Zero Spent Wash Discharge Technologies

8th October, 2015
Mahesh Kulkarni,
Praj Industries Limited, Pune
In Focus

- Options for Zero Spent Wash Discharge Technology
  - Raw Spent Wash
  - Biomethanated Spent Wash
  - Recycle, Reuse Technologies

- Value Maximization- Zero Spent Wash Discharge Technologies
Sustainability Drivers

- Stringent Pollution control Norms
- Rising Energy & Water Cost
- Volatility in Feedstock & Ethanol Prices
- Policy Uncertainty
Sustainability Demands.....

- Reduce effluent generation at source itself
- Recover energy, recycle and reuse the water
- Integrate the effluent treatment systems with main process plant
Sugar Factory Streams - Value Maximization

Cane → 1st mill

- Primary Juice

RVF

- Press Mud

Muddy Juice → Clarification

- Filtrate Juice

Bagaase → 2nd / 3rd / 4th / 5th mill

- Mixed Juice

- Secondary Juice

Evaporation

- Syrup

Crystallization

1st/2nd / 3rd / 4th Centrifuge

- B- Molasses

- C- Molasses

Bagasse → Power

Water Recovery?

Sugar → Packaging

Composting/power generation
## Typical Sugar Juice Stream Composition

<table>
<thead>
<tr>
<th>Stream</th>
<th>Primary Juice</th>
<th>Secondary Juice</th>
<th>Mixed Juice</th>
<th>Filtrate Juice</th>
</tr>
</thead>
<tbody>
<tr>
<td>% w/w on Cane</td>
<td>55</td>
<td>45</td>
<td>100</td>
<td>15</td>
</tr>
<tr>
<td>% Pol</td>
<td>14 - 16</td>
<td>6 - 9</td>
<td>10 - 12</td>
<td>8 - 10</td>
</tr>
<tr>
<td>°Brix</td>
<td>18 - 20</td>
<td>8 - 11</td>
<td>14 - 16</td>
<td>15 - 16</td>
</tr>
<tr>
<td>FS</td>
<td>15.5 - 17.5</td>
<td>7 - 10</td>
<td>11 - 13</td>
<td>9 - 11</td>
</tr>
</tbody>
</table>
## Typical Properties of Concentrated Streams

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Syrup</th>
<th>Molasses- B</th>
<th>Molasses- C</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDS (%w/w)</td>
<td>45-50</td>
<td>73.42</td>
<td>73-76</td>
</tr>
<tr>
<td>FS (%w/w)</td>
<td>40-45</td>
<td>50-60</td>
<td>45-50</td>
</tr>
<tr>
<td>TSS (%w/w)</td>
<td>0.2-0.5</td>
<td>1.0-1.5</td>
<td>2.0-3.0</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.19</td>
<td>1.39</td>
<td>1.39</td>
</tr>
<tr>
<td>Volatile Acidity (ppm)</td>
<td>1000-1500</td>
<td>1500-2000</td>
<td>3000-5000</td>
</tr>
</tbody>
</table>
Distillery Effluent Streams

- **Main effluent stream**
  - Spent wash / Vinasse for Molasses feedstock

- **Other dilute streams**
  - Spent Lees
  - Process Condensate
  - CIP washing effluents
  - Floor washing
  - Cooling tower Blow down
### Why Spent Wash or Vinasse is Challenge?

#### Organic Residual Sugar:

- **Carbohydrates, polymers, starch, gums**
- **Nitrogenous: proteins**
- **Waxes**
- **Vitamins**

#### Organic Solids:

- **Organic acids:**
  - Acetic
  - Butyric
  - Propionic
  - Valeric
- **Colouring substances**

#### Inorganic Solids:

- **Cations:**
  - Calcium
  - Potassium
  - Sodium
  - Magnesium
  - Silica
  - Iron
  - Manganese
- **Anions:**
  - Sulfates
  - Carbonates
  - Phosphates
  - Chlorides
  - Nitrates
  - Oxides
## Distillery Spent Wash Characteristics

