A NEW APPROACH TO IMPROVE THE HYDROGEN YIELD FOR HI_X SYSTEM OF I-S PROCESS

by

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Objectives

- India is planning to study the I-S process for production of hydrogen in conjunction with high temperature nuclear reactor. This requires optimization of parameters for improved efficiency.

- I-S process involves three major steps

- Bunsen reaction
- Sulfuric acid decomposition
- Hydrogen production by HI_X reactive distillation

Overview of I-S (Iodine-Sulfur) process

- Overall efficiency of the process is dictated by individual Stage performance
- Improvement in the yield of hydrogen production by various design options of HI_X system will lead to overall performance enhancement of I-S process
- No conclusive design data from literature is available for HI_X system
- All theoretical parametric estimations are subjected to uncertainty due to lack of experimental data

Complexities involved in HI_X system

- HI_X system is multi-component, multi-phase system forming hetro-azeotrope at normal temperature and pressure
- To have reasonable driving force for distillation High temperature (>300 ºC) and high pressure (>22 bar) operation is necessary
- HI_X System is highly corrosive at this temperature thus sealing material and system component fabrication require special care
- Direct measurement of equilibrium vapor and liquid compositions is an analytical challenge

Experience in reactive and distillation field

- Experience gained in multiphase H_2-H_2O isotopic exchange is utilized while designing HI_X system
- In both the cases though overall reaction is between liquid and gas phase actual reaction takes place in the vapor phase alone and requires Pt/Pd loaded catalyst
- Total isotopic transfer rate enhancement in liquid phase catalytic exchange mode compared to vapor phase catalytic exchange mode is due to replenishment of gas phase reactant from liquid phase
- Catalyst gets poisoned with excessive liquid loading. Introduction of segregated bed addresses this problem and reduces HETP

Design basis of the study

- Hydrogen is produced by direct decomposition of HI in the gas phase
- Equilibrium tray concept is used for reactive as well as physical distillation stages based on standard free energy change
- Equilibrium yield is taken as the ratio of hydrogen production to feed HI content
- Equilibrium yield is estimated by parametric variation having fixed re-boiler load
- NRTL three parameter model is taken for vapor-liquid equilibrium

Parametric study for equilibrium yield enhancement

- Analysis of already published case studies
- Effect of the number of theoretical plates
- Effect of side stream location
- Influence of in-situ flushing of iodine from vapor phase
- Influence of scrubbed liquid recycling to replenish decomposed HI
- Column concentration profile in the absence of reaction

