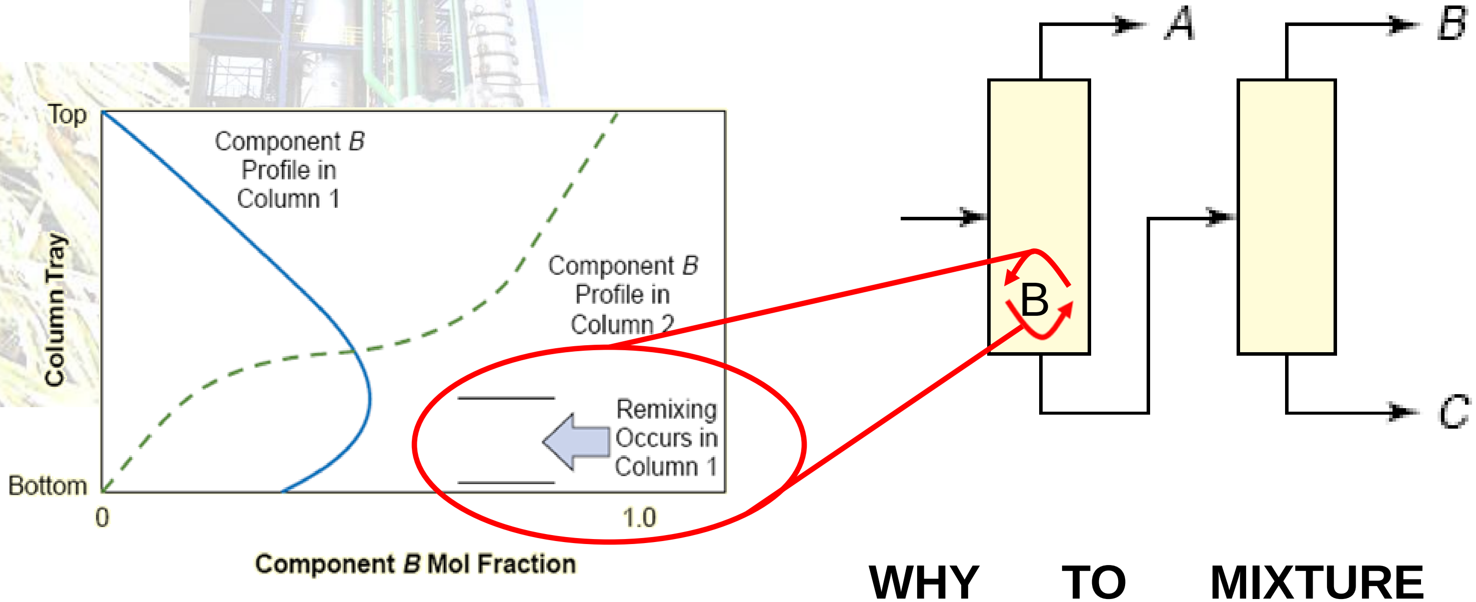
Professor Maria Regina Wolf Maciel, 10/09/2009

UNICAMP

CONVENTIONAL SEQUENCE

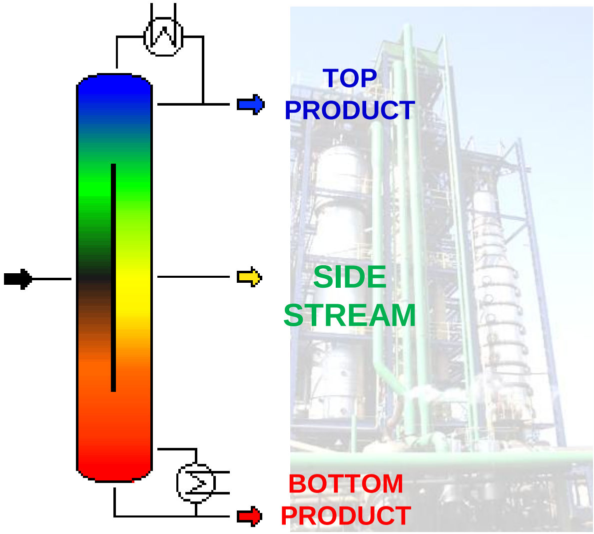


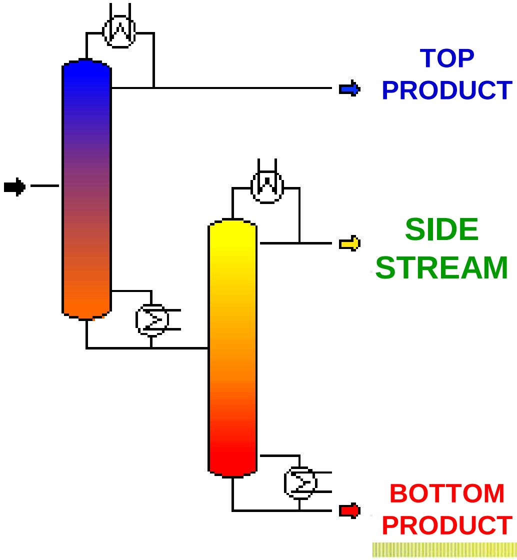
MAXIMUM OF B

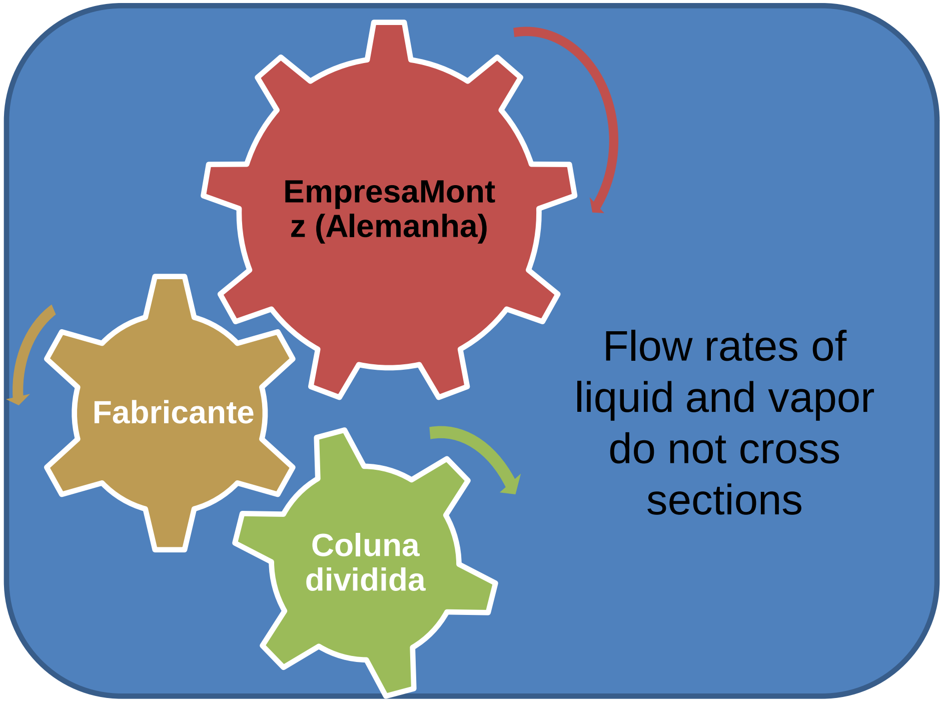


WHY TO MIXTURE IT AGAIN???

WALL DIVIDED VS. CONVENTIONAL







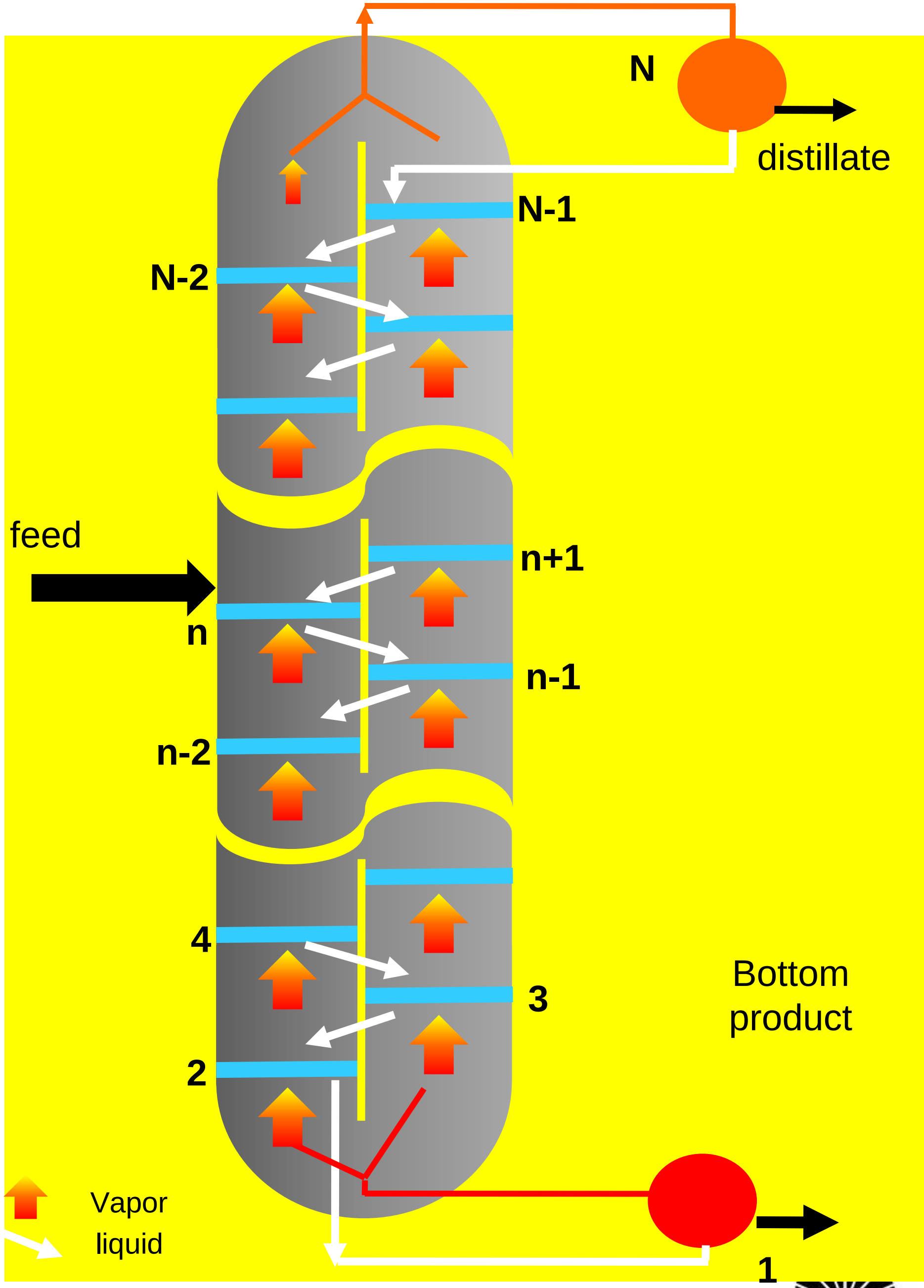
Flow rates of liquid and vapor do not cross sections

CARACTERÍSTICAS OPERACIONAIS

- Costs: Reduction of **30% in investiments and of 25% em utilities**

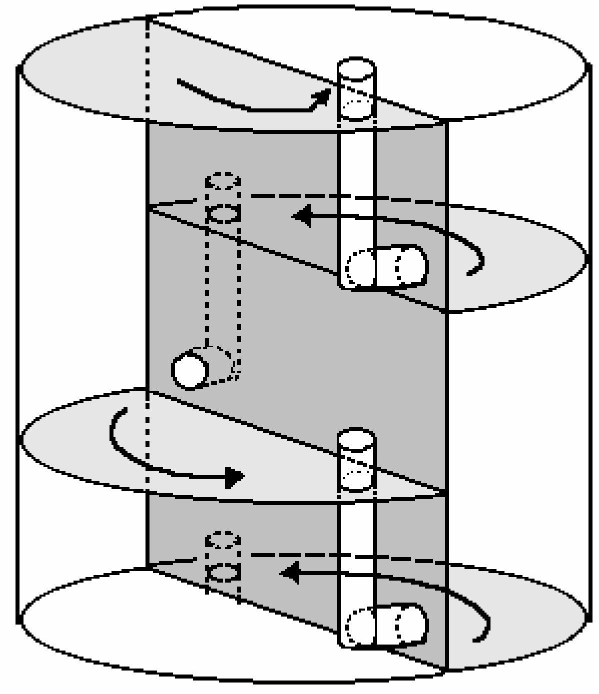
PARA DISTILLATION

- HIGHER EFFICIENCY
- DIVIDED WALL COLUMN
- VAPOR DIVIDED
- DOWNCOMERS TAKE THE LIQUID FROM ONE SIDE TO THE OTHER
- INCREASE MASS TRANSFER