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Sugar Cane Molasses</th>
<th>Sugar Cane/SS Juice</th>
<th>Sugar Cane/SS Syrup</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wastewater Generation, L/L of AA</td>
<td>11.0 – 13.0</td>
<td>11.0 – 13.0</td>
<td>2.5 – 3.5</td>
</tr>
<tr>
<td>pH</td>
<td>3.5 – 4.5</td>
<td>3.5 – 4.5</td>
<td>3.5 – 4.5</td>
</tr>
<tr>
<td>COD, mg/L</td>
<td>110000-130000</td>
<td>25000 – 35000</td>
<td>100000-130000</td>
</tr>
<tr>
<td>BOD, mg/L</td>
<td>40000 – 55000</td>
<td>15000 – 18000</td>
<td>55000 – 65000</td>
</tr>
<tr>
<td>BOD/COD ratio</td>
<td>0.35 – 0.45</td>
<td>0.50 – 0.60</td>
<td>0.50 – 0.60</td>
</tr>
<tr>
<td>TS, % w/w</td>
<td>11.0 – 13.0</td>
<td>2.0 – 2.5</td>
<td>8.0 – 10.0</td>
</tr>
<tr>
<td>TVS, % w/w</td>
<td>7.5 – 9.0</td>
<td>1.5 – 2.0</td>
<td>6.5 – 8.0</td>
</tr>
<tr>
<td>TVS/TS, % w/w</td>
<td>0.65 – 0.75</td>
<td>0.80 – 0.85</td>
<td>0.80 – 0.85</td>
</tr>
</tbody>
</table>
## Distillery Spent Wash Characteristics

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Vinsasse</th>
<th>Sugar Cane Molasses</th>
<th>Sugar Cane/SS Juice</th>
<th>Sugar Cane/SS Syrup</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Kjeldhal Nitrogen, mg/L</td>
<td>3000 - 3500</td>
<td>1000 - 1500</td>
<td>4000 - 5000</td>
<td></td>
</tr>
<tr>
<td>Phosphorous, mg/L</td>
<td>100 - 200</td>
<td>50 - 100</td>
<td>700 - 1500</td>
<td></td>
</tr>
<tr>
<td>Potassium, mg/L</td>
<td>8000 - 12000</td>
<td>2000 - 3000</td>
<td>6000 - 7000</td>
<td></td>
</tr>
<tr>
<td>Sulphates, mg/L</td>
<td>4000 - 5000</td>
<td>1000 - 1500</td>
<td>3000 - 4000</td>
<td></td>
</tr>
<tr>
<td>Ratio of COD to Sulphates</td>
<td>27</td>
<td>20</td>
<td>34</td>
<td></td>
</tr>
</tbody>
</table>
Zero Process Discharge—Need of the Hour . . .

- Zero Spent Wash Discharge Technology
- Maximum Usable Water Recovery
- High Steam Economy
- Reliability
- Lower Down time
- Low Capex
Combinations of treatment methods can be used in accordance with local norms and economics.
ZSD - Raw Spent Wash Evaporation + Incineration Boiler
Combinations of treatment methods can be used in accordance with local norms and economics
ECOVAP™-Raw Spent Wash Evaporation Technology

FEED → E-1 → CP-1 → TP-1

STEAM → E-2 → CP-2 → TP-2

E-3 → CP-3 → TP-3

E-4 → CP-4 → TP-4

CONDENSER

CW → VACUUM PUMP

FINISHER → PRODUCT

ECOVAP™ - Raw Spent Wash Evaporation Technology
Zero Process Discharge for Molasses Based Distillery - Vinasse Boiler
Why Vinasse Boiler?

1. CPCB approved method for distillery spent wash in all new distilleries in India as ZPD requirement.

2. Rapid destruction of polluting organic material to small volume of sterile ash

3. Suitable for sites with constraint on land
1. COAL (local/imported Indonesia/S. Africa) (low moisture)
2. RICE HUSK (silica ash is abrasive)
3. BAGASSE (low ash, but high moisture)

Auxiliary fuel required for startups, shutdowns, and in normal operation to partially counter clinkering tendency due to low melting point of Potassium salts.