Reference Scheme for HI_x Reactive Distillation

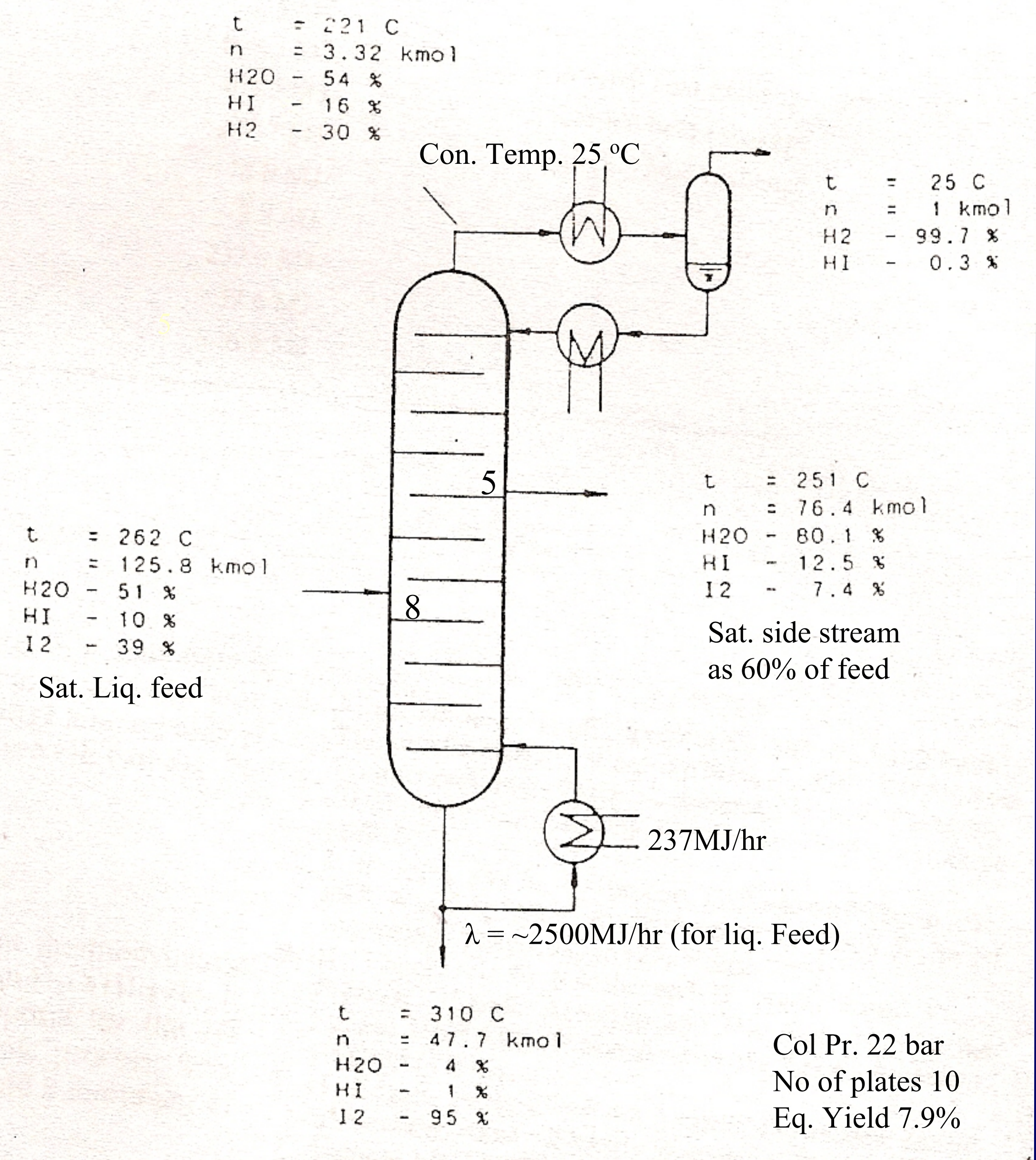