Paradistillation

Professor Maria Regina Wolf Maciel, 10/09/2009

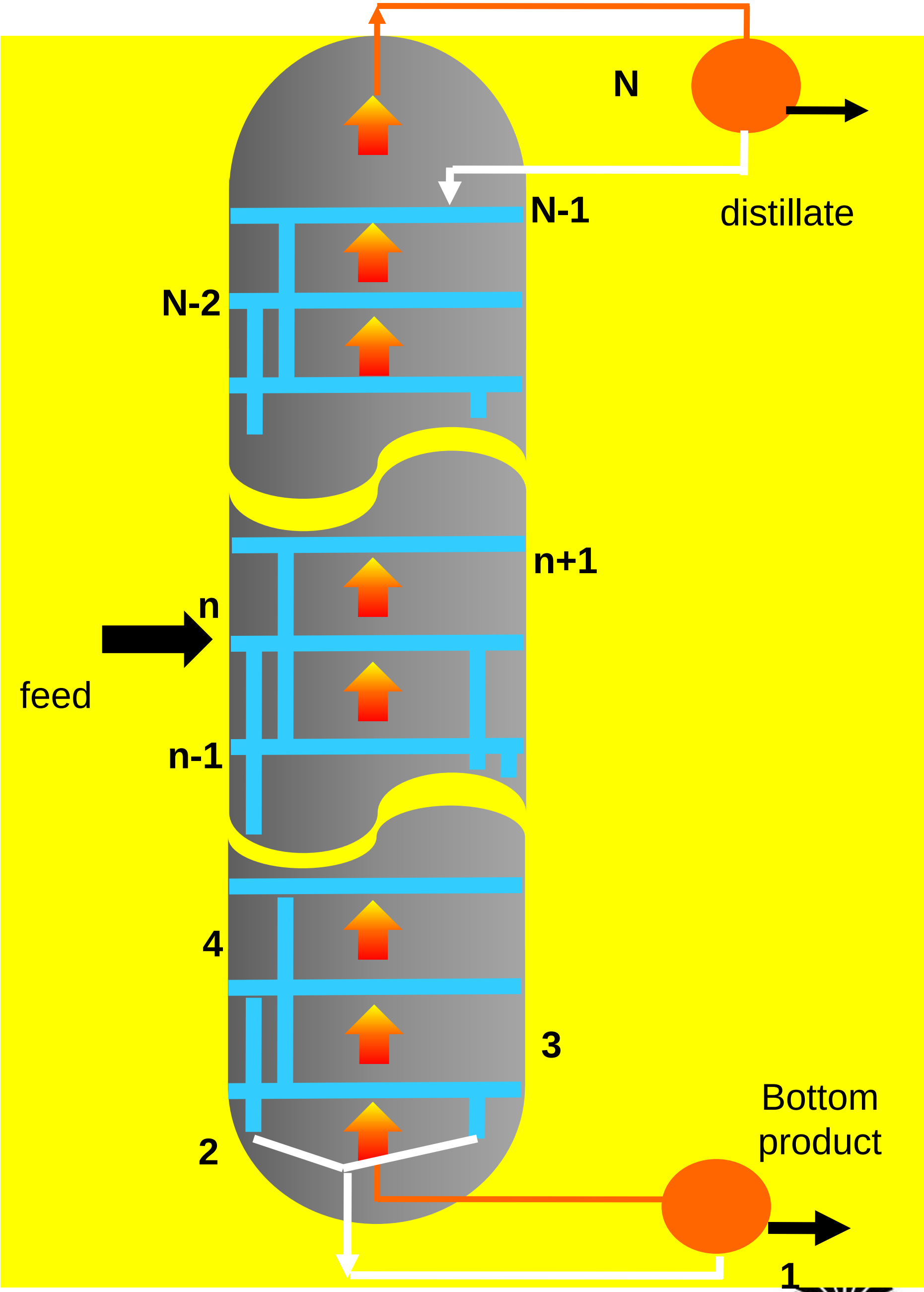


- COLUMN CORRESPOND TO

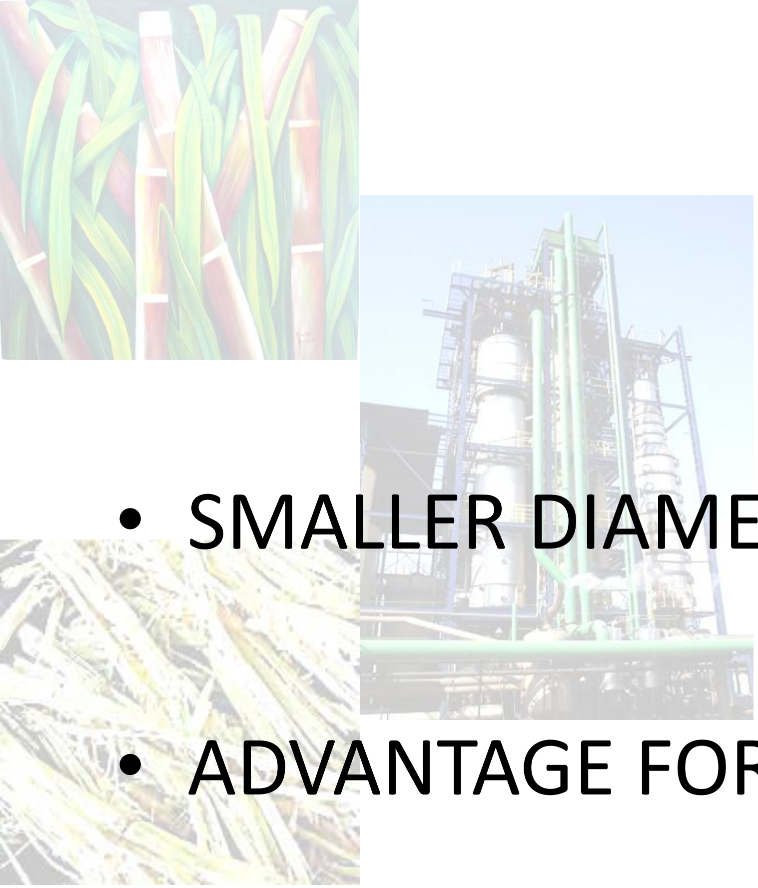
- 25% SMALLER PRESSURE DROP
- 30% SMALLER
- GOOD FOR LOW PRESSURE

META DISTILLATION

- HIGHER EFFICIENCY
- LIQUID IS DIVIDED.
- SMALLER NST THAN PARA DISTILLATION

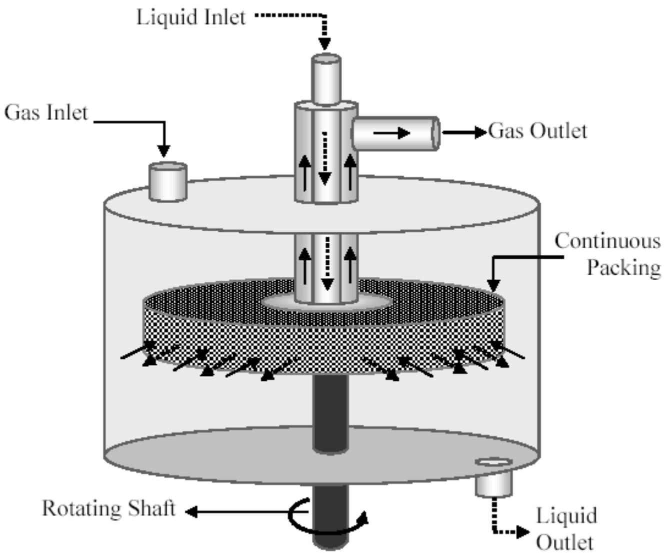


Professor Maria Regina Wolf Maciel, 10/09/2009



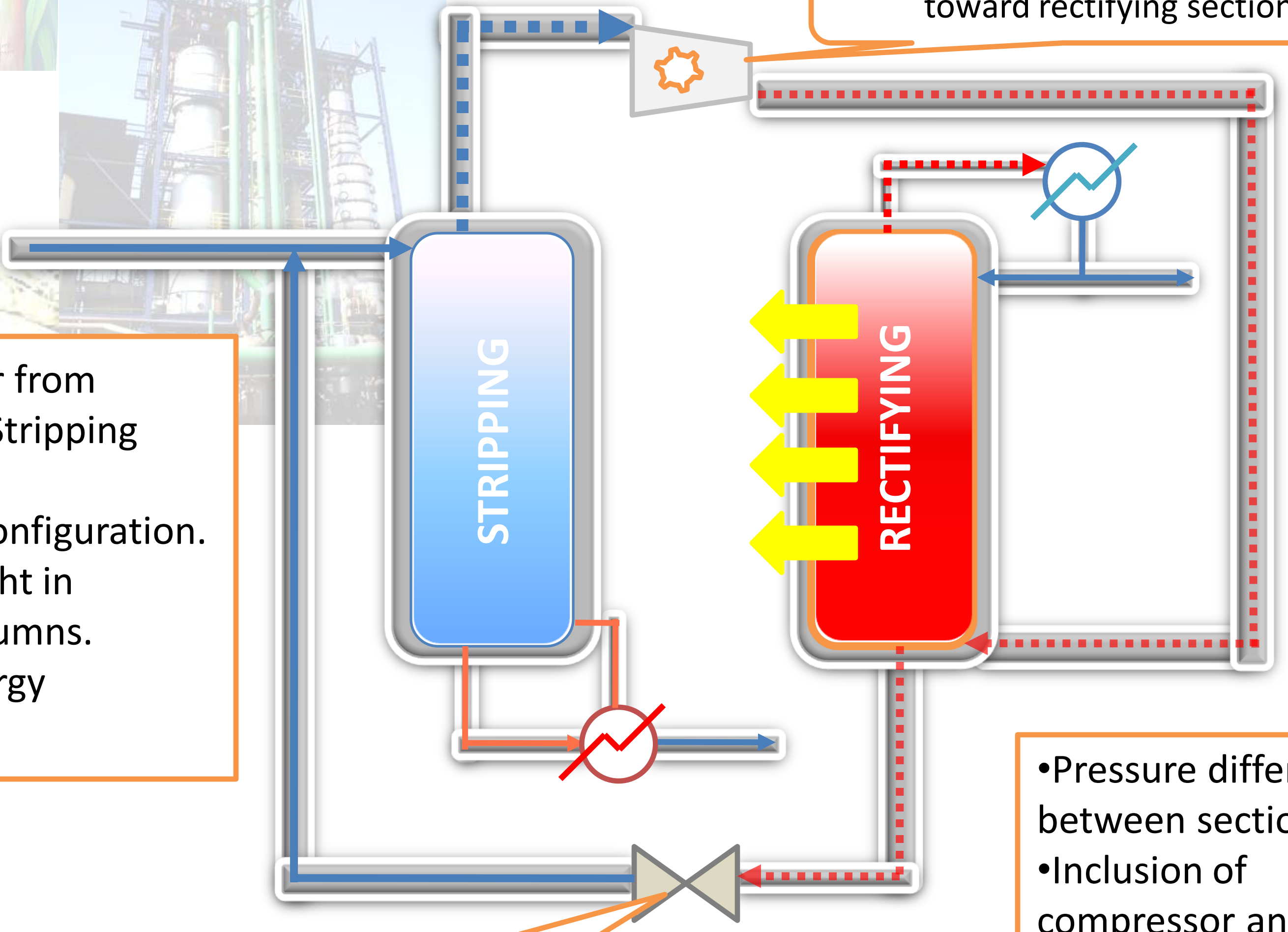
- SMALLER DIAMETER- 8%
- ADVANTAGE FOR HIGH LIQUID FLOW RATE

Coluna HIGEE
(*High Integrated Gravitational*)



Ramshaw e Mallinson, 1981	**Rotating Packed Column – centrífugal forces over to 1000 times the gravity. High efficiency**
Lang 2005	Smaller equipments

HEAT INTEGRATED DISTILLATION COLUMN HIDIC



Compressor : pressure increases toward rectifying section.

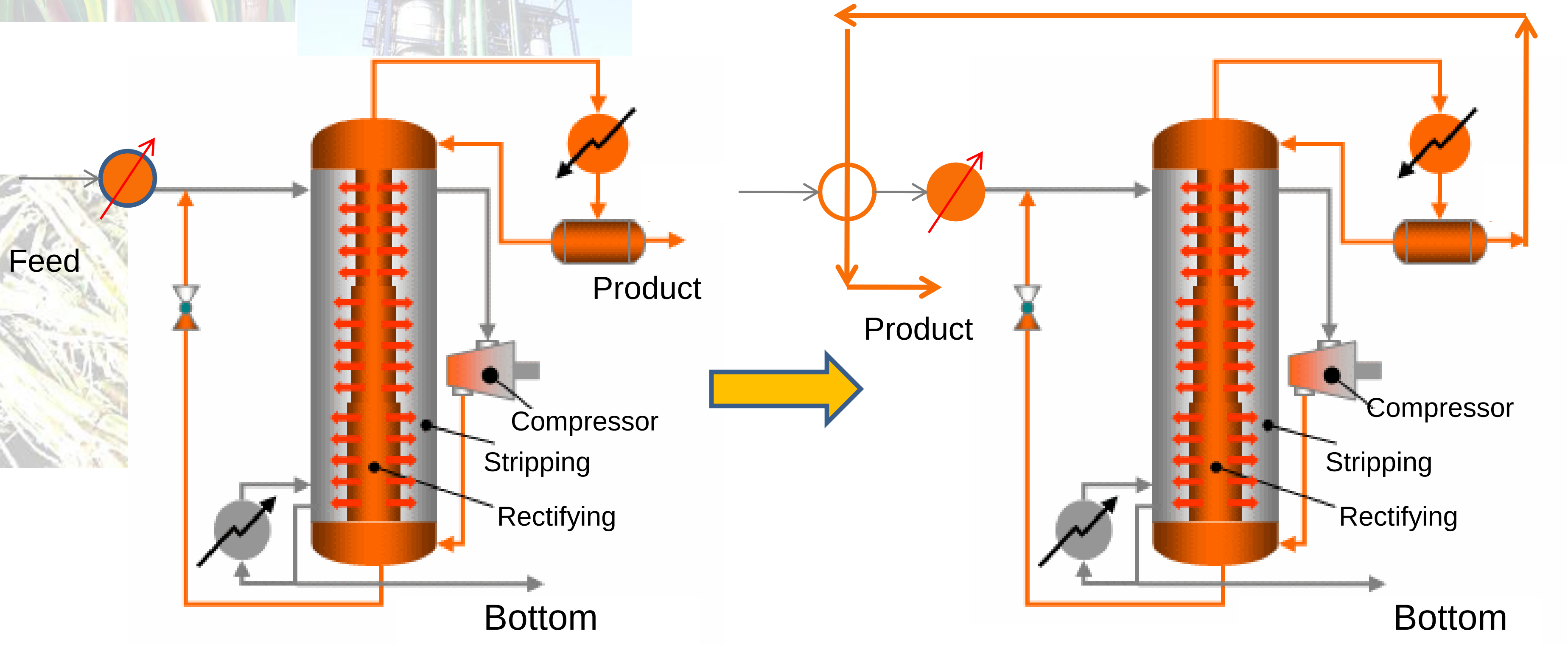
- Heat Transfer from Rectifying to Stripping section.
- Concentric configuration.
- Reduced height in distillation columns.
- Potential energy reduction.

- Pressure difference between sections.
- Inclusion of compressor and valves for the operation of the system.

Valve: pressure decreases toward stripping section

DEVELOPMENT TODAY

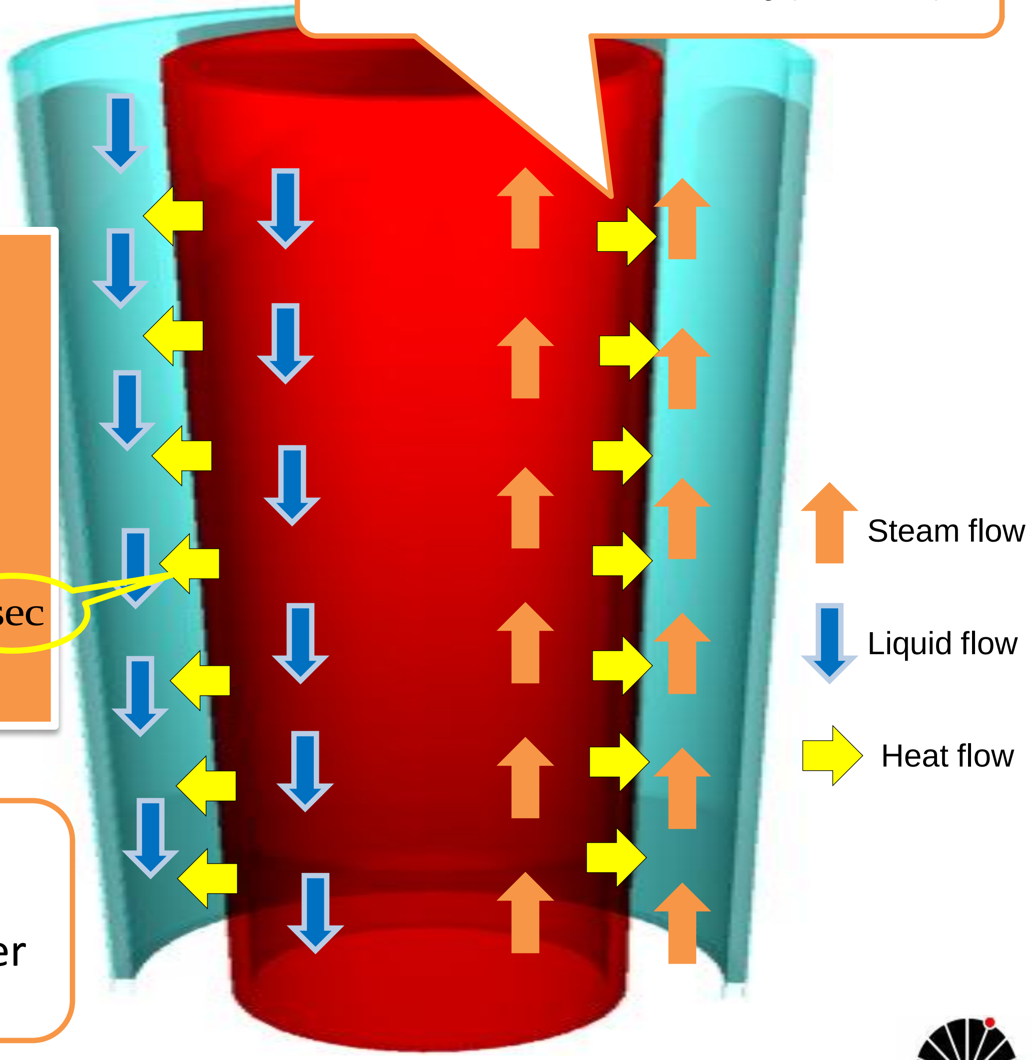
Totally Heat Integrated Distillation Column (THIDIC)



HEATING FEED

CONCENTRIC CONFIGURATION OF HIDIC

- *Qsec* = Heat section = *f*(A,U,ΔT)



Mass and Heat Transfer
Stage n

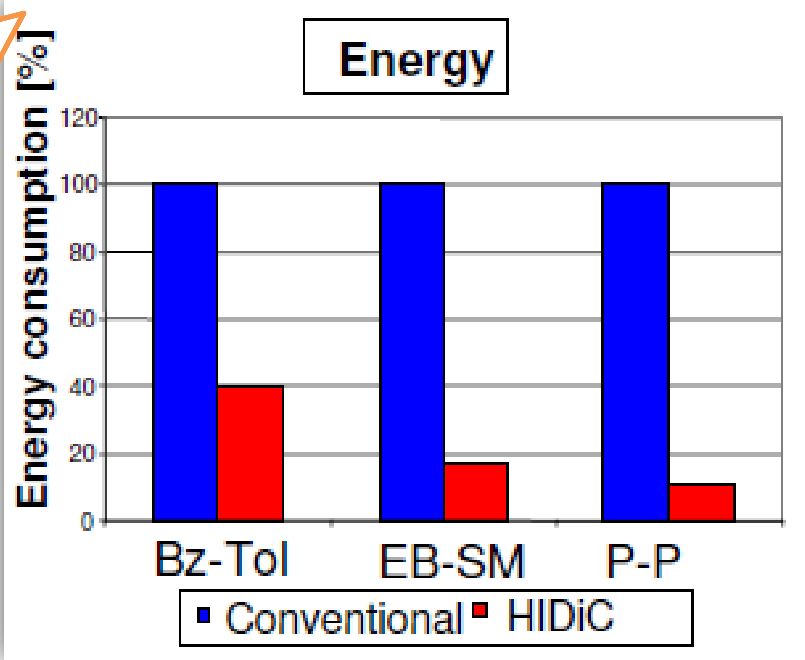
$$V_{n-a}y_{i,n-1}+L_{n+1}X_{i,n+1}=V_n y_{i,n}+L_n X_{i,n}$$

$$Fv_{n-1}Hv_{n-1}+Fl_{n+1}Hl_{n+1}=Fv_n Hv_n+Fl_n Hl_n+Q\sec$$

- Based on heat integrated transfer.
- Behavior in terms of geometry.
- Decline in consumption in the reboiler and condenser.