All auxiliary fuels stored under covered shed. Availability during full year to be checked.
## Vinasse Boiler - Ash Characteristics

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>COAL</th>
<th>SPENT WASH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>19.63</td>
<td>0.34</td>
</tr>
<tr>
<td>CaO</td>
<td>2.65</td>
<td>9.74</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5.80</td>
<td>0.6</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.98</td>
<td>35.55</td>
</tr>
<tr>
<td>MgO</td>
<td>1.11</td>
<td>12.73</td>
</tr>
<tr>
<td>MnO</td>
<td>0.11</td>
<td>0.02</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.47</td>
<td>6.08</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.10</td>
<td>1.68</td>
</tr>
<tr>
<td>SiO₂</td>
<td>60.70</td>
<td>0.32</td>
</tr>
<tr>
<td>SO₃</td>
<td>1.44</td>
<td>8.58</td>
</tr>
<tr>
<td>TiO₂</td>
<td>2.48</td>
<td>0.02</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.18</td>
<td>0.01</td>
</tr>
<tr>
<td>Cl</td>
<td>0.08</td>
<td>5.32</td>
</tr>
</tbody>
</table>

*Note: E I D Parry Ltd., sample*
ECOPHOTOx-Photochemical Oxidation Technology

**Complex Organic Compounds** → **Intermediates** → **CO₂ + H₂O**

- **RSW Evap. Condensate + Spent Lees** → **Filtration Unit (Sand Filtration)** → **Activated Carbon Filter** → **Treated Water**
- **Filtration Unit (Micron Filtration)** → **UV Activation Oxidant**

**UV Activation Oxidant**

- **Intermediate**
- **ECOPHOTOx Unit**
Benefits of ECOPHOTOx

- Modular skid mounted system - Occupies lesser floor space
- No secondary sludge generation - Reduced disposal load
- Easy to start and stop - Can start & stop whenever feed is available
- Capacity augmentation is simple.
- Treat COD & Toxic chemicals.
Biomethanation based Integrated Zero Spent Wash Discharge Technology
Biomethanation

Degradation of organic matter by anaerobic bacteria in absence of $O_2$, yielding valuable biogas.
Biomethanation-A anaerobic Reaction

Complex organic material
(proteins, polysaccharides, etc.)

Mono and oligomers
(amino acids, sugar, peptides, etc.)

Intermediary products
(alcohols, fatty acids, lactic acids, etc.)

H$_2$+CO$_2$

Acetic acid

H$_2$+CO$_2$

CH$_4$+CO$_2$

Hydrogenotrophic methanogenesis

Acetotrophic methanogenesis

Anaerobic oxidation

Fermentation

Hydrolysis
Combinations of treatment methods can be used in accordance with local norms and economics
<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Parameter</th>
<th>Unit</th>
<th>BMSW</th>
<th>BMSW RO Reject</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TS % w/w</td>
<td>w/w</td>
<td>3 - 7 %</td>
<td>6 - 14%</td>
</tr>
<tr>
<td>2</td>
<td>pH</td>
<td>-</td>
<td>6.8 - 8</td>
<td>7 - 8</td>
</tr>
<tr>
<td>3</td>
<td>Alkalinity</td>
<td>mg/L</td>
<td>8000-17000</td>
<td>15000-22000</td>
</tr>
<tr>
<td>4</td>
<td>NH$_3$-N</td>
<td>Mg/L</td>
<td>1500-2000</td>
<td>3000-4000</td>
</tr>
<tr>
<td>5</td>
<td>Calcium</td>
<td>mg/L</td>
<td>300-1000</td>
<td>600-2000</td>
</tr>
<tr>
<td>6</td>
<td>Potassium</td>
<td>mg/L</td>
<td>5000-10000</td>
<td>8000-20000</td>
</tr>
<tr>
<td>7</td>
<td>Sulphate</td>
<td>mg/L</td>
<td>1500-3000</td>
<td>3000-6000</td>
</tr>
<tr>
<td>8</td>
<td>Chlorides</td>
<td>mg/L</td>
<td>5000-10000</td>
<td>8000-15000</td>
</tr>
<tr>
<td>9</td>
<td>Phosphates</td>
<td>mg/L</td>
<td>100-120</td>
<td>150-200</td>
</tr>
<tr>
<td>10</td>
<td>Ash</td>
<td>w/w</td>
<td>1-2%</td>
<td>2-4%</td>
</tr>
</tbody>
</table>

