ADVANCES IN ETHANOL PURIFICATION:

ALTERNATIVES

AND

PERSPECTIVES
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(Full Professor)
REAL

- EQUILIBRIUM PROCESS
- NON EQUILIBRIUM APPROACH
Block flow diagram – conventional bioethanol production process

Sugarcane

Harvest

Cleaning

Extraction of sugars

Juice treatment

Juice concentration

Sugar cane Trash

Sand, dirt, metals

Cogeneration

Bioelectric Energy

CO₂

Sugarcane Bagasse

Sand, fibers, filter cake

Juice sterilization

Fermentation

Centrifugation

Yeast Treatment

Absorption

Gases

Yeast

Wine

Distillation and Rectification

Hydrous Bioethanol

Dehydration

2nd grade ethanol, Vinassee, Phlegmasse, Fusel oil

Anhydrous Bioethanol
Block flow diagram – bioethanol production process from bagasse

1. **Sugarcane Bagasse**
   - Cleaning
   - Sand, impurities
   - Pre-hydrolysis
   - Pentose liquor
   - Delignification
     - Cellulose
   - Hydrolysis
     - Lignin
     - Concentration
   - Solvent recovery
     - Organosolv solvent

2. **Glucose liquor**
   - Fermentation
     - Gases
     - Yeast
     - Centrifugation
     - Wine
   - Absorption
     - CO₂
   - Distillation and Rectification
     - 2nd grade ethanol, Vinassee, Phlegmasse, Fusel oil
   - Yeast Treatment
     - Hydrous Bioethanol
   - 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

<table>
<thead>
<tr>
<th>Component</th>
<th>Composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conventional</td>
</tr>
<tr>
<td>Water</td>
<td>79.181</td>
</tr>
<tr>
<td>Glucose</td>
<td>0.607</td>
</tr>
<tr>
<td>Impurities</td>
<td>2.824</td>
</tr>
<tr>
<td>Ethanol</td>
<td>10.064</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.129</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>0.005</td>
</tr>
<tr>
<td>Succinic Acid</td>
<td>0.001</td>
</tr>
<tr>
<td>Yeast</td>
<td>7.181</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>0.008</td>
</tr>
<tr>
<td>Pentose</td>
<td>-</td>
</tr>
<tr>
<td>Furfural</td>
<td>-</td>
</tr>
<tr>
<td>HMF</td>
<td>-</td>
</tr>
</tbody>
</table>
WINE

• HAS SEVERAL OTHER COMPONENTS (CONTAMINANTS) BEYOND WATER AND ETHANOL

• **ALCOHOLS**: METHANOL, PROПANOL, 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
EXAMPLE FOR SIMPLE COLUMNS
<table>
<thead>
<tr>
<th>Model</th>
<th>EQ</th>
<th>EQ70</th>
<th>NEQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column A reboiler (kJ/kg Product)</td>
<td>4503</td>
<td>4712</td>
<td>4723</td>
</tr>
<tr>
<td>Column B-B1 reboiler (kJ/kg Product)</td>
<td>1150</td>
<td>2252</td>
<td>2259</td>
</tr>
<tr>
<td>Total energy consumption (kJ/kg Product)</td>
<td>5653</td>
<td>6964</td>
<td>6982</td>
</tr>
</tbody>
</table>

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

Graph showing the relationship between x and y with data points for literature, NRTL, and UNIQUAC models.
Ethanol/Water
Acetaldehyde/Glucose
Acetaldehyde/Sucrose
Ethyl Acetate/Isoamyllic alcohol
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
None of the models represent properly

Acetaldehyde (1) / Ethyl Acetate (2) : $T=50 \, ^\circ\text{C}$  

Water (1) / Glycerol (2): $P=101.3 \, \text{kPa}$
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°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

<table>
<thead>
<tr>
<th>Component</th>
<th>Benzene</th>
<th>Cyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>0.3358</td>
<td>0.0768</td>
</tr>
<tr>
<td>Water</td>
<td>0.0517</td>
<td>0.0015</td>
</tr>
<tr>
<td>Entrainer</td>
<td>0.6126</td>
<td>0.9217</td>
</tr>
</tbody>
</table>
# Aqueous Phase Composition (Mole Fraction) when Using Benzene and Cyclohexane