HIDIC Vs Conventional Column

- Saving 90% for Propylene- Propane mixture.
- Lower compression ratio than heat pump.
- Decrease of the power required by the compressor and condenser.
- Favorable for mixtures with low volatilities.
- Decline in consumption in the reboiler and condenser.
- Study mixing Benzene-Toluene, Ethylbenzene-Styrene and Propylene-Propane.

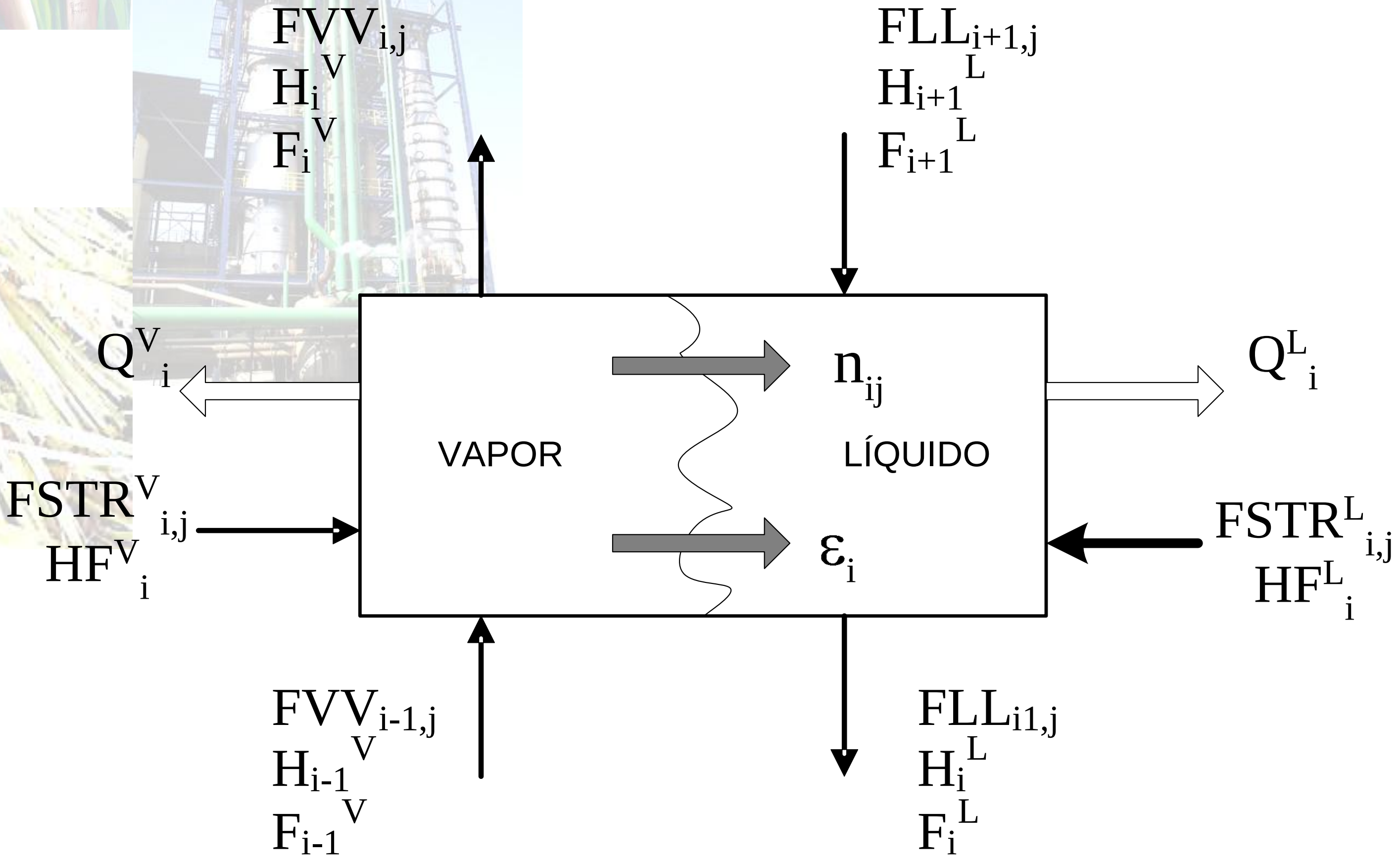


Delft University of Technology 2007

These studies have been developed by Japanese research groups (1998) and groups Dutchmen (2001), currently of great importance in Brazil (2008).

NON EQUILIBRIUM STAGE MODEL VS EFFICIENCY

- Taylor et al. (2003) refer as the real world



$FVV_{i,j}$
H_i^V
F_i^V

$FLL_{i+1,j}$
H_{i+1}^L
F_{i+1}^L

Q^V_i

n_{ij}

Q^L_i

VAPOR

LÍQUIDO

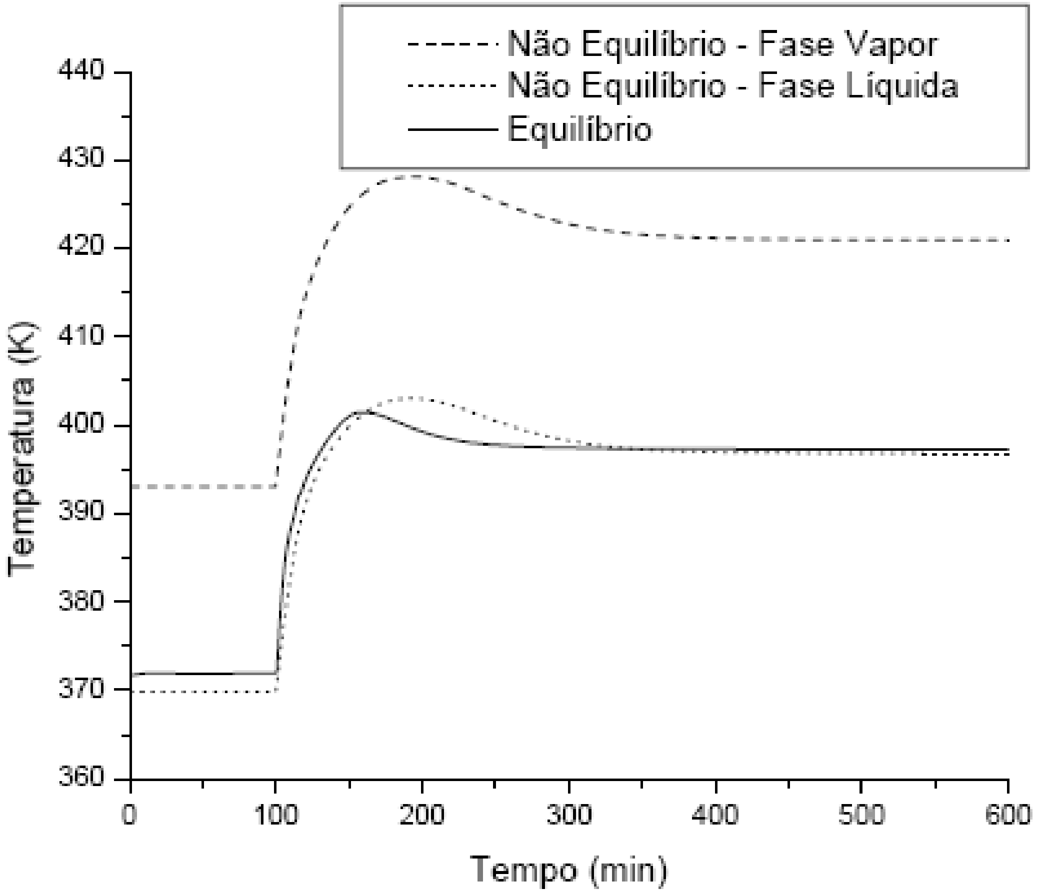
$FSTR^V_{i,j}$
HF^V_i

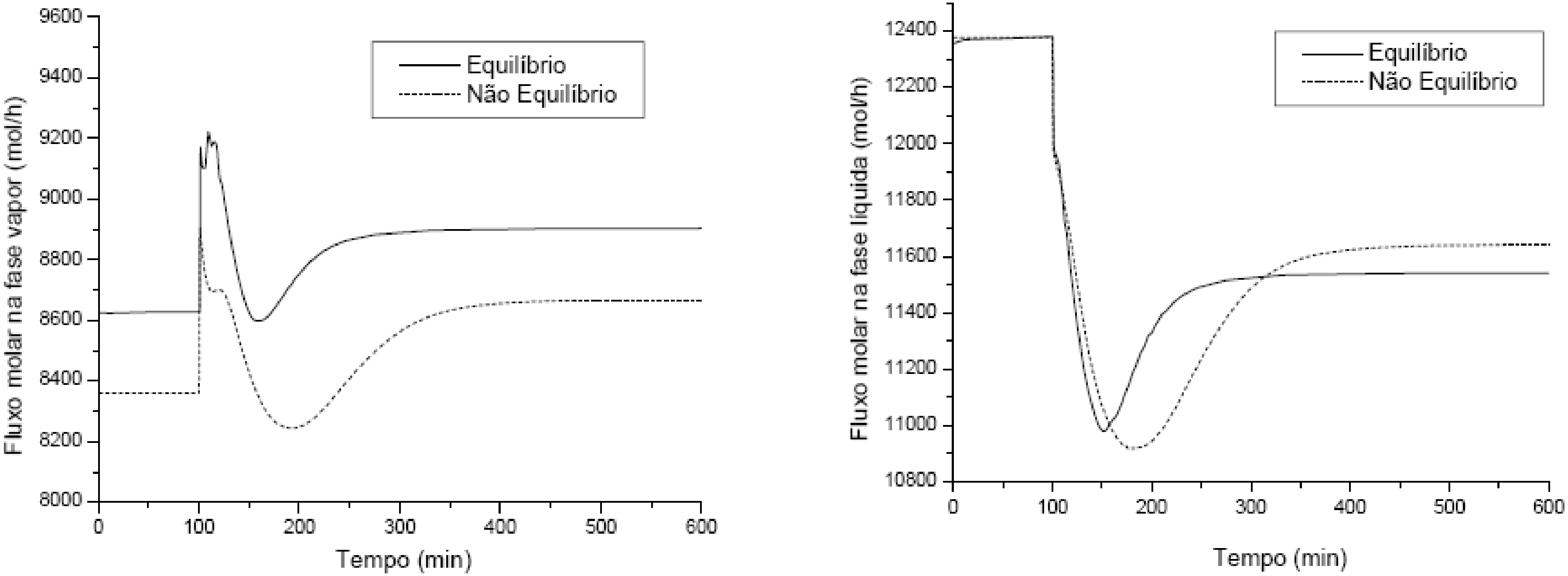
ε_i

$FSTR^L_{i,j}$
HF^L_i

$FVV_{i-1,j}$
H_{i-1}^V
F_{i-1}^V

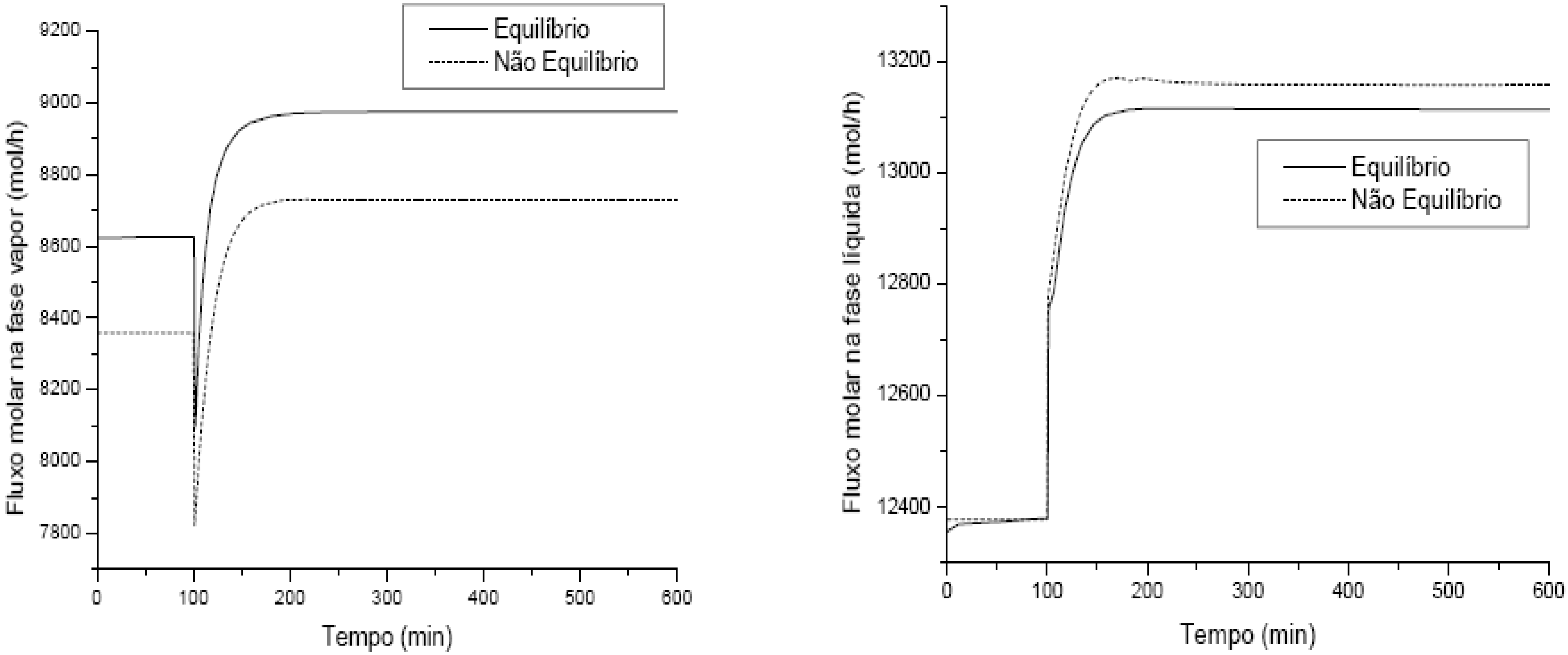
$FLL_{i1,j}$
H_i^L
F_i^L


Não Equilíbrio - Fase Vapor
Não Equilíbrio - Fase Líquida
Equilíbrio
Temperatura (K)
440
430
420
410
400
390
380
370
360
Tempo (min)
0
100
200
300
400
500
600



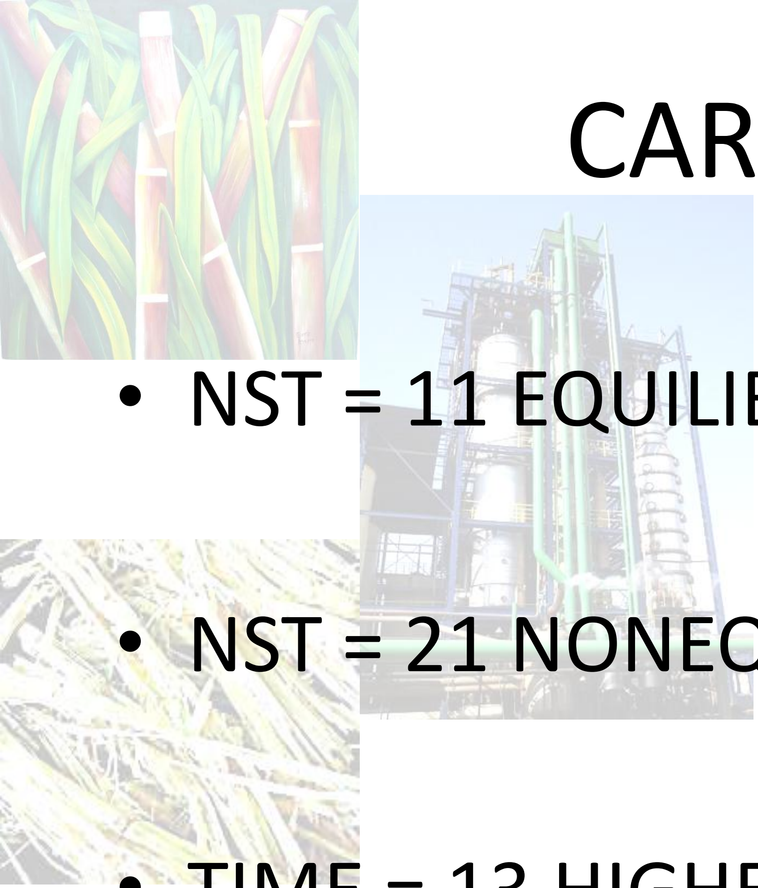
(b) (c)

