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***Research Article***

# COST ESTIMATION & OPTIMUM ROUTE SELECTION FOR THE PRODUCTION OF ACONITIC ACID

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## ABSTRACT

Among the notable materials found in cane molasses there is, 1, 2, 3-propenetricarboxylic acid better known as aconitic acid. Trans aconitic acid (TAA) is the predominant organic acid in cane leaf matter (CLM) juice. TAA content ranged between 2.1-3.1 kg / t. Several resins, adsorbents & techniques were tested for their potential use in recovery of aconitic acid from a sugarcane liquor prepared by extraction and fermentation of the juice of sugar cane. There are three main techniques for the extraction of Aconitic acid from molasses namely, Precipitation (conventional method), Solvent-extraction, Ion-exchange method. The report is a detailed description of all the three methods. Our work also contains material balance for the ion-exchange method, design of fluidized bed ion exchanger, cost estimation for all the three methods and finally the optimum route selection.

***Key Words:*** *Aconitic, Precipitation, Molasses, Trans Aconitic Acid (TAA) Fermentation*

## INTRODUCTION

Aconitic acid, ($C_6H_6O_6$), MW 174g/gmol, an unsaturated tribasic aliphatic acid exists in two geometric forms, the trans- isomer, TAA, and the cis- isomer. TAA is a white to yellowish crystalline solid, with melting point 195 °C. It is soluble in water and alcohol. Its solubility in water increases from 18.6 g/100 mL at 13 °C to 110.7 g/100 mL at 90°C. In sugarcane juice aconitic acid is present to the extent of 0.1% to 0.2% & its concentration goes on increasing, as the juice is concentrated to syrup stage & finally into molasses, it is present to the extent of 3%-7% on dry basis.

## MATERIALS AND METHODS

### *1.1 Precipitation Method*

Molasses were diluted to 50° Brix by adjusting the solution pH and adding the precipitation agent solution. The calcium hydroxide solution was added to the molasses to raise the pH from 6.2 to 6.8. Salt solutions of calcium chloride were prepared dissolving 7 to 11.5 g of $CaCl_2$ or 5 g of $MgCl_2$ in 120 mL distilled water according to the salt solubility. 250 g of treated molasses were introduced in the reactor and heated at 60 or 90 °C under reflux. Mechanic stirring (300 rpm) was applied during 30 min before adding the salt solution, which is the starting point of the precipitation reaction. After 1 or 7 h, stirring and heating were stopped and the reactor was cooled at room temperature during 1 h. The precipitated molasses were centrifuged 15 min at 5500 G. The tricalcium aconitate solid was washed with 150 mL of deionized water and centrifuged again. Finally, the solid was dried 12 hours at 106 °C. 1 g of the precipitate was dissolved in 30 mL of 25 % sulphuric acid, heated 30 min at 80°C under mechanic stirring, cooled 30 min in fresh water and filtered under vacuum to eliminate $CaSO_4$ solid wastes. Filtration cake was washed with deionized water in order to adjust the filtrate to 50 mL.

First of all, precipitation was tested on model solutions. Once the optimal temperature, pH, $CaCl_2$ quantity and aconitic acid concentration were determined using Doehlert experimental design, experiences on molasses were carried out.

### *1.2 Model solution experiments*

Model solutions containing trans-aconitic acid from 1.5 to 4 % in mass were prepared and the pH was adjusted to 6.3 with a solution of sodium hydroxide at 12 % in mass. 250 g of the model solutions were introduced in a three necks reactor and heated under reflux about 15 min with stirring (300 rpm) from 50 to 90 °C. Salt solutions of calcium chloride were prepared dissolving 0.7 to 14 g of $CaCl_2$ in 1 to 20 mL of distilled water according to the salt solubility. The precipitation started when the salt solution was added to the solution of trans-aconitic acid,

then temperature and stirring were maintained from 1 to 9 hours. At the end, stirring was stopped and the three necks reactor was left one hour at 25 °C in order to finalize the precipitation and decantate the solid. Finally, the solution was filtered under vacuum and the tricalcium aconitate was dried at 50 °C almost two days.