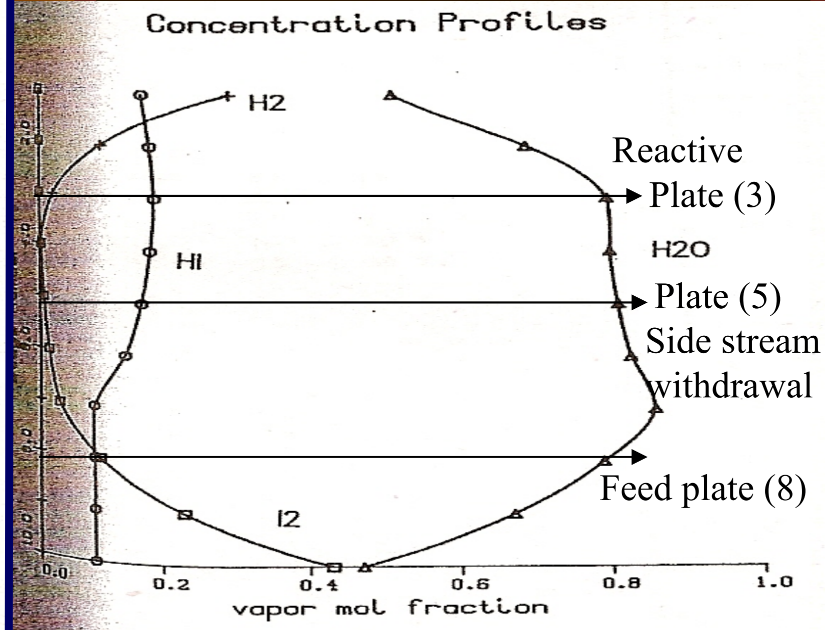
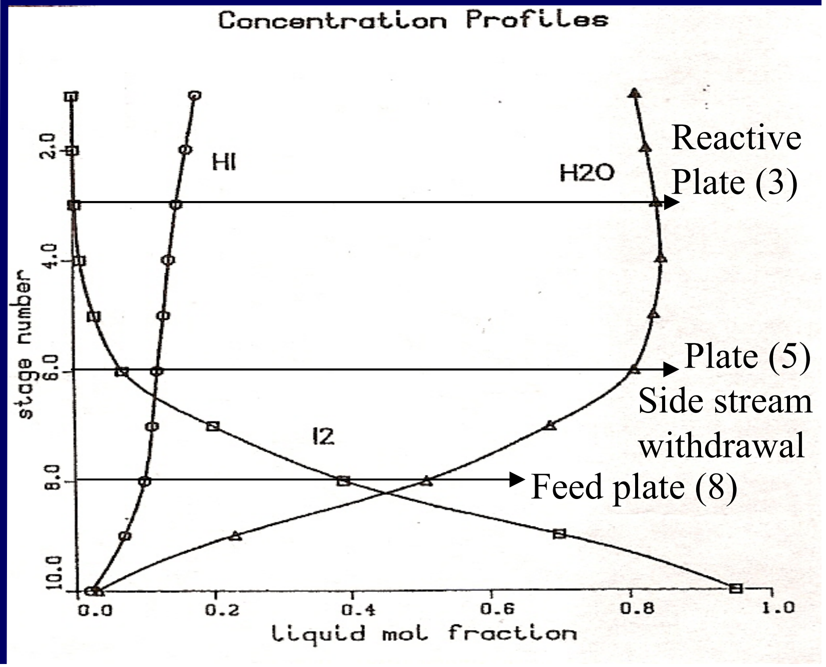