Note: Above mentioned ranges are avg. values. Actual may vary depending on plant performance.

BMSW RO reject concentration will be ~ 2 times the BMSW feed.
Typical Biomethanated Spent Wash Composition

<table>
<thead>
<tr>
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<th>Parameter</th>
<th>Unit</th>
<th>BMSW</th>
</tr>
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<td>TS % w/w</td>
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<td>2</td>
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<td>-</td>
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</tr>
<tr>
<td>3</td>
<td>Alkalinity</td>
<td>mg/L</td>
<td>8000-17000</td>
</tr>
<tr>
<td>4</td>
<td>NH₃-N</td>
<td>Mg/L</td>
<td>1500-2000</td>
</tr>
<tr>
<td>5</td>
<td>Calcium</td>
<td>mg/L</td>
<td>300-1000</td>
</tr>
<tr>
<td>6</td>
<td>Potassium</td>
<td>mg/L</td>
<td>5000-10000</td>
</tr>
<tr>
<td>7</td>
<td>Sulphate</td>
<td>mg/L</td>
<td>1500-3000</td>
</tr>
<tr>
<td>8</td>
<td>Chlorides</td>
<td>mg/L</td>
<td>5000-10000</td>
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<tr>
<td>9</td>
<td>Phosphates</td>
<td>mg/L</td>
<td>100-120</td>
</tr>
<tr>
<td>10</td>
<td>Ash</td>
<td>w/w</td>
<td>1-2%</td>
</tr>
</tbody>
</table>

Note: Above mentioned ranges are avg. values actual may vary depending on plant performance.
Challenges of BMSW Concentration

- Foaming
- Scaling and fouling
- Dissolved gases
- Viscosity at higher concentration
- Higher inorganic salts
BMSW Concentration - The Complete Solution

Pretreatment

- Objective
  1. Remove Dissolved Gases
  2. Reduce Scaling

Concentration

- Objective
  1. Concentration
  2. Less Contaminated Condensate

Condensate Treatment

- Objective
  1. Remove Ammonia
  2. Remove Hydrogen Sulfide
EcoVap™ BMSW- BMSW Evaporation Technology

BMSW Pretreatment - Steps

- **Flashing** – Remove non-bound gases
- **Stripping** – Remove thermally unstable bound gas forming compounds and reduce alkalinity.
- **Acidification** – Increase the solubility of dissolved bicarbonate and stabilize the residual heat sensitive compounds.
BMSW Evaporation

- Multiple Effect Evaporator with or without TVR.
- Flow scheme may be forward feed / Backward feed or mixed feed depending upon process requirement.
- Maximum number of effects up to 7 from stand alone and up to 3 for integrated BMSW evaporation (On Analyzer Vapors)
- Operational Philosophy will be 20 hr working and 4 hr CIP.