In order to evaluate the reaction yield (Equation 1), concentrations of initial trans-aconitic solution ([AAco]initial) and filtrate ([AAco]filtrate) were determined by HPLC.

*Equation 1:* Yp (%) = (([AAco]initial - [AAco]filtrate)/ [AAco]initial ) x 100

### *1.3 By-product solution experiments*

Molasses were diluted to 50° Brix by adjusting the solution pH and adding the precipitation agent solution. The calcium hydroxide solution was added to the molasses to raise the pH from 6.2 to 6.8. Salt solutions of calcium chloride were prepared dissolving 7 to 11.5 g of $CaCl_2$ or 5 g of $MgCl_2$ in 120mL distilled water according to the salt solubility. 250 g of treated molasses were introduced in the reactor and heated at 60 or 90 °C under reflux. Mechanic stirring (300 rpm) was applied during 30 min before adding the salt solution, which is the starting point of the precipitation reaction. After 1 or 7 h, stirring and heating were stopped and the reactor was cooled at room temperature during 1 h. The precipitated molasses were centrifuged 15 min at 5500 G. The tricalcium aconitate solid was washed with 150 mL of deionized water and centrifuged again. Finally, the solid was dried 12 hours at 106 °C. 1 g of the precipitate was dissolved in 30 mL of 25 % sulphuric acid, heated 30 min at 80°C under mechanic stirring, cooled 30 min in fresh water and filtered under vacuum to eliminate $CaSO_4$ solid wastes. Filtration cake was washed with deionized water in order to adjust the filtrate to 50 mL.

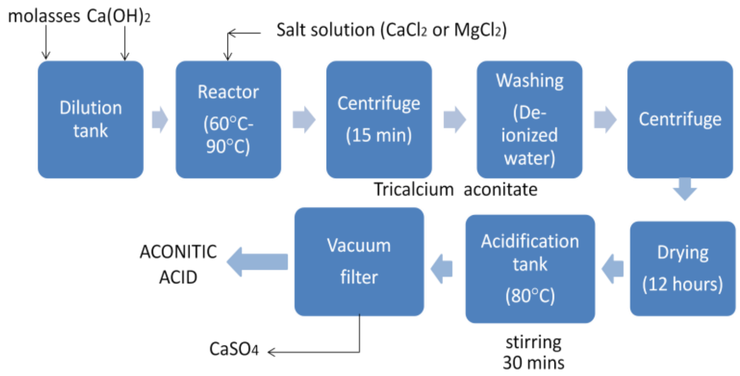

**Figure 2: Flow diagram of Precipitation**

According to the concentration of acids in the filtrate and the initial solutions, solid purity (Equation 2) and precipitation yield (Equation 3) were calculated.

*Equation 2:* P (%) = ([AAco]filtrate x Wfiltrate) / Wprecipitate) x 100

*Equation 3:* Yp (%) = ( ($W_{precipitate}$ total x P) /([AAco]molasses x Wmolasses) ) x 100

AAco]filtrate is the aconitic acid concentration in the filtrate; Wfiltrate is the mass of filtrate; Wprecipitate is the mass of dissolved precipitate; Wprecipitate total is the whole mass of precipitate obtain after precipitation;

[AAco]molasses is the aconitic acid concentration in the molasses and Wmolasses is the mass of molasses introduced initially.

### *1.4 Liquid Extraction or Solvent Extraction*

This separation technique is based on the different distribution of the components to be separated etween liquid phases. In this process, the component to be extracted is transferred from first liquid phase to second one. In the liquid- liquid extraction process, it is common to use the terms feed or aqueous phase for the solution that contains the component to be separated, in this case the fermentation broths called A; the transferred component (the organic acid) called C, and the solvent or organic phase named B which is the liquid used to extract the component C, from the stream feed. The out streams of this process are the extract stream which mainly contains solvent and the solute and raffinate stream which is the liquid remaining from the feed after the solute is removed (Figure 2.4). The component extracted dissolves in the solvent (organic phase) until its concentration in water and organic phase are in equilibrium. Liquid-liquid extraction (LLE) is used in the separation of components with low volatility such as di and tri-carboxylic acids (Muller, 2002). Two additional steps of liquid-liquid extraction are solvent recovery and raffinate cleanup.