Fig. 6. The distillation column.

Ref.: ROTH M. et. al. Int. J. Hydrogen Energy. 1989



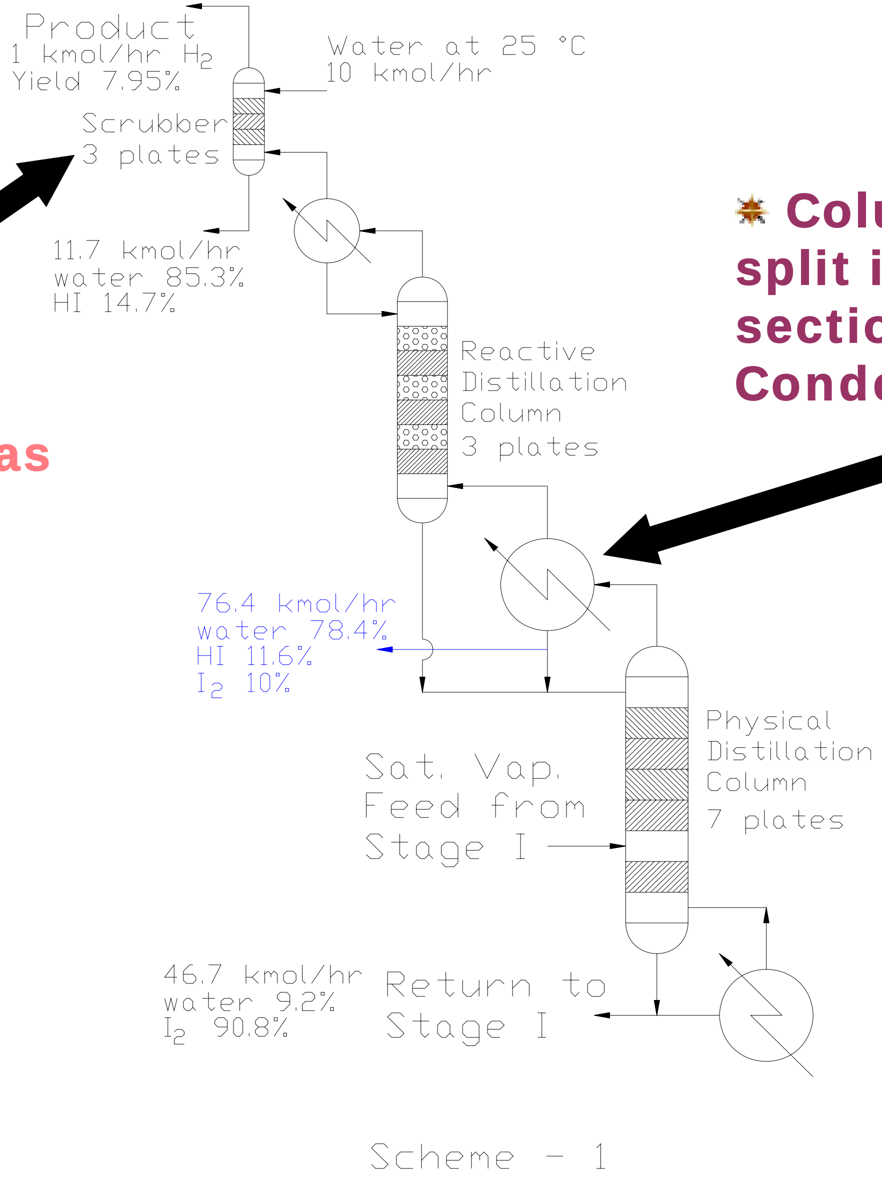


Analysis of most elaborate published scheme as Reference Scheme

- This is the only published scheme depicting complete column vapor-liquid composition profile
- Column pressure is based on driving force i.e. difference between the feed and azeotropic composition
- Azeotropic composition of HI decreases from 10% to 1% for iodine concentration of 39% to 95%
- Hydrogen production is significant only for iodine depleted vapors
- Stripping section plates of the column follows azeotropic compositions corresponding to the iodine concentration

Problems associated with the Reference Scheme

- Overall and individual component material balance are not matching
- Internal reflux for the column is not clearly brought out
- Re-boiler load is insufficient for saturated liquid feed
- Based on this analysis Scheme-1 is proposed for same design objectives with minor modifications



- **Water scrubber has been added to get Product hydrogen purity**

- **Column has been split into two distinct sections with a partial Condenser in between**