DYNAMIC PROFILES AFTER INCREASING REBOILER DUTY

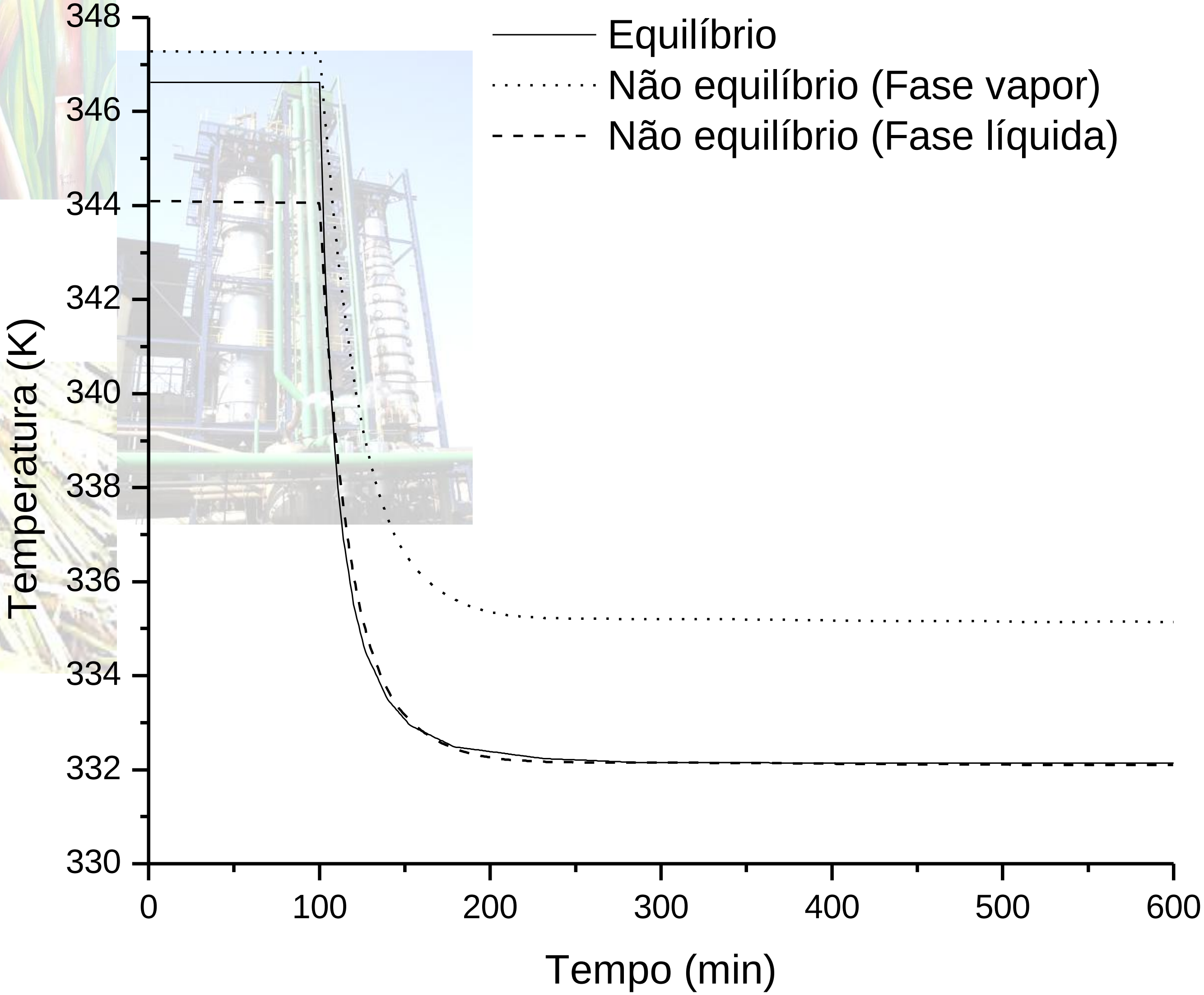


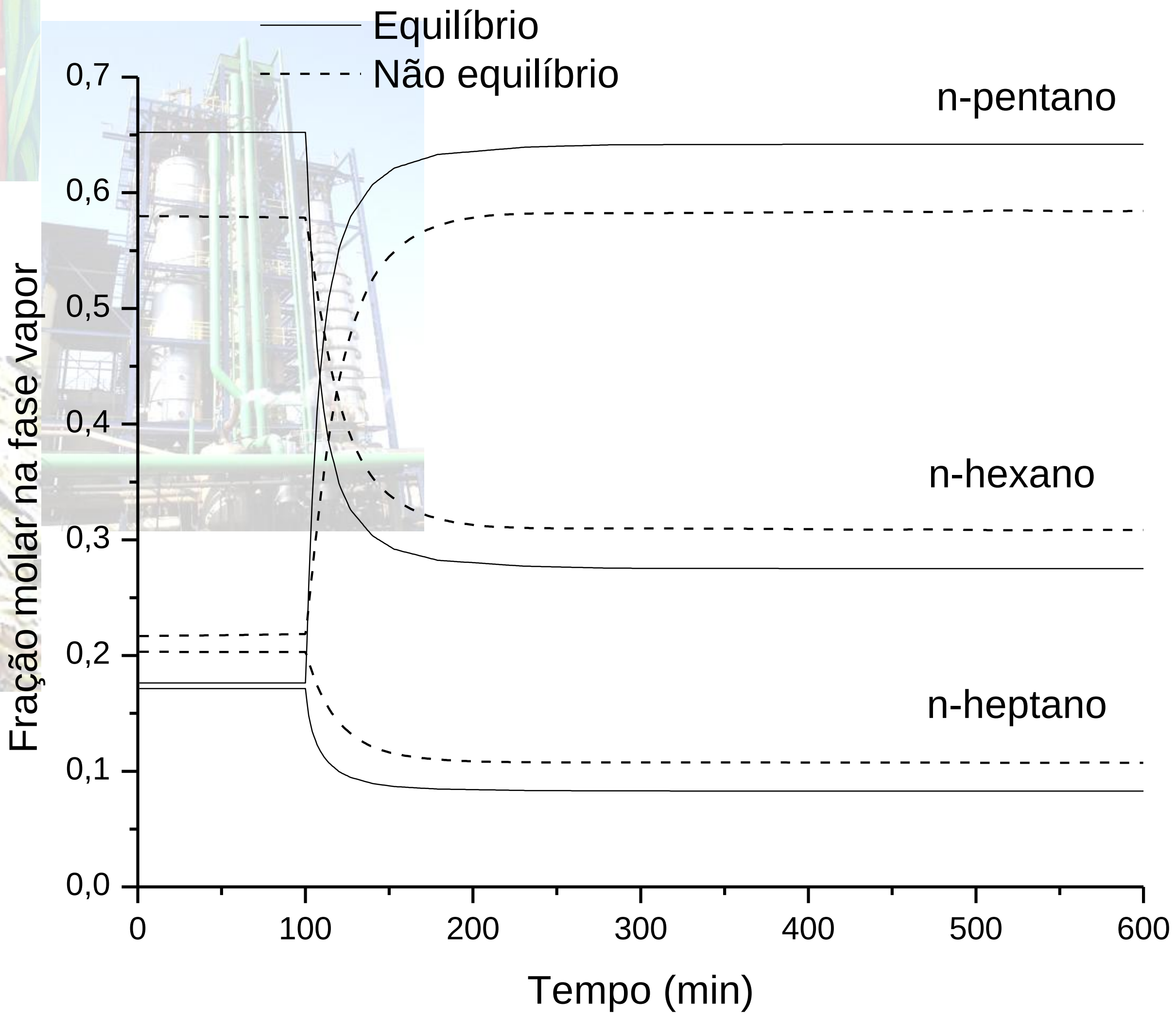
DYNAMIC PROFILES AFTER DECREASING REBOILER DUTY

CARACTERISTICS

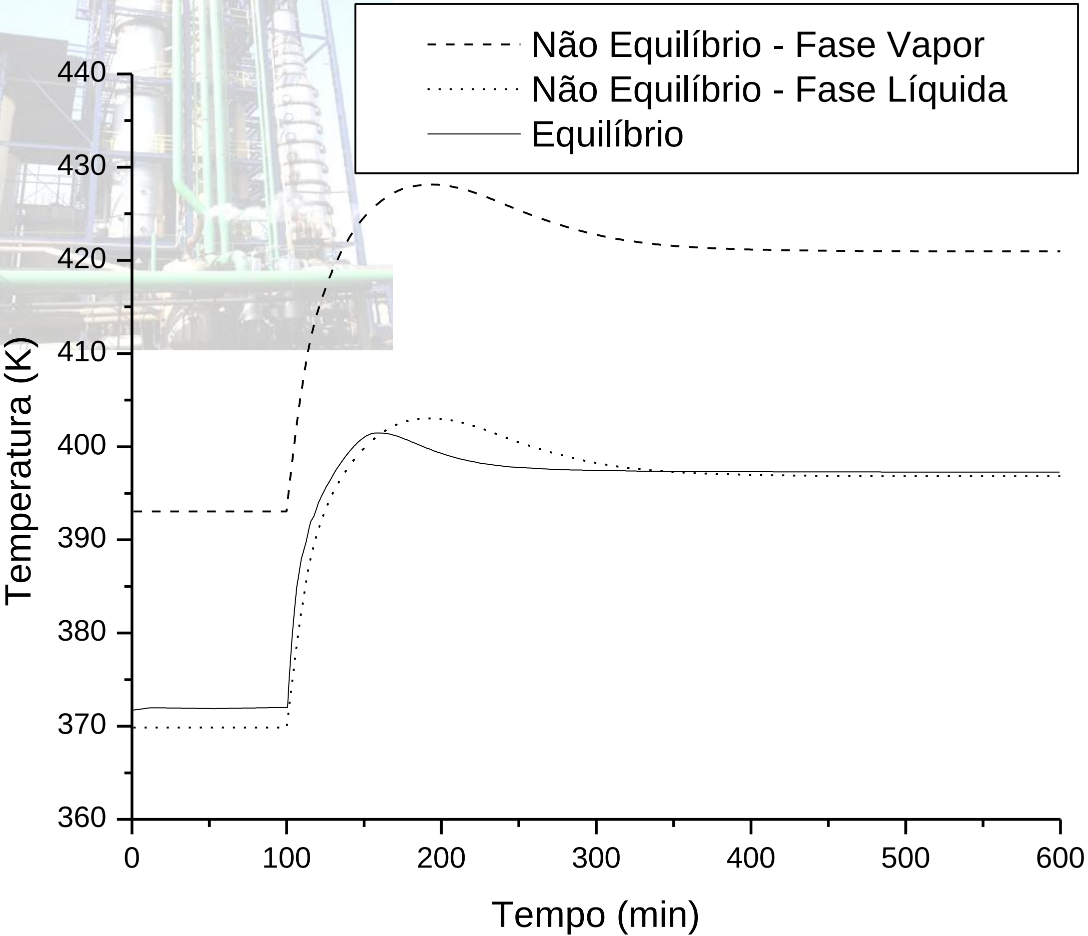


- NST = 11 EQUILIBRIUM
- NST = 21 NONEQUILIBRIUM
- TIME = 13 HIGHER

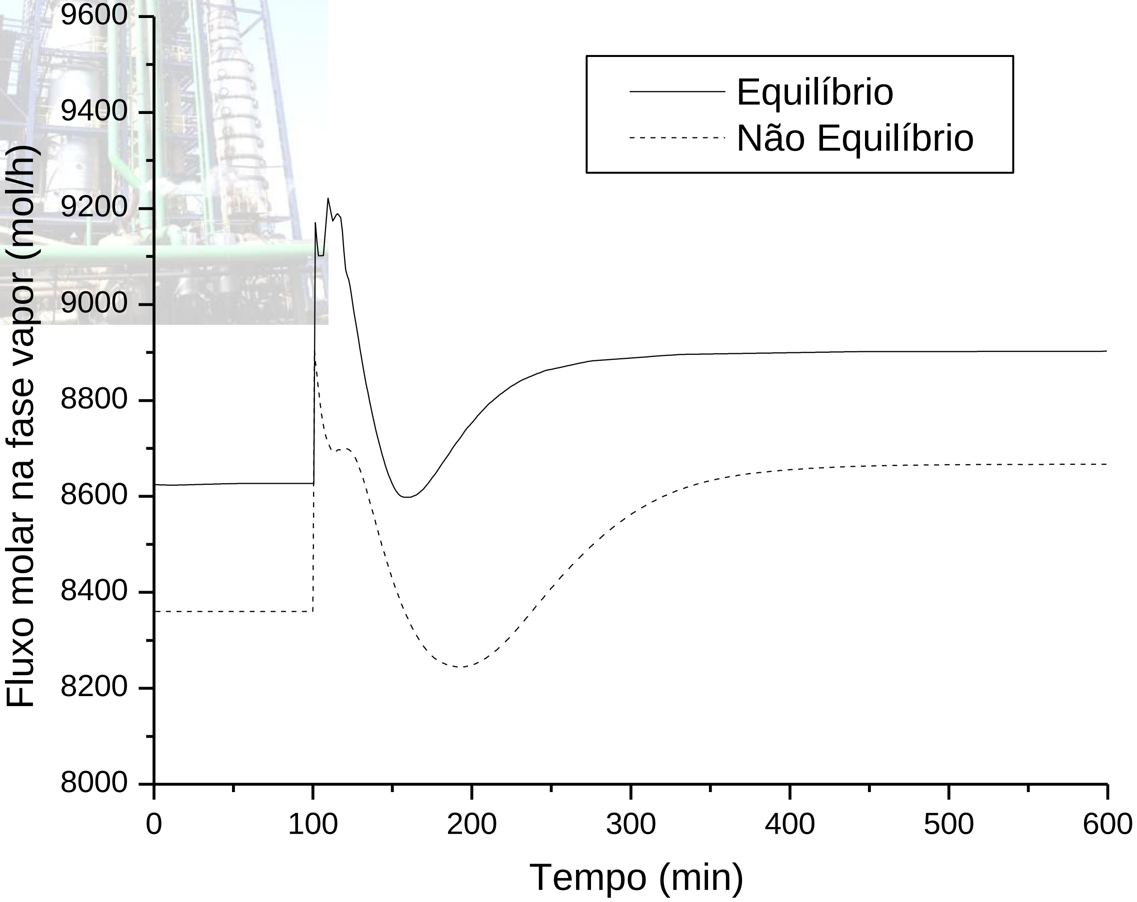

Equilíbrio
Não equilíbrio (Fase vapor)
Não equilíbrio (Fase líquida)
Temperatura (K)
348
346
344
342
340
338
336
334
332
330
0
100
200
300
400
500
600
Tempo (min)


Equilíbrio
Não equilíbrio
n-pentano
n-hexano
n-heptano
Fração molar na fase vapor
0,0
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0
100
200
300
400
500
600
Tempo (min)

ETHANOL + WATER + ETHYLENEGLICOL



ETHANOL + WATER + ETHYLENEGLICOL



Sugarcane Processing and Engineering

BIOEN WORKSHOP ON PROCESSES FOR ETHANOL PRODUCTION

Professor Maria Regina Wolf Maciel, 10/09/2009

CORRELATION OF BARROS & WOLF FOR EFFICIENCY OF STAGES AND COMPONENTS

- DISTILLATION COLUMNS: FROM SIMPLE TO COMPLEX

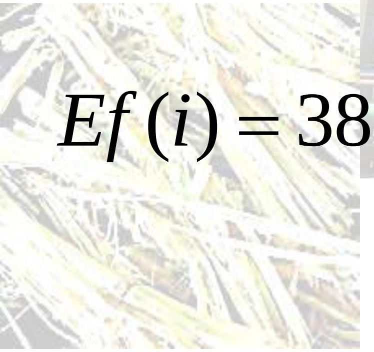


PLATE EFFICIENCY

- Dependent on mixture properties

$$Ef(i) = 38.5309 * \left[\frac{klm(i)}{cplm(i)} * \frac{dlm(i) * diflm(i) * pmm(i)}{\left(mlm(i) \right)^2} \right]^{-0.04516}$$

Molecular weight (pmm)

Thermal conductivity (klm)

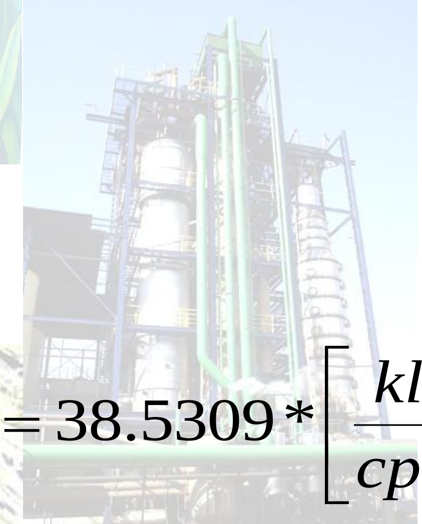
Heat capacity (cplm)

Viscosity (mlm)

Diffusivity (diflm)