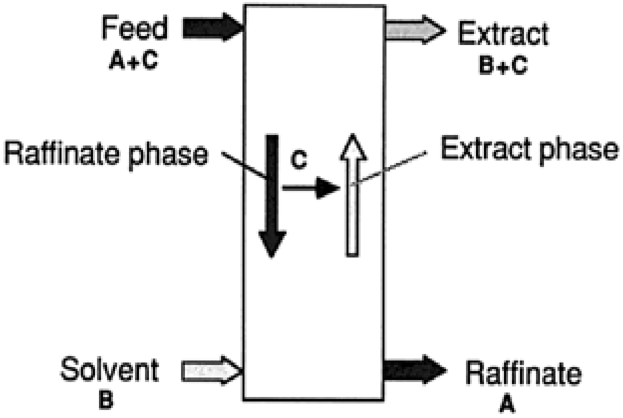

**Figure 3: Schematic representation of Solvent-Extraction**

***Process description***

Molasses is pumped to the dilution & acidification tank, where it is mixed with wash water containing concentrated sulphuric acid. The amount of acid used is equivalent to the ash content of the molasses & the dilution is to attain 60 % solids. A reaction period of 0.5 hour is allowed, after which the molasses solution is pumped to a continuous centrifugal machine to remove calcium sulphate & other insoluble materials. The wash water is for dilution of next batch of molasses. The extractor is a packed tower into which the treated molasses is fed from the top & the 88% Methyl Ethyl ketone-12% water solution as extracting solvent at the bottom.

The raffinate leaves the bottom of the tower & enters a horizontal settling tank, wherein in one hour hold up is allowed, before the molasses is pumped to the neutralization tanks. Lime slurry is added to neutralize the excess Sulphuric acid contained in the molasses, which, after a one hour reaction time, is pumped to a continuous centrifugal machine for removal of calcium sulphate . Then the molasses is discharge into a hold tank, from where it is pumped through a pre heater to a batch vacuum evaporator. The concentrated molasses contain essentially invert sugar & may be used for fermentation to produce Ethyl alcohol or used as animal feed. The solvent vapours in the form of MEK-water azeotrope are condensed in a surface condenser & are pumped to the solvent storage tank.

The extract passes from the top of the extraction tower to a settler, which allows raffinate to settle & also serves as a feed tank to the extract evaporator. The washed solids are dissolved in a decolorizing tank, where carbon is added in the ratio of 1:10 parts of aconitic acid. The carbon slurry is fed to a filter press to remove carbon, as well as all insoluble solids. The clear aconitic acid solution is discharged to a hold tank serving as a feed tank for batch vacuum crystallizer.

From the crystallizer, the mother liquor/ crystals slurry is discharged to a centrifugal to separate the crystals , which are given a water rinse before being discharged for drying.

The overall yield assumed in this process is 90%. The solvent extraction process has certain definite advantages over the precipitation process. It is a direct process.

Disadvantage, when treating silicate containing molasses, which tend to hold the aconitate in the suspension despite centrifuging