Extension of reference scheme

Scheme-1: Extension of Reference Scheme

Common features as of reference Scheme

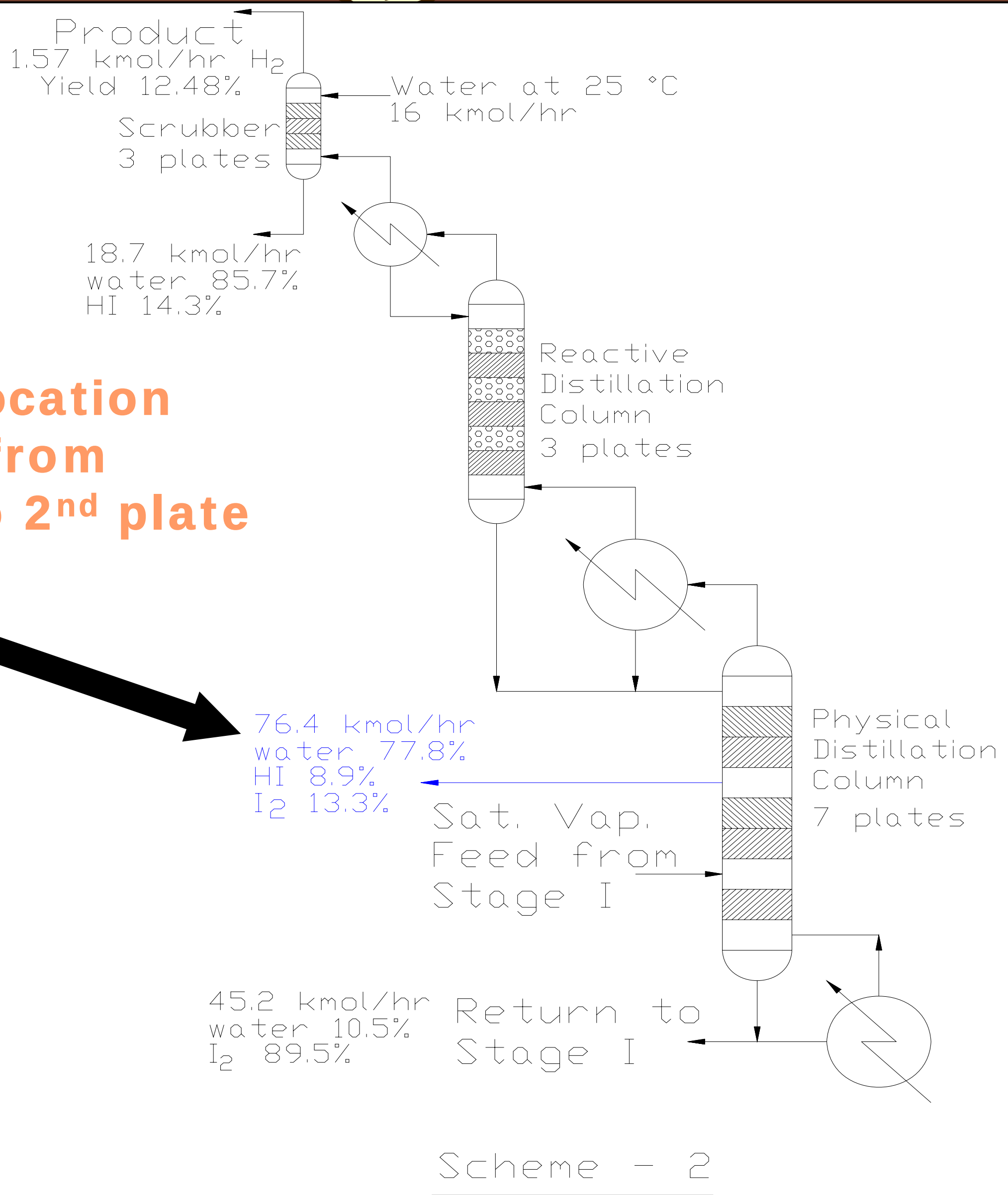
- Total number of plates and reaction zone plates are kept same
- Feed and side stream plate locations are unchanged
- Re-boiler load and Column operating pressure are same
- All feed and product streams flow and compositions are unchanged
- Equilibrium hydrogen yield and product hydrogen purity is kept same

Modifications to reference Scheme

- Feed quality is changed to saturated vapor as against saturated liquid
- Reference column is split into two columns to take care of internal reflux to meet the design objectives
- Scrubber is added to meet the requirement of product hydrogen purity

Observations from scheme-1 analysis

- Bottom product is enriched to more than 90% of iodine by removing water content of the feed as side stream
- Removal of water as side stream from enrichment section of the column leads to significant loss of HI
- Improvement in equilibrium yield is possible by shifting the side stream downwards
- In view of the above side stream plate location is shifted downwards in Scheme-2



- Side stream Withdrawal plate location has been changed from condenser reflux to 2nd plate from top