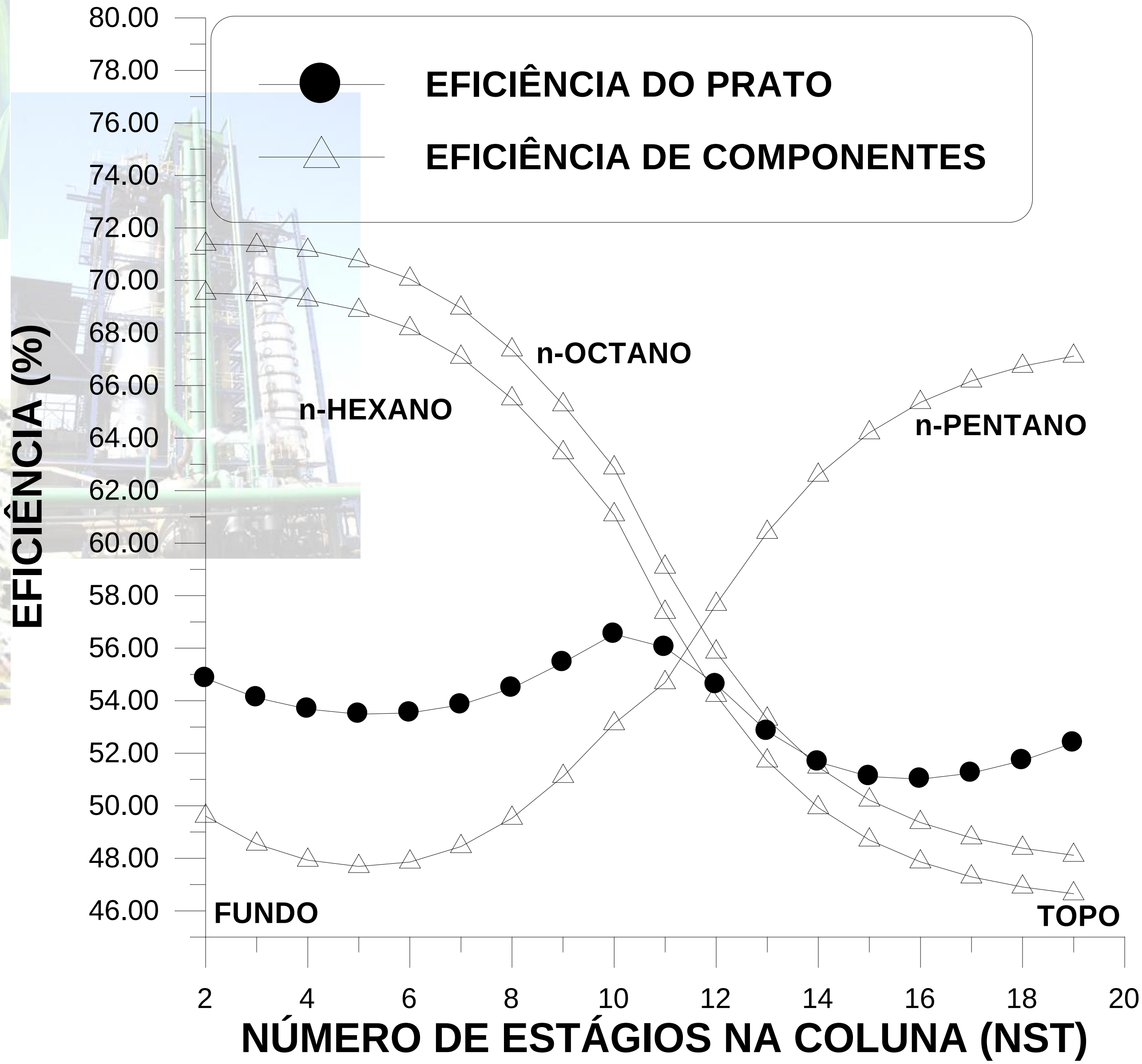
Density (dlm)

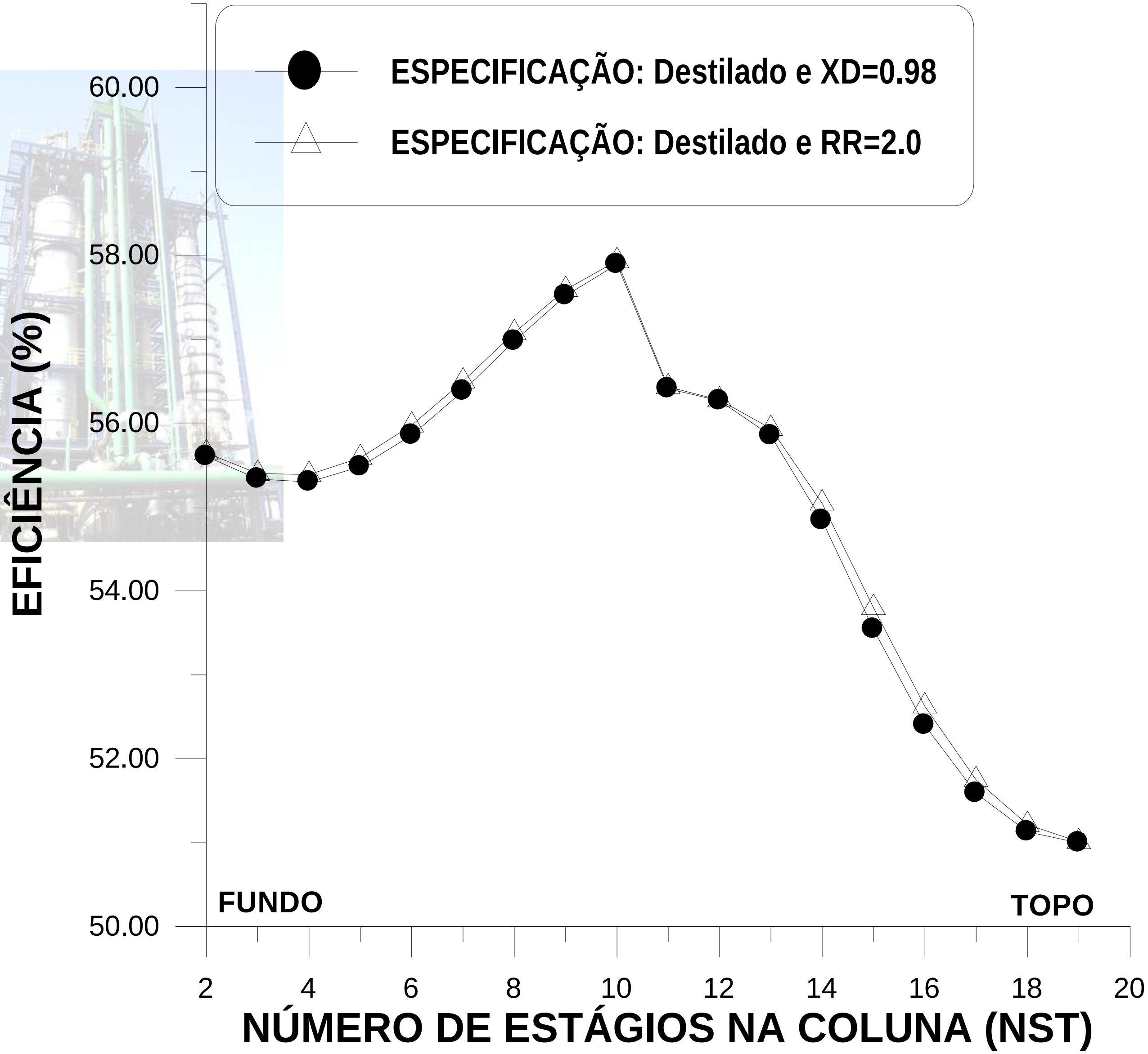
COMPONENT EFFICIENCY

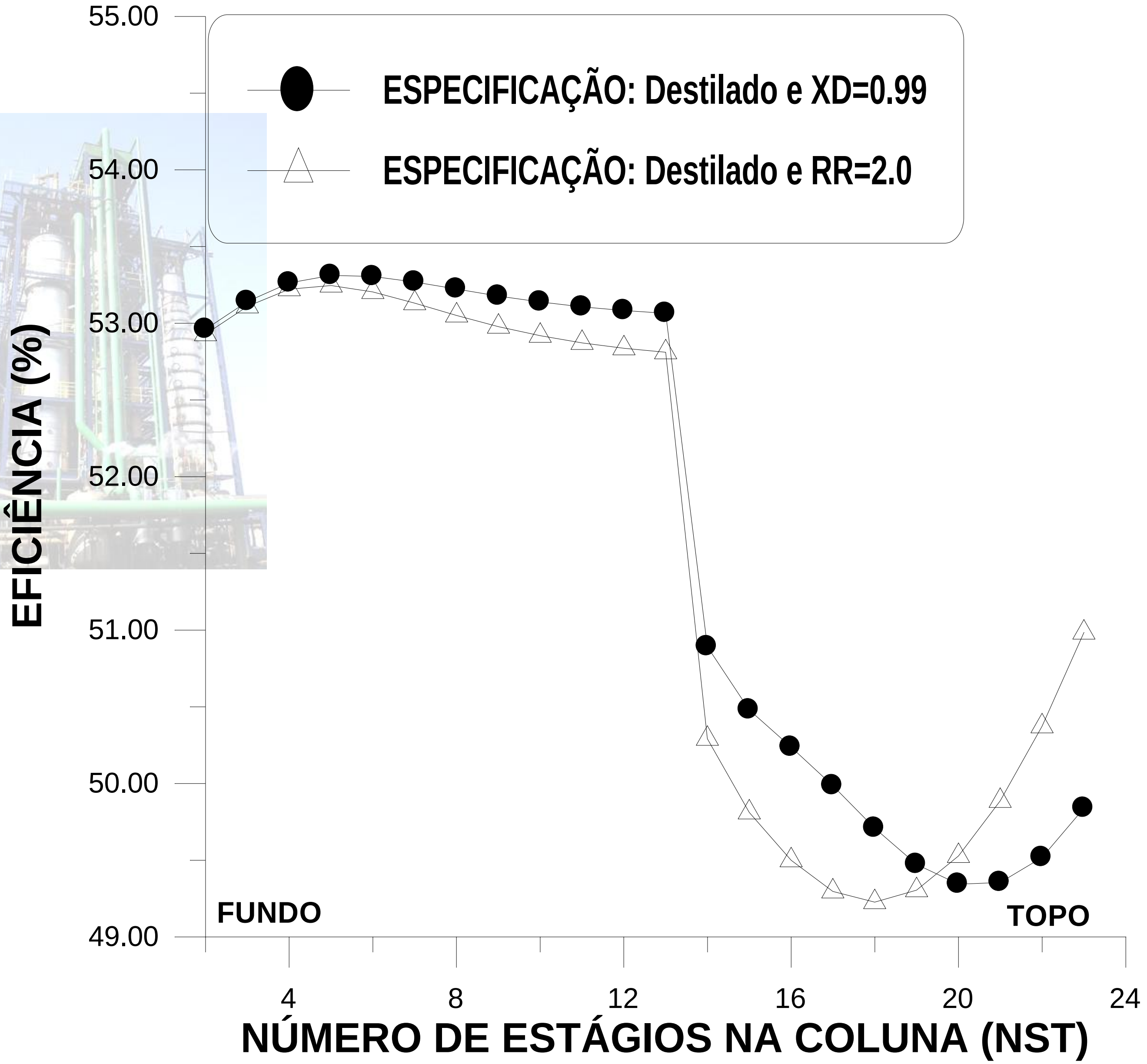


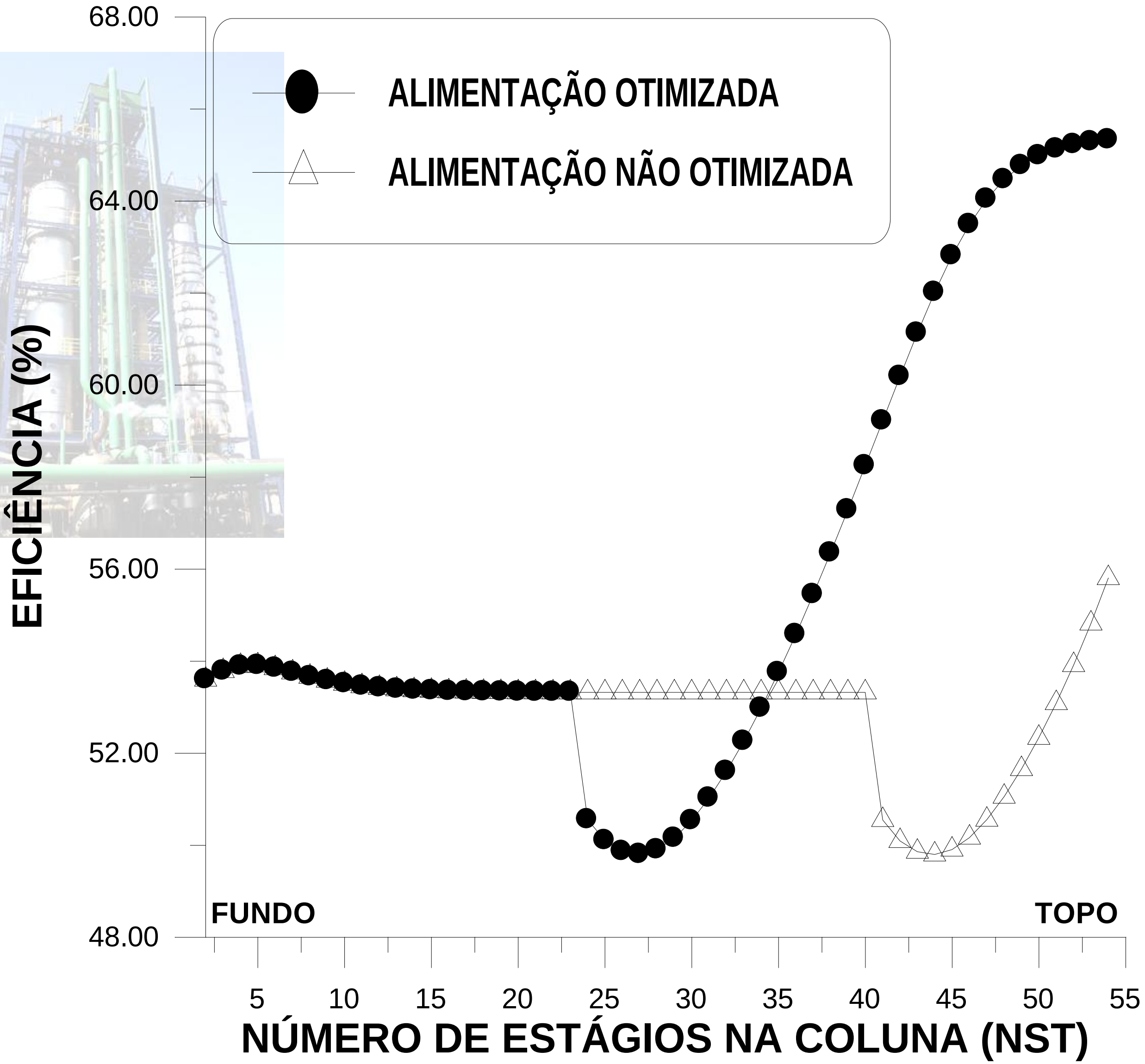
$$Eff(i,j) = 38.5309 * \left[\frac{kll(i,j)}{cpll(i,j)} * \frac{dll(i,j) * difl(i,j) * pm(j)}{\left(mll(i,j)\right)^{2}} \right]^{-0.04516}$$