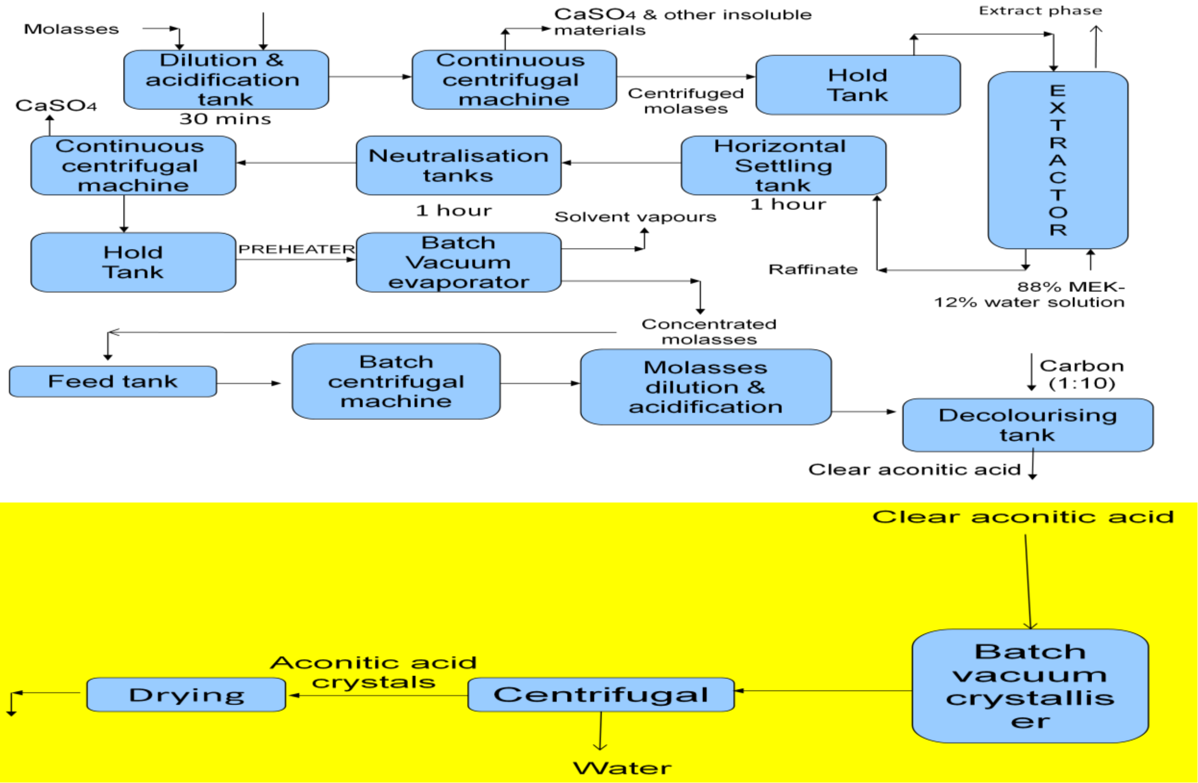

**Figure 4: Flow diagram of Solvent-Extraction**

### *1.5 Ion Exchange Method*

"In ion exchange, ions of a given charge (either cations or anions) in a solution are adsorbed on a solid material (the ion exchanger) and are replaced by equivalent quantities of other ions of the same charge that are released by the solid" . The solids are the ion exchange resin; they may be a salt, acid or base that is insoluble in water but hydrated. Among some of the applications of ion exchange resins are water purification and separation of antibiotics and organic acids from fermentation broths.

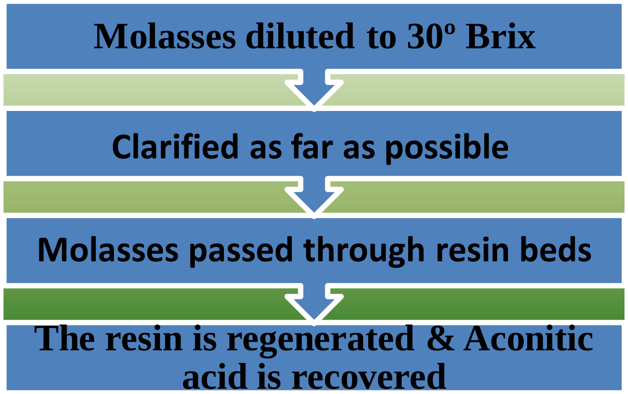

**Figure 5: Schematic representation of Ion-exchange method**

Ion exchangers are made of resins; polymers with 0.5 to 15 % of cross-linking (connections between long carbon chains in a polymer by adding i.e. divinyl benzene). The resin has active groups in the form of electrically charged sites. Ions of opposite charge are attracted but may be replaced by other ions depending on their relative concentrations and affinities for the sites.

Final molasses is diluted to 15° Brix & clarified as far as possible by simple methods. Diluted molasses is then passed through a series of ion-exchange resin beds, previously exhausted with mineral acid. When the resin bed is exhausted to aconitic acid in the diluted molasses, the bed is washed with water until the wash water contains less than 0.1 % of sugar. A fresh portion of mineral acid is then passed over the bed. The bed is thus regenerated & the mineral acid solution containing aconitic acid is concentrated & the crude aconitic acid is crystallized under vacuum. The crude aconitic acid is purified by is purified by recrystallisation. The resin bed is washed free of mineral acid is now ready for treating more fresh molasses. Clarification of molasses avoids the clogging of the resin bed & allows much more molasses to be treated.