Design Parameters*

- 1\textsuperscript{st} Effect Boiling Temperature: 80-90 Deg. C
- 1\textsuperscript{st} Effect Jacket Temperature: 95-100 Deg. C
- Last Effect Boiling Temperature: 50-55 Deg. C
Ecofine CST™-BMSW Condensate Treatment Technology

Stripped BSW Condensate to ETP

BSW Sour condensate stripper

Heat recovery PHE

Reboiler

Steam @ 3.5 bar a & 140 °C

Vapour:

\[ \text{pp} \quad \downarrow \quad \text{NH}_3 \quad \downarrow \quad \text{NH}_3 \quad \uparrow \quad \text{pp} \quad \text{H}_2\text{S} \quad \uparrow \quad \text{H}_2\text{S} \]

Solution: \( \text{NH}_4^+ \quad + \quad \text{HS}^- \quad \leftrightarrow \quad \text{NH}_3 \quad + \quad \text{H}_2\text{S} \)

pp: partial pressure
BMSW Condensate Recycle

• 80 - 90% water is recovered as BMSW evaporation process condensate.

• BMSW process condensate can be recycled back to process or utilities application like cooling tower makeup etc.

• It will reduce the distillery water consumption by 6 - 8 lit / lit of Ethanol.
BMSW Evaporation - Key highlights

- No Cooling water requirement (with Adiabatic Evaporation)
- Simultaneous evaporative degassing system
- Less Foaming in evaporation system
- Less Scaling and fouling due preconditioned feed
- Clean water recovery for recycle and reuse
- Less operating cost
- Higher Plant availability
- Less Plant Downtime
- High reliability
Integrated BMSW ZLD Technology

- Reduction in distillation steam consumption from 3.2 kg/lit to 2.8 kg/lit
- 100% Recycle of Process condensate for process and Utility application
- BMSW Volume reduction by 75-80%
Dryers- Current Availability in market

- Spray Dryer
- Rotary Dryer
- Agitated Thin Film Dryer
# BMSW Dryer - Limitation of Spray and Rotary Dryer

<table>
<thead>
<tr>
<th>Spray Dryer</th>
<th>Rotary Dryer (Comparison against ATFD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Capital and Overhead Cost</td>
<td>Higher investment</td>
</tr>
<tr>
<td>Maintenance Issue</td>
<td>Higher power consumption</td>
</tr>
<tr>
<td>High Energy loss along with hot air</td>
<td>Higher steam consumption</td>
</tr>
<tr>
<td>Fuel like FO or LDO is required which create pollution</td>
<td>Energy recovery not possible</td>
</tr>
<tr>
<td>Integration / Energy Recovery is not possible</td>
<td>Higher foot print</td>
</tr>
<tr>
<td>Quality of product (Dried BMSW)</td>
<td>Higher HTA required for same duty</td>
</tr>
<tr>
<td>Frequent chocking of the Spray Dryer</td>
<td>Higher heat loss</td>
</tr>
<tr>
<td></td>
<td>Steam requirement is about 1.45 time of water evaporation</td>
</tr>
<tr>
<td></td>
<td>Open process: dusty atmosphere</td>
</tr>
</tbody>
</table>
### Advantage - PRAJ’s BMSW Drying Technology

- Low investment (low fix cost)
- Low power requirement
- Lower steam requirement
- Energy recovery is possible through Vapor Integration
- Lower foot print
- Much lesser HTA required for given duty
- Lower heat loss
- Steam requirement is about 1.1 to 1.2 time of water evaporation
- Easy Start-up and Shut down
- Enclosed process: Cleaner surroundings
Value Maximization - Praj’s Zero Process Discharge Technologies
## Composition of BioManure