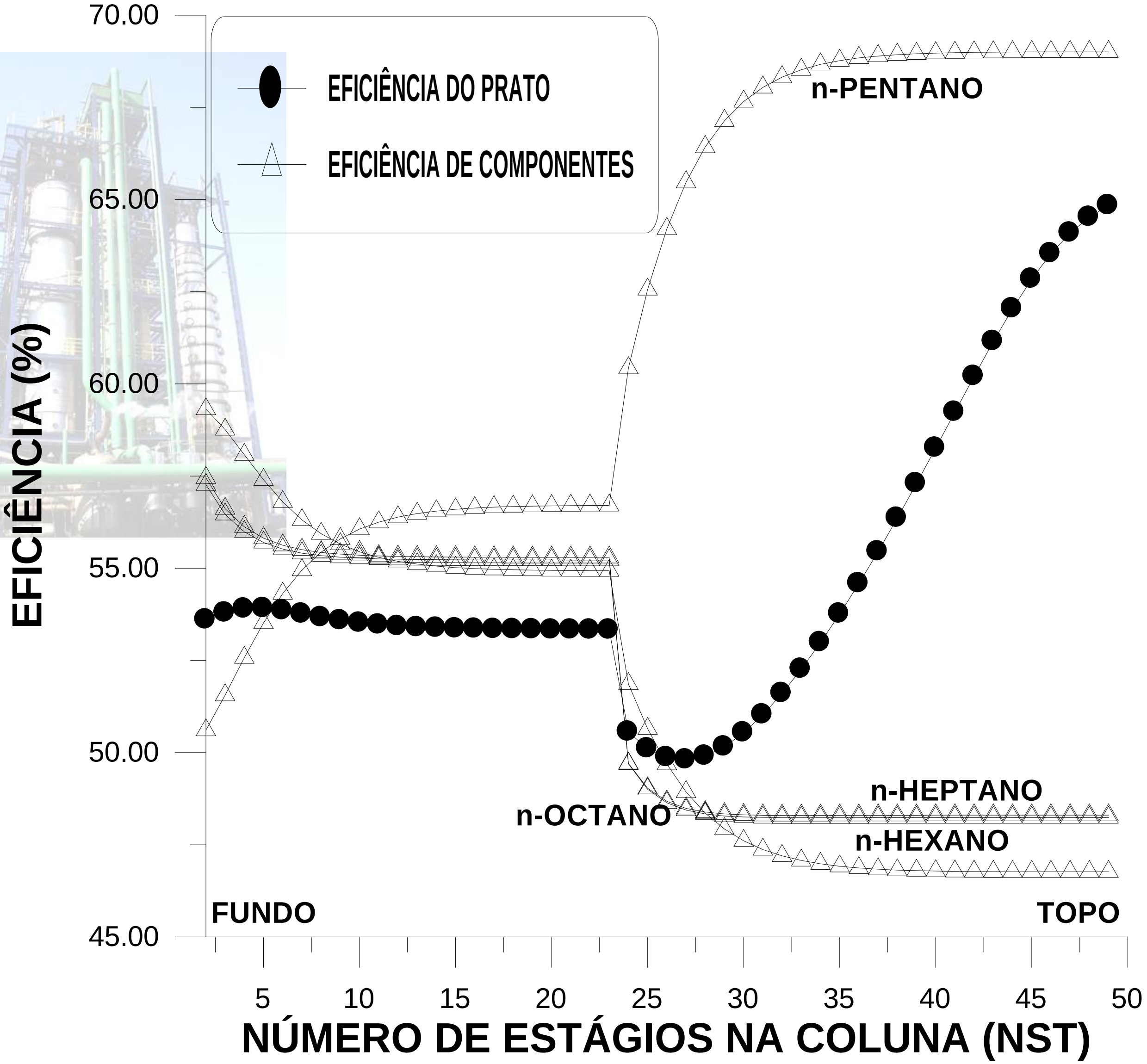
PURE COMPONENT PARAMETERS

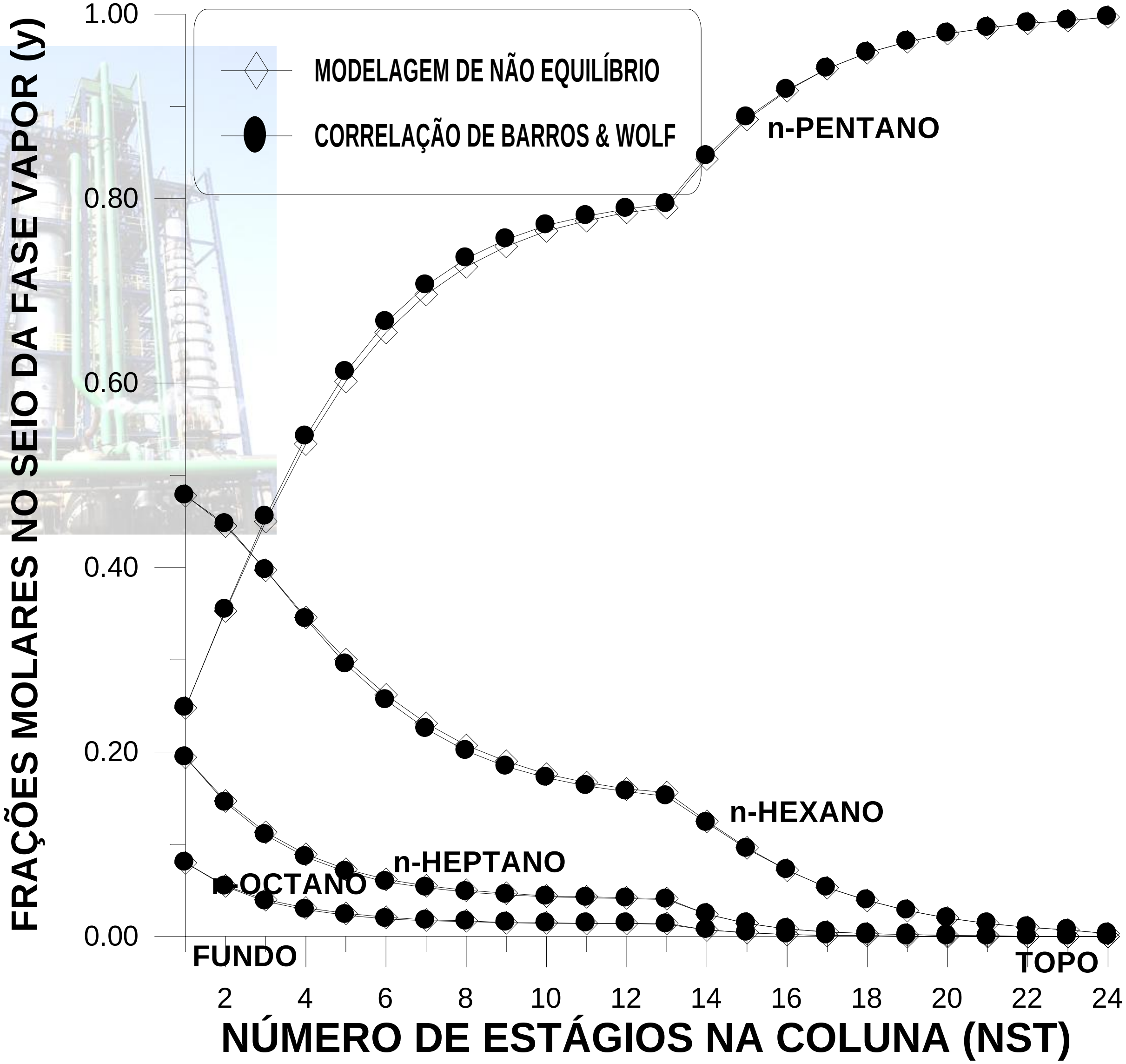

EFICIÊNCIA DO PRATO
EFICIÊNCIA DE COMPONENTES
n-OCTANO
n-HEXANO
n-PENTANO
FUNDO
TOPO
EFICIÊNCIA (%)
80.00
78.00
76.00
74.00
72.00
70.00
68.00
66.00
64.00
62.00
60.00
58.00
56.00
54.00
52.00
50.00
48.00
46.00
2
4
6
8
10
12
14
16
18
20
NÚMERO DE ESTÁGIOS NA COLUNA (NST)

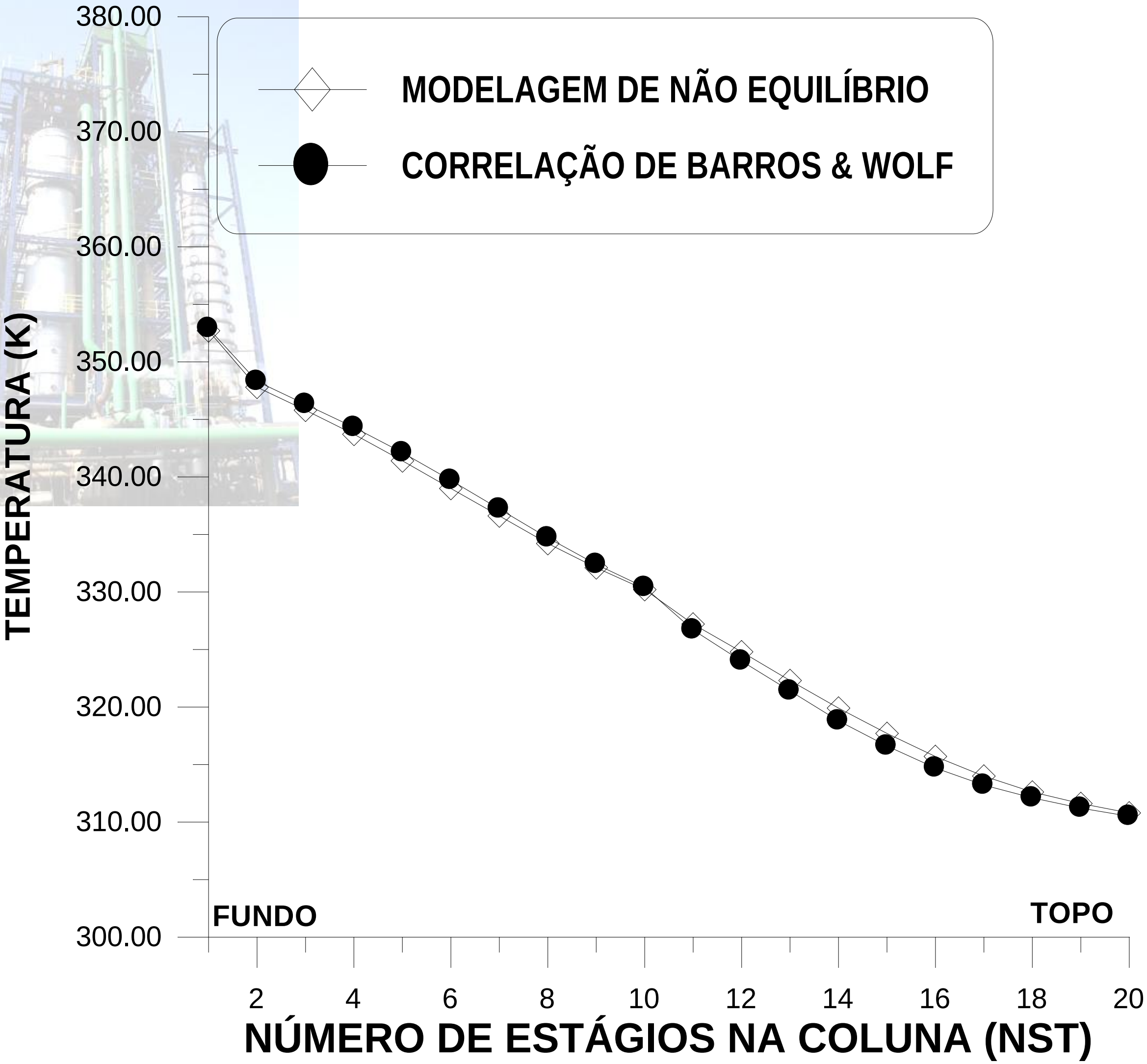

ESPECIFICAÇÃO: Destilado e XD=0.98
ESPECIFICAÇÃO: Destilado e RR=2.0
EFICIÊNCIA (%)
60.00
58.00
56.00
54.00
52.00
50.00
FUNDO
TOPO
2
4
6
8
10
12
14
16
18
20
NÚMERO DE ESTÁGIOS NA COLUNA (NST)

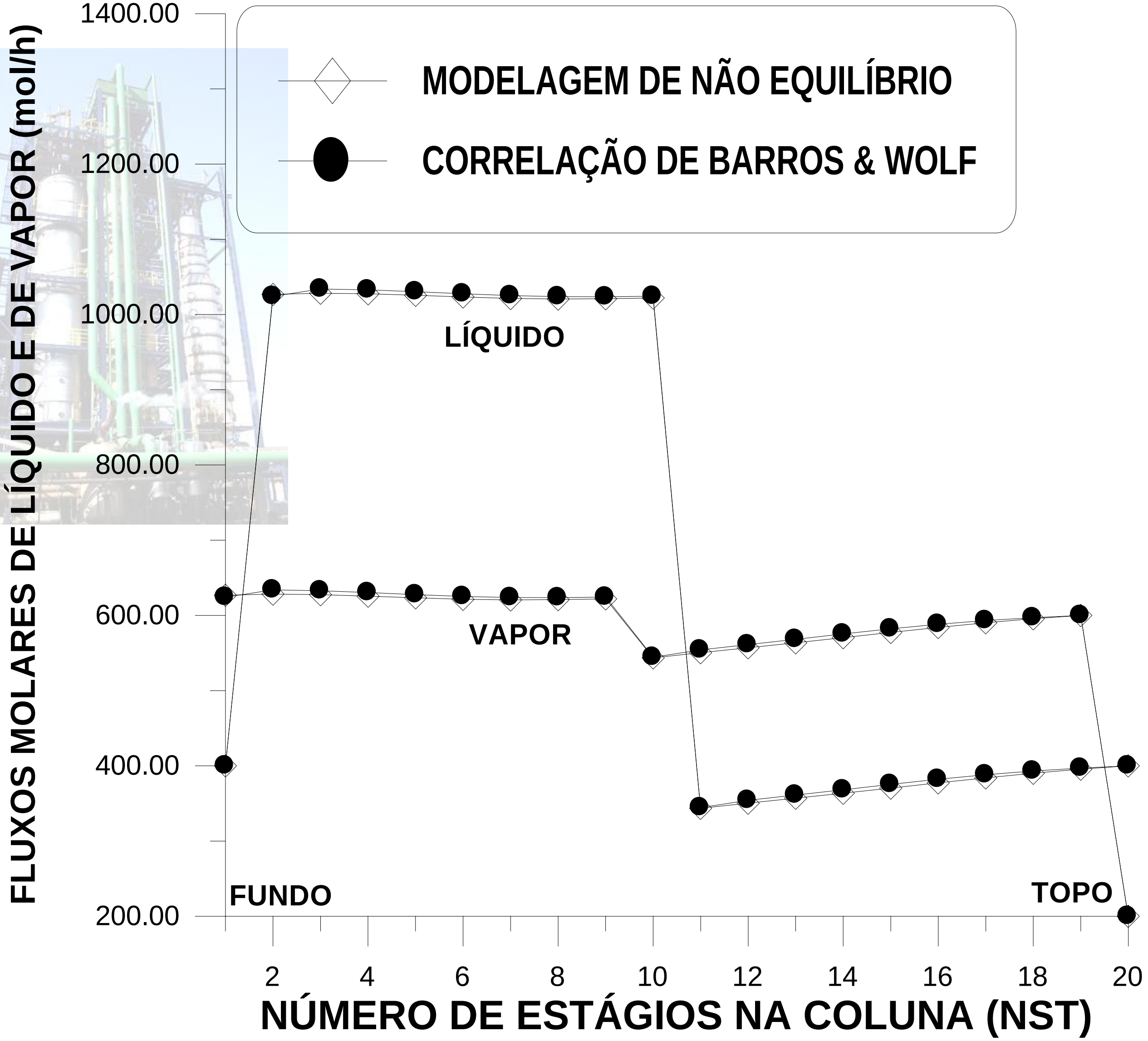

55.00
54.00
53.00
52.00
51.00
50.00
49.00
EFICIÊNCIA (%)
● ESPECIFICAÇÃO: Destilado e XD=0.99
△ ESPECIFICAÇÃO: Destilado e RR=2.0
FUNDO
TOPO
4
8
12
16
20
24
NÚMERO DE ESTÁGIOS NA COLUNA (NST)