After the recovery of aconitic acid from molasses, the molasses has the right density to be used in distillery.

## *2.0 Material Balance*

### *Basis & Assumptions*

Production: 1000 tonnes per year.
Molasses Used: Cuban Blackstrap molasses (85° Brix).
Resin Used : 1. Dowex Marathon MSA (Sulphate form)
2. Permutit SD-102 Eluent used : 10% $H_2SO_4$

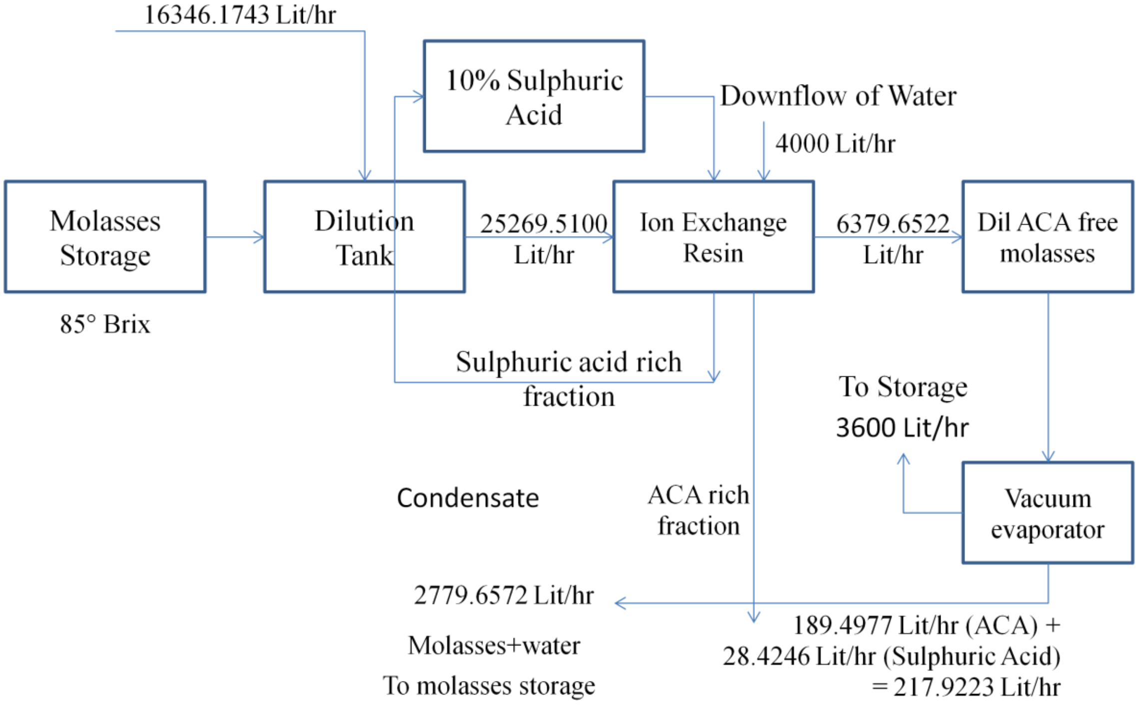

**Figure 6: Mass balance (part 1)**

## *3.0 Cost Estimation*

### *3.1 Basis & Assumptions*

- Production per year- 2000 Tonnes
- 1 $ = Rs 55.03

- General Expenses are same for all the three methods
- x= Cost of installed equipments
- Instrumentation and controls cost = 20 % of x
- Piping cost = 80 % of x
- Electrical Installation Cost = 12 % of x
- Buildings including Service Cost = 20 % of x
- Site Preparation Cost = 10 % of x
- Auxiliaries Cost = 30 % of x
- Land Cost = 4 % of x
- Engineering Cost = 35 % of x
- Contractor’s Fee = 5 % of x
- Contingencies = 10 % of x