<table>
<thead>
<tr>
<th>Component</th>
<th>Benzene</th>
<th>Cyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Etanol</td>
<td>0.4834</td>
<td>0.6766</td>
</tr>
<tr>
<td>Water</td>
<td>0.4773</td>
<td>0.2122</td>
</tr>
<tr>
<td>Entrainer</td>
<td>0.0394</td>
<td>0.1112</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Extractive Distillation</th>
<th>Azeotropic Distillation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conventional</td>
<td>Alternative</td>
</tr>
<tr>
<td></td>
<td>MEG Glyc.</td>
<td>MEG Glyc.</td>
</tr>
<tr>
<td>Vapor consumption (kg/L anydr ethanol)</td>
<td>0.43 0.47</td>
<td>0.41 0.56</td>
</tr>
<tr>
<td>Saturated steam pressure (bar)</td>
<td>6 10 / 65</td>
<td>6 65</td>
</tr>
<tr>
<td>Ethanol losses (%)</td>
<td>10^-5 10^-5</td>
<td>9x10^-5 6x10^-5</td>
</tr>
<tr>
<td>Solvent losses (%)</td>
<td>0.01 0.01</td>
<td>0.49 0.02</td>
</tr>
<tr>
<td>Solvent in anhydrous ethanol (wt%)</td>
<td>No contamination with solvent</td>
<td></td>
</tr>
</tbody>
</table>
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 (different pressures), increasing some times NST
DOUBLE EFFECT DISTILLATION

• Integrating Condenser and Reboiler
• Operating with 2 levels of pressure
• Vacuum (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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Distillation process</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conventional</td>
</tr>
<tr>
<td>2.5bar steam consumption – column A</td>
<td>1.53</td>
</tr>
<tr>
<td>2.5bar steam consumption – column B</td>
<td>0.27</td>
</tr>
<tr>
<td>6bar steam consumption – extractive column</td>
<td>0.35</td>
</tr>
<tr>
<td>6bar steam consumption – recovery column</td>
<td>0.07</td>
</tr>
<tr>
<td>Total steam consumption</td>
<td>2.21</td>
</tr>
</tbody>
</table>

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

HYDROUS BIOETHANOL
93 wt%

SUPERHEATER

RECTIFYING COLUMN
(CONVENTIONAL)

99.5 wt%

ANHYDROUS BIOETHANOL

VACUUM CONDENSER

ZEOLITES – 3 Å
ETHANOL – 4.4 Å
WATER – 2.8 Å

Professor Maria Regina Wolf Maciel, 10/09/2009
Disadvantages:

- High investment cost
- Zeolites are imported
- High vacuum 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 nonequilibrium 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 millions 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

<table>
<thead>
<tr>
<th>Tecnologia Empregada</th>
<th>Consumo de vapor Kg/m³ de AEHC</th>
<th>Consumo de Energia Elétrica KWh/m³ de AEAC</th>
<th>Energia primaria total Kcal/m³ de AEAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Destil com cicloexano convencional</td>
<td>1750</td>
<td>-</td>
<td>1272,5</td>
</tr>
<tr>
<td>Destil com cicloexano otimizada</td>
<td>1450</td>
<td>-</td>
<td>1062,5</td>
</tr>
<tr>
<td>Destil. com cicloexano a 3 efeitos</td>
<td>580</td>
<td>23</td>
<td>435,5</td>
</tr>
<tr>
<td>Absorção com MEG</td>
<td>750</td>
<td>15</td>
<td>572,5</td>
</tr>
<tr>
<td>Pervaporação</td>
<td>110</td>
<td>34,5</td>
<td>124,5</td>
</tr>
<tr>
<td>Peneiras moleculares</td>
<td>550</td>
<td>19</td>
<td>432,5</td>
</tr>
</tbody>
</table>

**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

IL + H₂O

Ethanol (99.8%)

H₂O

H₂O + Air

Air

IL + H₂O

IL
• 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

Chemical Formula: C₃H₈O₃
Molecular Weight: 92,09
### Summary of dehydration technologies of extractive distillation with different agents