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Total Solids</td>
<td>% w/w</td>
<td>97.55</td>
</tr>
<tr>
<td>2 Ash</td>
<td>% w/w</td>
<td>47.58</td>
</tr>
<tr>
<td>3 Kjeldahl Nitrogen</td>
<td>% w/w</td>
<td>3.76</td>
</tr>
<tr>
<td>4 Phosphorus</td>
<td>% w/w</td>
<td>1.7</td>
</tr>
<tr>
<td>5 Phosphorus as P2O5</td>
<td>% w/w</td>
<td>3.89</td>
</tr>
<tr>
<td>6 Potassium</td>
<td>% w/w</td>
<td>10.9</td>
</tr>
<tr>
<td>7 Potassium as K2O</td>
<td>% w/w</td>
<td>13.13</td>
</tr>
<tr>
<td>8 Magnesium</td>
<td>% w/w</td>
<td>2.58</td>
</tr>
<tr>
<td>9 Calcium</td>
<td>% w/w</td>
<td>2.17</td>
</tr>
<tr>
<td>10 Sulfur</td>
<td>% w/w</td>
<td>3.39</td>
</tr>
<tr>
<td>11 Sodium</td>
<td>% w/w</td>
<td>0.37</td>
</tr>
<tr>
<td>12 Zinc</td>
<td>ppm</td>
<td>54</td>
</tr>
<tr>
<td>13 Iron</td>
<td>ppm</td>
<td>692</td>
</tr>
<tr>
<td>14 Manganese</td>
<td>ppm</td>
<td>46</td>
</tr>
<tr>
<td>15 Copper</td>
<td>ppm</td>
<td>100</td>
</tr>
<tr>
<td>16 Calorific Value</td>
<td>Kcal/kg</td>
<td>1800-2400</td>
</tr>
</tbody>
</table>
Value Added Co-products-EcoClean™ Technologies

- **Bio-methanation**
  - H₂S Scrubbing
  - CO₂ Scrubbing

- **Boiler**
  - Steam / Power

- **Gas Engine**
  - Power

- **Compressor**
  - BioCNG
# Ecoclean™ Technologies-Biogas Quality

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Biogas quality for Boiler application</th>
<th>Biogas quality for Power</th>
<th>Biogas quality for BioCNG</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>60 - 65 %</td>
<td>60 - 65%</td>
<td>92-95 %</td>
</tr>
<tr>
<td>CO₂</td>
<td>30 - 35 %</td>
<td>30 - 35 %</td>
<td>2-8%</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.1 - 3.0 %</td>
<td>&lt; 200ppm</td>
<td>&lt; 20ppm</td>
</tr>
<tr>
<td>Moisture</td>
<td>&lt;1 %</td>
<td>RH&lt;80</td>
<td>&lt;-40° C DP</td>
</tr>
</tbody>
</table>

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Process Water-Distillery Sustainability

- 80 - 90% water is recovered as RSW/BMSW evaporation process condensate.
- Water suitable for fermentation and Utility (Cooling Tower)
- It will reduce the distillery water consumption by 6 - 8 lit / lit of Ethanol.
Integrated distillery for value added products

- High Gravity Fermentation
- Treatment
- Bio-Distillation & Dehydration
- Biomethanation
- Evaporation
- Bio-Composting/BMSW Dryer
- Boiler/Turbine
- Power/BioCNG
- Fertilizer

- Ethanol
- Lees
- Condensate
- Steam
- Steam & Electricity
- Biogas

Molasses

20% w/w

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Performance Benchmarking
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Radico NV Distilleries Maharashtra Ltd, Aurangabad

- 1000 TPD BMSW Evaporation plant
- Concentration from 4 % w/w to 19.5 % w/w
- 7 effect falling film type mixed feed evaporation system.
- Feed flow scheme is 7-6-5-4-Stripper – Reactor -1-2-3
- Condensate Stripping and polishing unit for condensate recycle in fermentation and cooling tower.
Performance Benchmarking......

Nava Bharat Ventures Ltd, Samlkota Andrapradesh

- 170 TPD BMSW RO Reject Evaporation plant
- Concentration from 10 % w/w to 17.5 % w/w
- Feed Stripper for feed conditioning is provided.
- Standalone two effect falling film evaporation system.
- Provision of Integration with analyzer column.
Waste water treatment plant to Bio-refinery...

Waste is no more a waste

Power

Bio compost

Steam

BMV Power

Bio CNG

Recover Water

Distillery Waste water

It is valuable Co-product
“Effluent is a problem, if not used at appropriate place with appropriate technology”

“Effluent is useful resource, if used at appropriate place with appropriate technology”