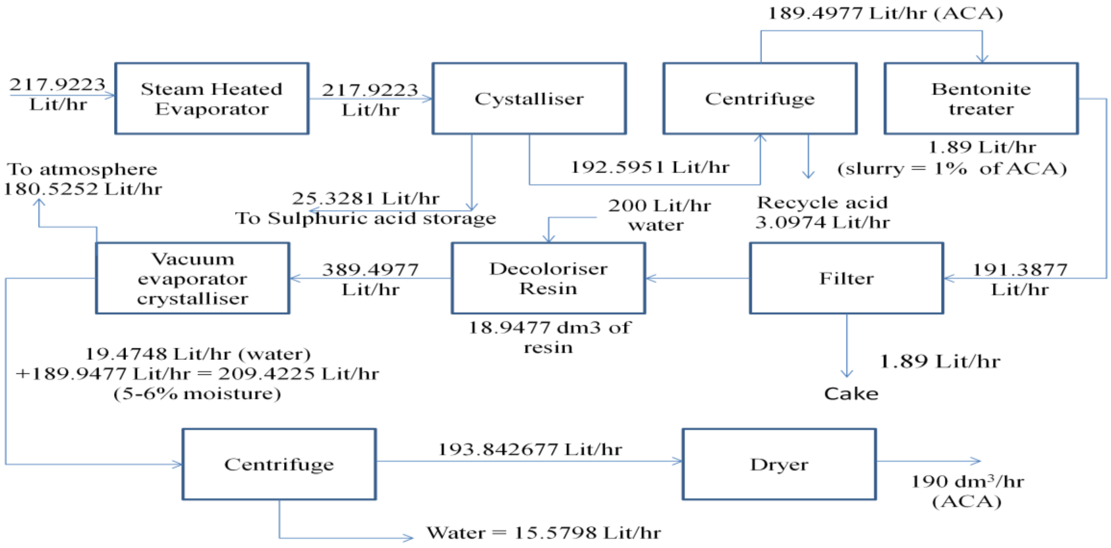

**Figure 7: Mass balance (part 2)**

### *3.2 Utilities per tonne of aconitate for precipitation process*

- Steam-34 tonnes
- Electricity-1440 kWh
- Gas-132 $m^3$
- Water-35600 litres

### *3.3 Approximate cost for production by all three methods*

**Table 1: Approximate cost for production by all three methods**

| Parameters | Precipitation | Solvent Extraction | Ion Exchange |
|---|---|---|---|
| **Manufacturing Cost** | Rs 38,521 | Rs 32,742.85 | Rs 39,346.45 |
| **Cost of installed equipments** | Rs 3,95,11,540 | Rs 3,38,98,480 | Rs 3,79,70,700 |
| **Total Cost of production** | Rs 38,521 + $C_{GEC}$ | Rs 32,742.85 + $C_{GEC}$ | Rs 39,346.45 + $C_{GEC}$ |

### *4. Cost distribution*

### *4.1 For Precipitation*

1. Instrumentation and controls cost = Rs 79,02,308
2. Piping cost Rs 3,16,09,232
3. Electrical Installation Cost = Rs 47,41,384.8
4. Buildings including Service Cost = Rs 79,02,308
5. Site Preparation Cost = Rs 39,51,154
6. Auxiliaries Cost = Rs 1,18,53,462
7. Land Cost = Rs 1580461.6
8. Engineering Cost = Rs 1,38,29,039
9. Contractor's Fee = Rs 19,75,577
10. Contingencies = Rs 39,51,154

### 4.2 For Solvent-Extraction

1. Instrumentation and controls cost = Rs 67,79,696
2. Piping cost = Rs 2,71,18,784
3. Electrical Installation Cost = Rs 40,67,817.6
4. Buildings including Service Cost = Rs 67,79,696
5. Site Preparation Cost = Rs 33,89,848
6. Auxiliaries Cost = Rs 1,01,69,544
7. Land Cost = Rs 13,55,939.2
8. Engineering Cost = Rs 1,18,64,468
9. Contractor's Fee = Rs 16,94,924
10. Contingencies = Rs 33,89,848