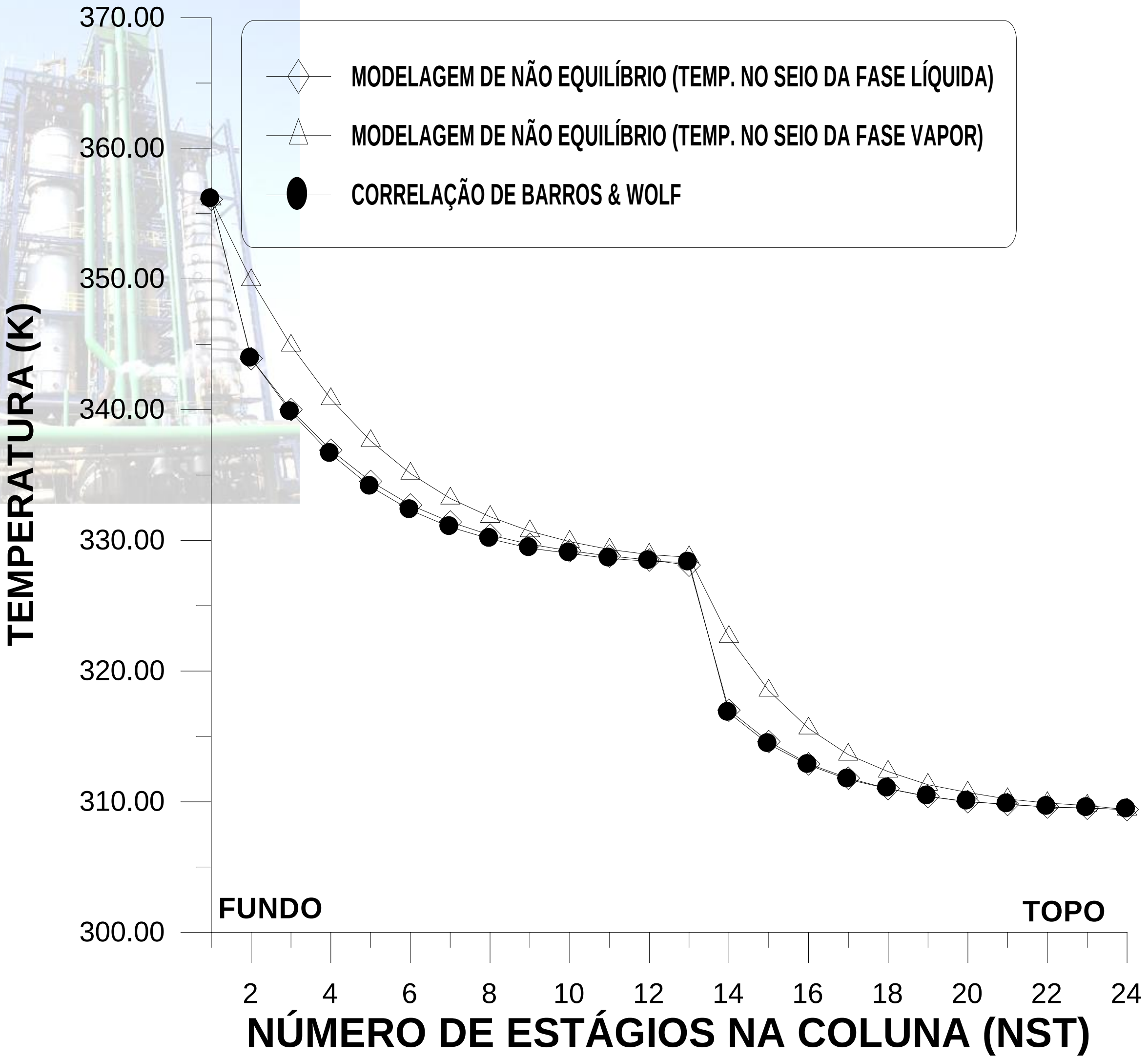

68.00
64.00
60.00
56.00
52.00
48.00
EFICIÊNCIA (%)
ALIMENTAÇÃO OTIMIZADA
ALIMENTAÇÃO NÃO OTIMIZADA
FUNDO
TOPO
5
10
15
20
25
30
35
40
45
50
55
NÚMERO DE ESTÁGIOS NA COLUNA (NST)


70.00
65.00
60.00
55.00
50.00
45.00
EFICIÊNCIA (%)
● EFICIÊNCIA DO PRATO
△ EFICIÊNCIA DE COMPONENTES
n-PENTANO
n-HEPTANO
n-OCTANO
n-HEXANO
FUNDO
TOPO
5
10
15
20
25
30
35
40
45
50
NÚMERO DE ESTÁGIOS NA COLUNA (NST)


MODELAGEM DE NÃO EQUILÍBRIO
CORRELAÇÃO DE BARROS & WOLF
FRAÇÕES MOLARES NO SEIO DA FASE VAPOR (y)
1.00
0.80
0.60
0.40
0.20
0.00
n-PENTANO
n-HEXANO
n-HEPTANO
n-OCTANO
FUNDO
TOPO
2
4
6
8
10
12
14
16
18
20
22
24
NÚMERO DE ESTÁGIOS NA COLUNA (NST)


380.00
370.00
360.00
350.00
340.00
330.00
320.00
310.00
300.00
TEMPERATURA (K)
◇ MODELAGEM DE NÃO EQUILÍBRIO
● CORRELAÇÃO DE BARROS & WOLF
FUNDO
TOPO
2
4
6
8
10
12
14
16
18
20
NÚMERO DE ESTÁGIOS NA COLUNA (NST)

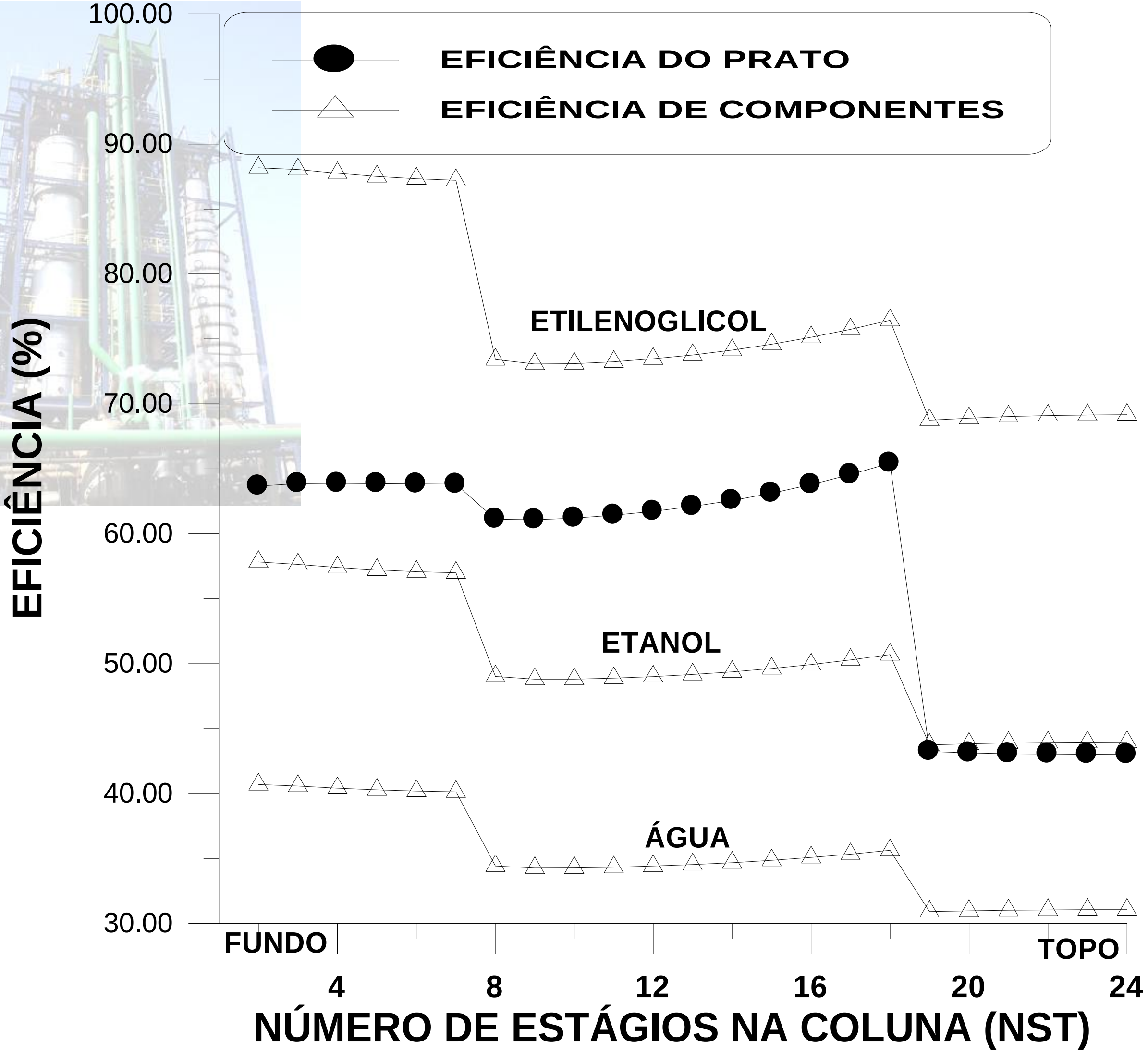

1400.00
1200.00
1000.00
800.00
600.00
400.00
200.00
FLUXOS MOLARES DE LÍQUIDO E DE VAPOR (mol/h)
◇ MODELAGEM DE NÃO EQUILÍBRIO
● CORRELAÇÃO DE BARROS & WOLF
LÍQUIDO
VAPOR
FUNDO
TOPO
2
4
6
8
10
12
14
16
18
20
NÚMERO DE ESTÁGIOS NA COLUNA (NST)


370.00
360.00
350.00
340.00
330.00
320.00
310.00
300.00
TEMPERATURA (K)
MODELAGEM DE NÃO EQUILÍBRIO (TEMP. NO SEIO DA FASE LÍQUIDA)
MODELAGEM DE NÃO EQUILÍBRIO (TEMP. NO SEIO DA FASE VAPOR)
CORRELAÇÃO DE BARROS & WOLF
FUNDO
TOPO
2
4
6
8
10
12
14
16
18
20
22
24
NÚMERO DE ESTÁGIOS NA COLUNA (NST)

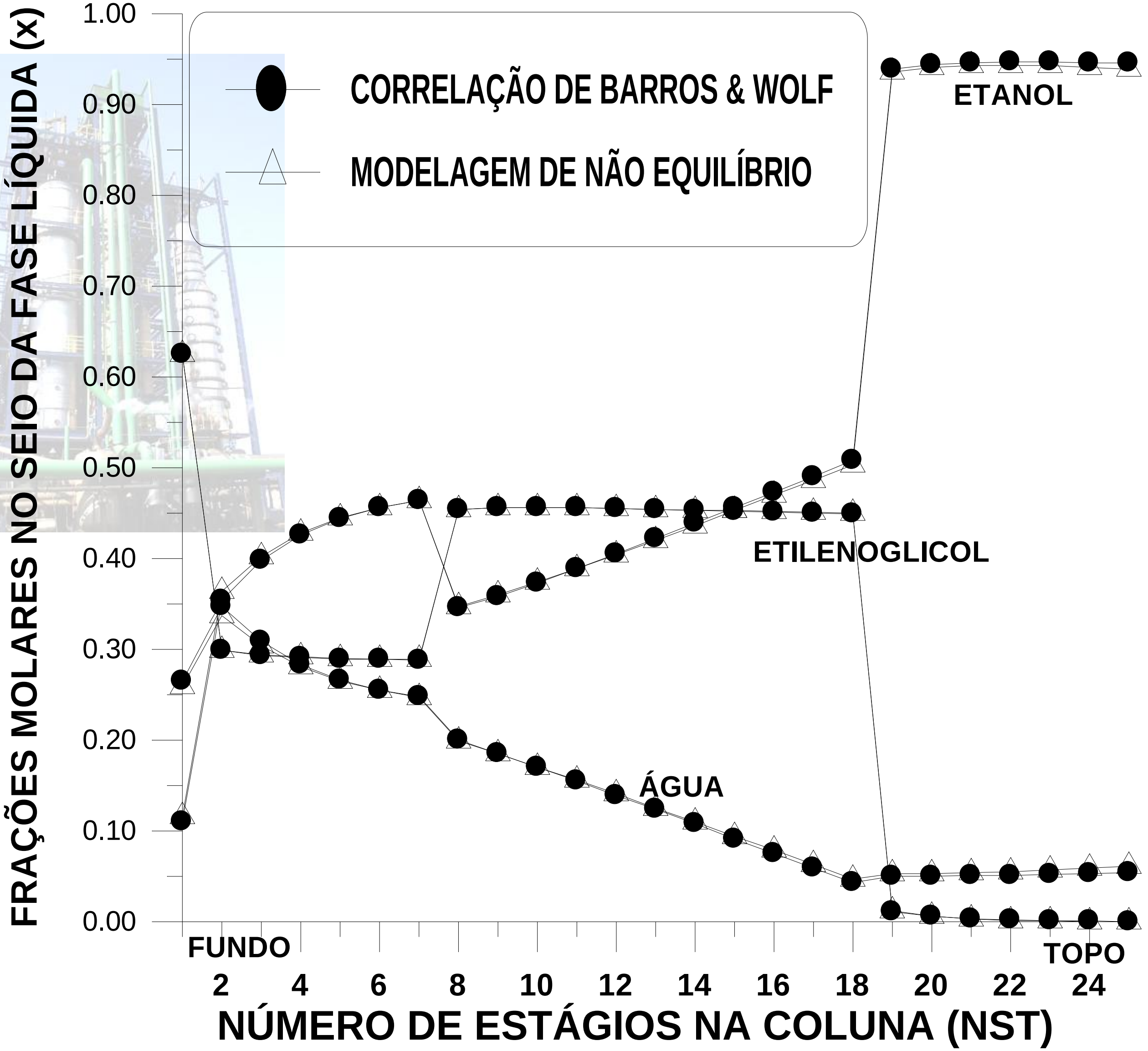
EXTRACTIVE DISTILLATION EFFICIENCY

$$Ef(i) = 19.37272\left(\frac{klm(i)}{cplm(i)} * \frac{dlm(i) * diflm(i) * pmm(i)}{mlm(i)^2}\right)^{-0.109588}$$

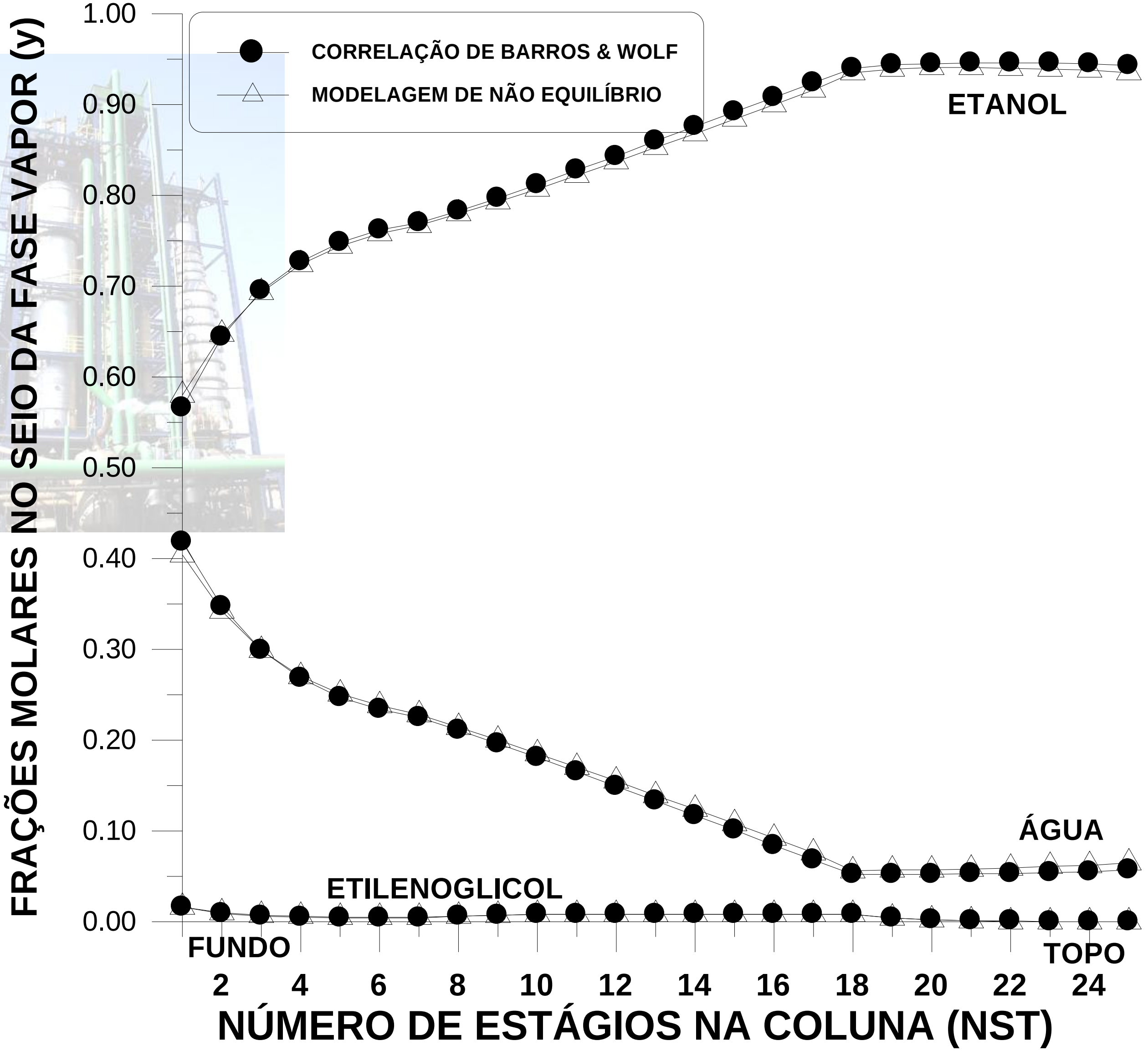
$$Eff(i,j) = 19.37272\left(\frac{kll(i,j)}{cpll(i,j)} * \frac{dll(i,j) * difl(i,j,k) * pm(j)}{mll(i,j)^2}\right)^{-0.109588}$$