<table>
<thead>
<tr>
<th>Technologies</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extractive distillation with liquid solvent</td>
<td>Less energy consumption than azeotropic distillation because of the high boiling point of the added solvent; flexible selection of the possible solvents.</td>
<td>Very high solvent/feed mass ratio, up to 5–8, leading to much consumption of energy.</td>
</tr>
<tr>
<td>Extractive distillation with dissolved salt</td>
<td>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.</td>
<td>Potential problems in dissolution, transport and recycle of salt; potential jam and erosion to equipment.</td>
</tr>
<tr>
<td>Extractive distillation with the mixture of liquid extractant and dissolved salt</td>
<td>Integrates the advantages of both liquid solvent (easy operation) and dissolved salt (high separation ability).</td>
<td>Less availability of suitable salts; potential corrosion of salts to the equipment; possible contaminant of the overhead product by liquid extractants.</td>
</tr>
<tr>
<td>Extractive distillation with ionic liquid (IL)</td>
<td>(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.</td>
<td>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.</td>
</tr>
<tr>
<td>Extractive distillation with hyperbranched polymers</td>
<td>(1) Excellent separation efficiency and selectivity; (2) entrainers can not contaminate the top product.</td>
<td></td>
</tr>
</tbody>
</table>
Table 4: Input data, simulation results and specific parameters for a new distillation column with [mmim][DMP]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Input data</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed flow rate</td>
<td>kmol/h</td>
<td>100</td>
</tr>
<tr>
<td>Ionic liquid feed flow rate</td>
<td>kmol/h</td>
<td>1.5</td>
</tr>
<tr>
<td>Feed ethanol composition</td>
<td>molar %</td>
<td>11</td>
</tr>
<tr>
<td>Feed water composition</td>
<td>molar %</td>
<td>89</td>
</tr>
<tr>
<td><strong>Specified design and operating parameters</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Theoretical stage number</td>
<td>-</td>
<td>28</td>
</tr>
<tr>
<td>Operating pressure</td>
<td>atm</td>
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<tr>
<td>Distillate flow rate</td>
<td>kmol/h</td>
<td>11</td>
</tr>
<tr>
<td>Reflux ratio</td>
<td>-</td>
<td>1.8</td>
</tr>
<tr>
<td>Feed stage number</td>
<td>-</td>
<td>21</td>
</tr>
<tr>
<td>Ionic liquid feed stage number</td>
<td>-</td>
<td>4</td>
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<tr>
<td><strong>Simulation results for distillate and reboiler</strong></td>
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<tr>
<td>Ethanol flow rate</td>
<td>kmol/h</td>
<td>10.95</td>
</tr>
<tr>
<td>Water flow rate</td>
<td>kmol/h</td>
<td>0.05</td>
</tr>
<tr>
<td>Ethanol weight fraction</td>
<td>%</td>
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<td>Water weight fraction</td>
<td>%</td>
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<tr>
<td>Reboiler duty (298 K, feed temperature)</td>
<td>kJ/kg ethanol</td>
<td>3080.1</td>
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<tr>
<td>Reboiler duty (358 K, feed temperature)</td>
<td>kJ/kg ethanol</td>
<td>3078.3</td>
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</tbody>
</table>
DIVIDED WALL DISTILLATION COLUMN

More than 2 pure products

The wall is introduced in part of the column

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CONVENTIONAL SEQUENCE
MAXIMUM OF B

WHY TO MIXTURE IT AGAIN???
WALL DIVIDED VS. CONVENTIONAL

CARACTERÍSTICAS OPERACIONAIS

• Costs: Reduction of 30% in investments and of 25% in utilities

Flow rates of liquid and vapor do not cross sections

EmpresaMontz (Alemanha)

Fabricante

Coluna dividida
PARA DISTILLATION

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

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Paradistillation

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• COLUMN CORRESPOND TO

• 25% SMALLER PRESSURE DROP
• 30% SMALLER
• GOOD FOR LOW PRESSURE
META DISTILLATION

• HIGHER EFFICIENCY

• LIQUID IS DIVIDED.

• SMALLER NST THAN PARADISTILLATION
• SMALLER DIAMETER - 8%

• ADVANTAGE FOR HIGH LIQUID FLOW RATE
Coluna HIGEE (High Integrated Gravitational)

- Ramshaw e Mallinson, 1981: Rotating Packed Column – centrifugal 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.

Valve: pressure decreases toward stripping section

- Pressure difference between sections.
- Inclusion of compressor and valves for the operation of the system.
CONCENTRIC CONFIGURATION OF HIDIC

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

Mass and Heat Transfer Stage $n$

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

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

$Q_{sec} = \text{Heat section} = f(A,U,\Delta T)$
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.

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
DYNAMIC PROFILES AFTER INCREASING REBOILER DUTY

(b)
DYNAMIC PROFILES AFTER DECREASING REBOILER DUTY
CARACTERISTICS

• NST = 11 EQUILIBRIUM

• NST = 21 NONEQUILIBRIUM

• TIME = 13 HIGHER
Fração molar na fase vapor

Tempo (min)

Equilíbrio

Não equilíbrio

n-pentano

n-hexano

n-heptano
ETANOL + WATER + ETHYLENEGLICOL

![Graph showing the molar flow rate in the vapor phase over time with equilibrium and nonequilibrium lines.](image-url)

- **Equilíbrio**
- **Não Equilíbrio**

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CORRELATION OF BARROS & WOLF FOR EFFICIENCY OF STAGES AND COMPONENTS