### *4.3 For Ion-Exchange*

1. Instrumentation and controls cost = Rs 75,94,140
2. Piping cost = Rs 3,03,76,560
3. Electrical Installation Cost = Rs 45,56,484
4. Buildings including Service Cost = Rs 75,94,140
5. Site Preparation Cost = Rs 3,79,70,700
6. Auxiliaries Cost = Rs 1,13,91,210
7. Land Cost = Rs 15,18,828
8. Engineering Cost = Rs 1,32,89,745
9. Contractor's Fee = Rs 18,98,535
10. Contingencies = Rs 37,97,070

## RESULTS AND DISCUSSION

### *5.1 Optimum Route Selection*

### *5.1.1 Factors Compared*

- Technical Factors
- Raw Materials
- Waste product and By products
- Equipment
- Costs

### *5.1.2 Comparison based on Technical factors*

**Table 2: Resin characteristics**

| Resin Type | Ionic Form | Final Concentration Brix | Color reduction | Aconitate reduction |
|---|---|---|---|---|
| Dowex Marathon SBA type I styrenic macroporous | Chloride | 12.5 | 81 | 37 |
| | Sulphate | 30.0 | 91 | 86 |
| Purolite MN-400 SBA styrenic | Chloride | 10.0 | 95 | 0 |
| | Sulphate | 10.5 | 94 | 8 |
| Tulsion A-30 MP SBA acrylic macroporous | Chloride | 13.3 | 21 | 32 |
| | Sulphate | 12.2 | 40 | 53 |

### *5.1.3 Comparison based on Raw materials*

**Table 3: Comparison based on Raw materials**

| Parameters | Precipitation | Solvent- Extraction | Ion- Exchange |
|---|---|---|---|
| Present and future availability | Plenty | Plenty | Plenty |
| Processing Required | Molasses-30° | Molasses- dilution to 60% solids<br>$H_2SO_4$- equivalent to ash content<br>MEK- 88% | Molasses-30° Brix<br>$H_2SO_4$ - 10%<br>Bentonite slurry- 1% of Aconitate |
| Material handling Problems | High | Low | Low |
| Storage requirement | Molasses- steel or concrete storage vessel with proper facilities,<br>$CaCl_2$- Carbon steel with epoxy based lining | Molasses- steel or concrete storage vessel with proper facilities,<br>$H_2SO_4$ - Cast iron, carbon steel, FRP composite tanks | Molasses- steel or concrete storage vessel with proper facilities,<br>$H_2SO_4$ - Cast iron, carbon steel, FRP composite tanks |

### *5.1.4 Comparison based on Equipments*

**Table 4: Comparison based on Equipments**

| Parameters | Precipitation | Solvent- Extraction | Ion- Exchange |
|---|---|---|---|
| **Cost of installed equipments** | Rs 3,95,11,540 | Rs 3,38,98,480 | Rs 3,79,70,700 |
| **Special Designs** | Vacuum Filter | Vacuum Crystalliser | Ion- Exchange cells |

### *5.1.5 Comparison based on Costs*

**Table 5: Comparison based on Costs**

| Parameters | Precipitation | Solvent Extraction | Ion Exchange |
|---|---|---|---|
| **Manufacturing Cost** | Rs 38,521 | Rs 32,742.85 | Rs 39,346.45 |
| **Cost of installed equipments** | Rs 3,95,11,540 | Rs 3,38,98,480 | Rs 3,79,70,700 |
| **Total Cost of production** | Rs 38,521 + $C_{GEC}$ | Rs 32,742.85 + $C_{GEC}$ | Rs 39,346.45 + $C_{GEC}$ |

### *Conclusion*

1. Extraction of Aconitic acid is only beneficial if its percentage is more than 4-5% in molasses if highest purity is the requirement then ion-exchange proves to be best method for extraction.
2. Of the several resins and adsorbents that were selected for testing recovery of aconitic acid from Sugarcane liquors Dowex Marathon MSA, a strong base anion resin in sulfate form was found good.
3. However resins are limited by their low capacity of extraction.
4. For commercial scale Solvent extraction is a better choice, however co-extraction of different other compounds reduces the purity of the product.

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