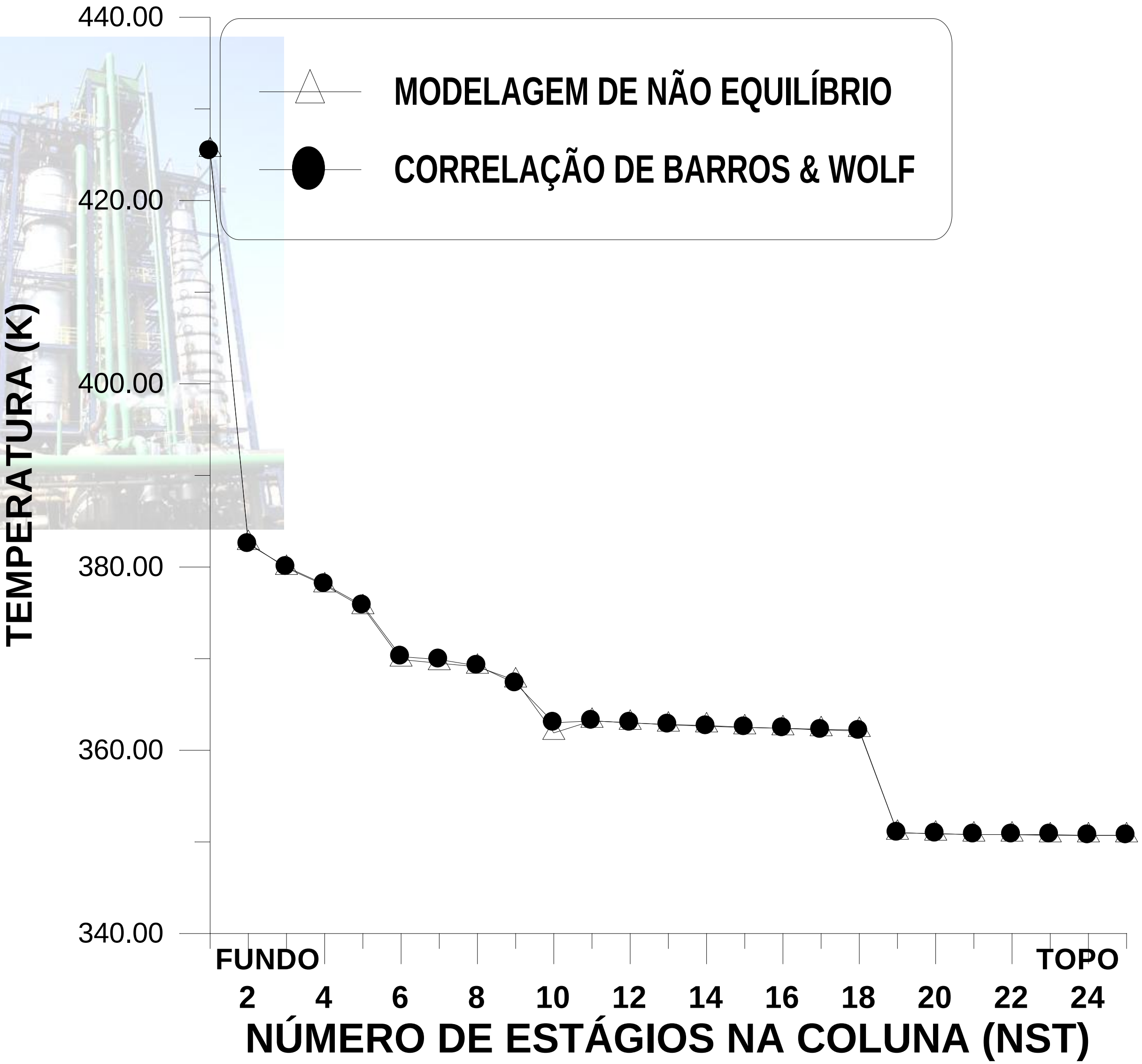
Professor Maria Regina Wolf Maciel, 10/09/2009

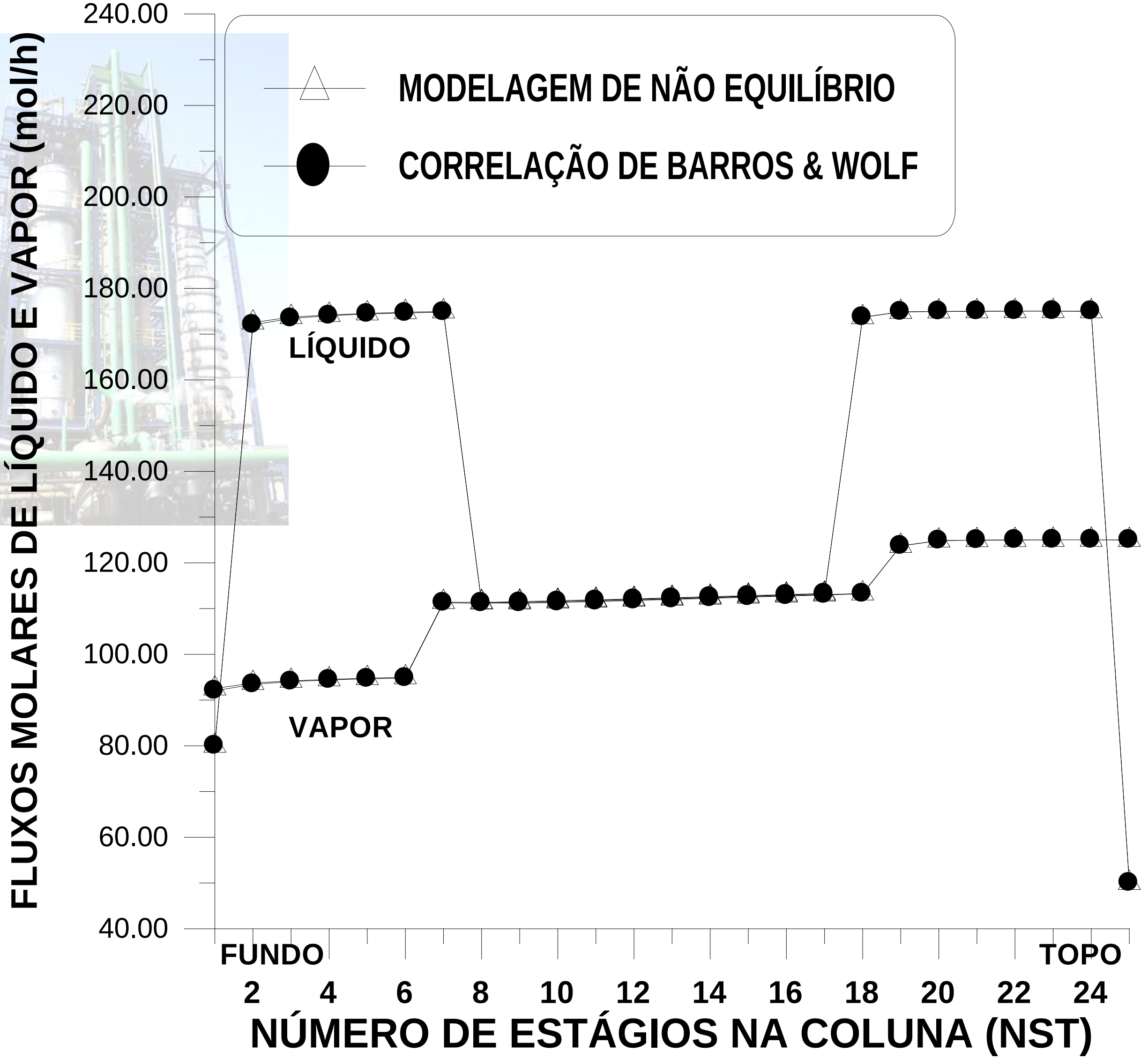


FRAÇÕES MOLARES NO SEIO DA FASE LÍQUIDA (x)
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
CORRELAÇÃO DE BARROS & WOLF
MODELAGEM DE NÃO EQUILÍBRIO
ETANOL
ETILENOGLICOL
ÁGUA
FUNDO
TOPO
2
4
6
8
10
12
14
16
18
20
22
24
NÚMERO DE ESTÁGIOS NA COLUNA (NST)

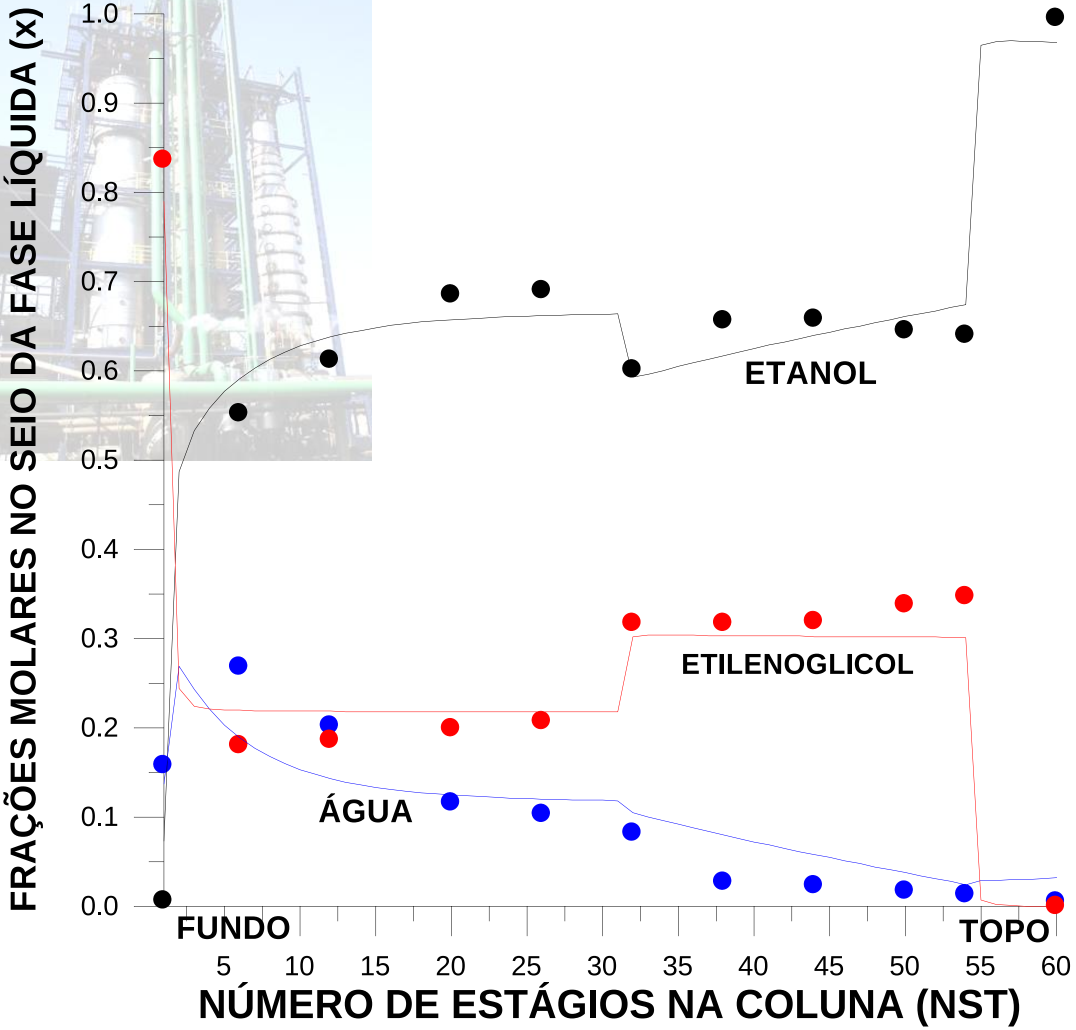


CORRELAÇÃO DE BARROS & WOLF
MODELAGEM DE NÃO EQUILÍBRIO
ETANOL
ÁGUA
ETILENOGLICOL
FUNDO
TOPO
FRAÇÕES MOLARES NO SEIO DA FASE VAPOR (y)
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
2
4
6
8
10
12
14
16
18
20
22
24
NÚMERO DE ESTÁGIOS NA COLUNA (NST)


440.00
420.00
400.00
380.00
360.00
340.00
TEMPERATURA (K)
MODELAGEM DE NÃO EQUILÍBRIO
CORRELAÇÃO DE BARROS & WOLF
FUNDO
TOPO
2
4
6
8
10
12
14
16
18
20
22
24
NÚMERO DE ESTÁGIOS NA COLUNA (NST)


MODELAGEM DE NÃO EQUILÍBRIO
CORRELAÇÃO DE BARROS & WOLF
FLUXOS MOLARES DE LÍQUIDO E VAPOR (mol/h)
240.00
220.00
200.00
180.00
160.00
140.00
120.00
100.00
80.00
60.00
40.00
LÍQUIDO
VAPOR
FUNDO
TOPO
2
4
6
8
10
12
14
16
18
20
22
24
NÚMERO DE ESTÁGIOS NA COLUNA (NST)

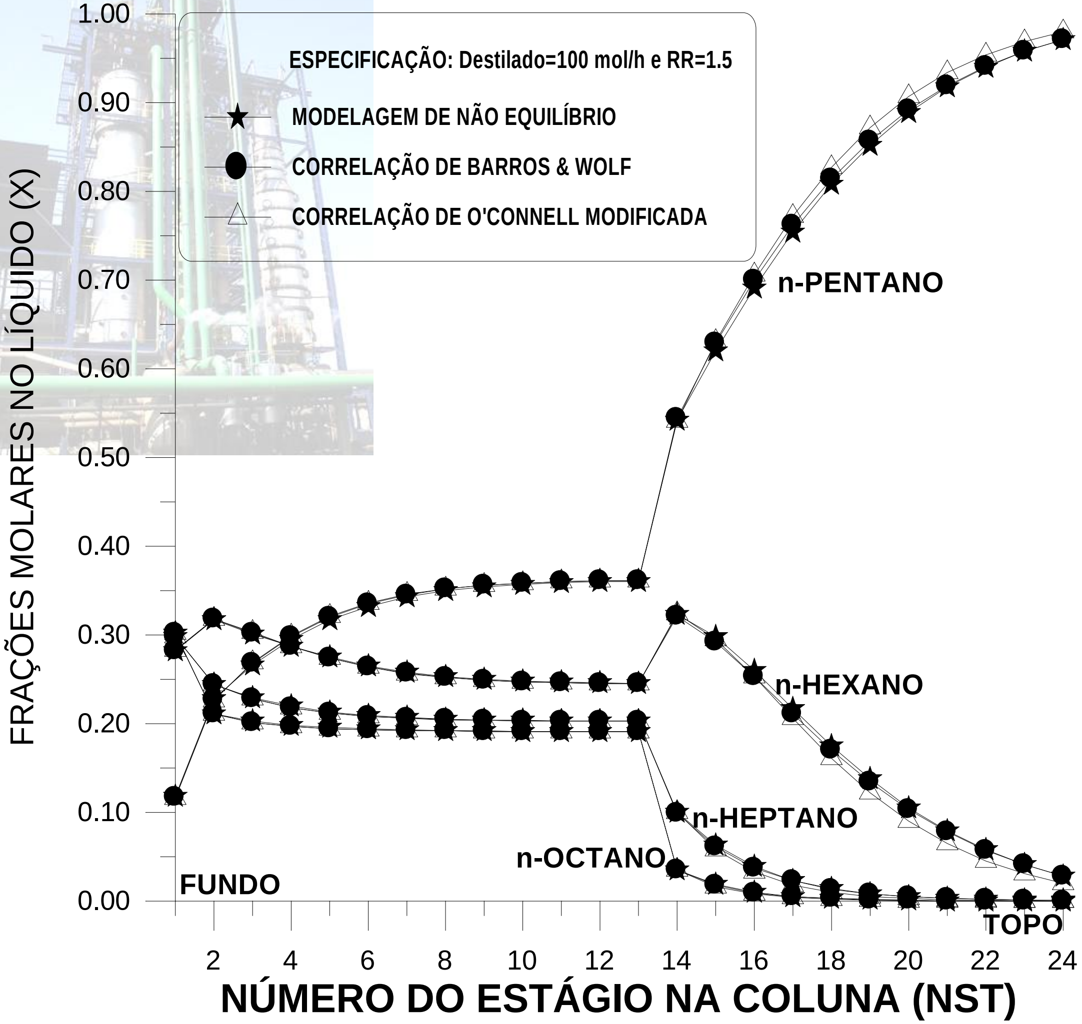
DD e RR


FRAÇÕES MOLARES NO SEIO DA FASE LÍQUIDA (x)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
ETANOL
ETILENOGLICOL
ÁGUA
FUNDO
TOPO
5
10
15
20
25
30
35
40
45
50
55
60
NÚMERO DE ESTÁGIOS NA COLUNA (NST)

COMPLEX COLUMNS

- **SIDE STREAMS – LIQUID AND VAPOR PHASES**

COMPARAÇÃO NÃO EQUILÍBRIO



THANKS

- MARINA DIAS
- TASSIA JUNQUEIRA
- LAURA PLAZAS
- JAIVER
- JEFREY
- PROFS.ROSSEL, MEIRELLES, KAKUTA