• DISTILLATION COLUMNS: FROM SIMPLE TO COMPLEX
PLATE EFFICIENCY

- Dependent on mixture properties

\[
Ef(i) = 38.5309 \times \left[ \frac{klm(i)}{cplm(i)} \times \frac{dlm(i) \times diflm(i) \times pmm(i)}{nlm(i)} \right]^{-0.04516}
\]

- Molecular weight (pmm)
- Thermal conductivity (klm)
- Heat capacity (cplm)
- Viscosity (mlm)
- Density (dlm)
- Diffusivity (diflm)
COMPONENT EFFICIENCY

\[ \text{Eff}(i, j) = 38.5309 \times \left[ \frac{kll(i, j)}{cpll(i, j)} \times \frac{dll(i, j) \times difl(i, j) \times pm(j)}{nll(i, j)} \right]^{-0.04516} \]

PURE COMPONENT PARAMETERS

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EFICIÊNCIA DO PRATO

EFICIÊNCIA DE COMPONENTES

n-HEXANO

n-OCTANO

n-PENTANO

NÚMERO DE ESTÁGIOS NA COLUNA (NST)

EFICIÊNCIA (%)
ESPECIFICAÇÃO: Destilado e XD=0.98

ESPECIFICAÇÃO: Destilado e RR=2.0

EFICIÊNCIA (%)

NÚMERO DE ESTÁGIOS NA COLUNA (NST)

FUNDO

TOPO

NÚMERO DE ESTÁGIOS NA COLUNA (NST)
ESPECIFICAÇÃO: Destilado e XD=0.99

ESPECIFICAÇÃO: Destilado e RR=2.0

EFICIÊNCIA (%)

NÚMERO DE ESTÁGIOS NA COLUNA (NST)

FUNDO

TOPO

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**EFICIÊNCIA DO PRATO**

**EFICIÊNCIA DE COMPONENTES**

- **n-PENTANO**
- **n-HEPTANO**
- **n-OCTANO**
- **n-HEXANO**

**NÚMERO DE ESTÁGIOS NA COLUNA (NST)**

<table>
<thead>
<tr>
<th>EFICIÊNCIA (%)</th>
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<tr>
<td>70.00</td>
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Frações molares no seio da fase vapor (y)

Número de estágios na coluna (NST)

Modelagem de não equilíbrio

Correlação de Barros & Wolf

n-Pentano

n-Hexano

n-Heptano

Octano

Fundo

Topo

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MODELAGEM DE NÃO EQUILÍBRIO

CORRELAÇÃO DE BARROS & WOLF

TEMPERATURA (K)

FUNDO

TOPO

NÚMERO DE ESTÁGIOS NA COLUNA (NST)

300.00
310.00
320.00
330.00
340.00
350.00
360.00
370.00
380.00
Nota de Correção

NÚMERO DE ESTÁGIOS NA COLUNA (NST)

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
EXTRACTIVE DISTILLATION EFFICIENCY

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

\[ Eff(i, j) = 19.37272 \left( \frac{kll(i, j)}{cpll(i, j)} * \frac{dll(i, j) * difl(i, j, k) * pm(j)}{mll(i, j)^2} \right)^{-0.109588} \]
CORRELAÇÃO DE BARROS & WOLF
MODELagem DE NÂO EQUILÍBRIO

NÚmero de estágios na coluna (NST)

Frações mólares no seio da fase líquida (x)

Funddo

Fundo Topo

Etanol

Etílenoglicol

Água
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TEMPERATURA (K)

NÚMERO DE ESTÁGIOS NA COLUNA (NST)

- MODELAGEM DE NÃO EQUILÍBRIO
- CORRELAÇÃO DE BARROS & WOLF

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FLUXOS MOLARES DE LÍQUIDO E VAPOR (mol/h)

MODELAGEM DE NÃO EQUILÍBRIO
CORRELAÇÃO DE BARROS & WOLF

NÚMERO DE ESTÁGIOS NA COLUNA (NST)

LÍQUIDO
VAPOR

FUNDO TOPO

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COMPLEX COLUMNS

• SIDE STREAMS – LIQUID AND VAPOR PHASES
COMPARAÇÃO NÃO EQUILÍBRIO

ESPECIFICAÇÃO: Destilado=100 mol/h e RR=1.5

MODELAGEM DE NÃO EQUILÍBRIO
CORRELAÇÃO DE BARROS & WOLF
CORRELAÇÃO DE O’CONNELL MODIFICADA

n-PENTANO
n-HEXANO
n-HEPTANO
n-OCTANO

FRAÇÕES MOLARES NO LÍQUIDO (X)

NÚMERO DO ESTÁGIO NA COLUNA (NST)
THANKS

• MARINA DIAS
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• JAIVER
• JEFREY
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