Effect of side stream position

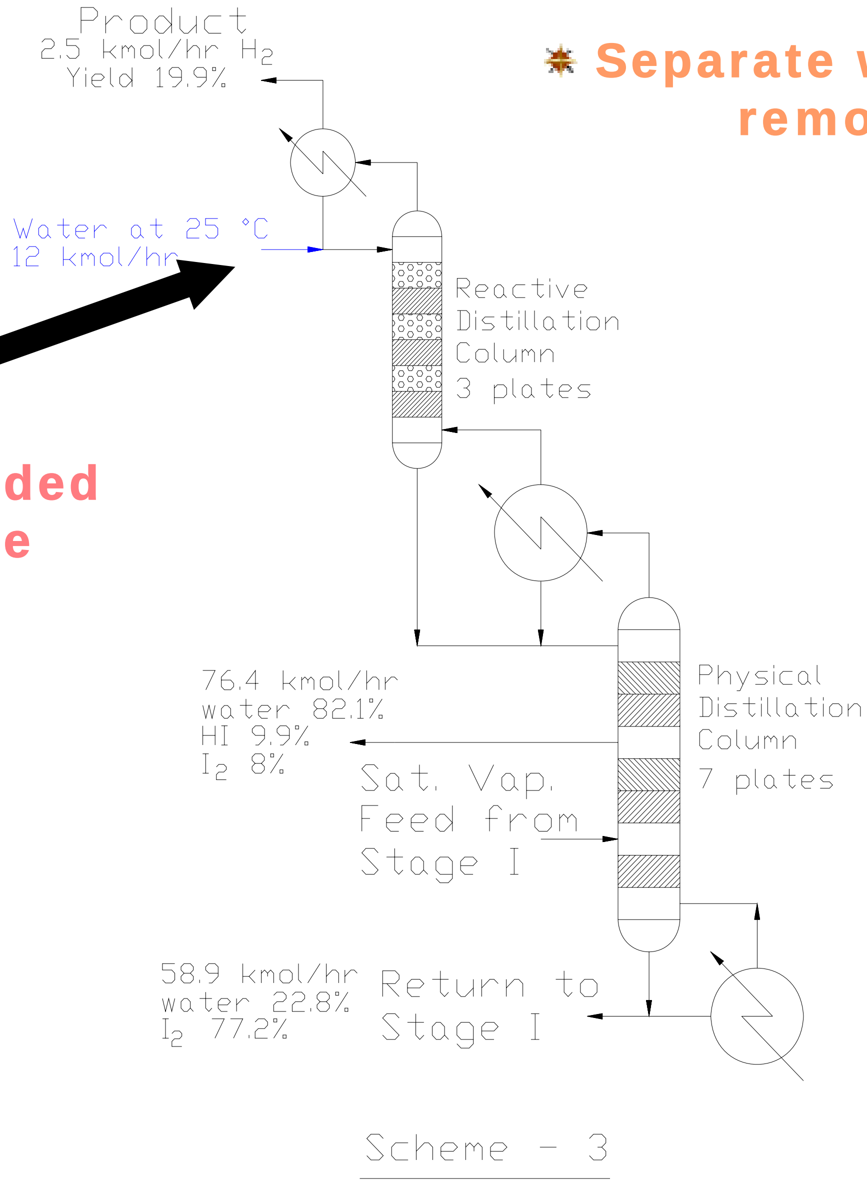
Salient features of side stream location: Scheme-2

- Except side stream location all design parameters are kept same
- Side stream withdrawal location has been changed from condenser reflux stream to 2nd plate from the top
- It reduces the HI content in the side stream which increases the total amount of HI going to reactive distillation column
- This modification led to increased yield of hydrogen in the product to 12.5 %

Observations from scheme-2 analysis

- Downward shifting of side stream increases water and HI content going to the reactive distillation section for a given iodine enrichment
- Lower iodine concentration improves equilibrium yield. Thus requires proper combination of water and HI
- Scrubber water is directly added to reactive distillation section in scheme-3 to see the effect of iodine flushing.

- Separate water scrubber removed



- Scrubbing water added directly in the reactive distillation section

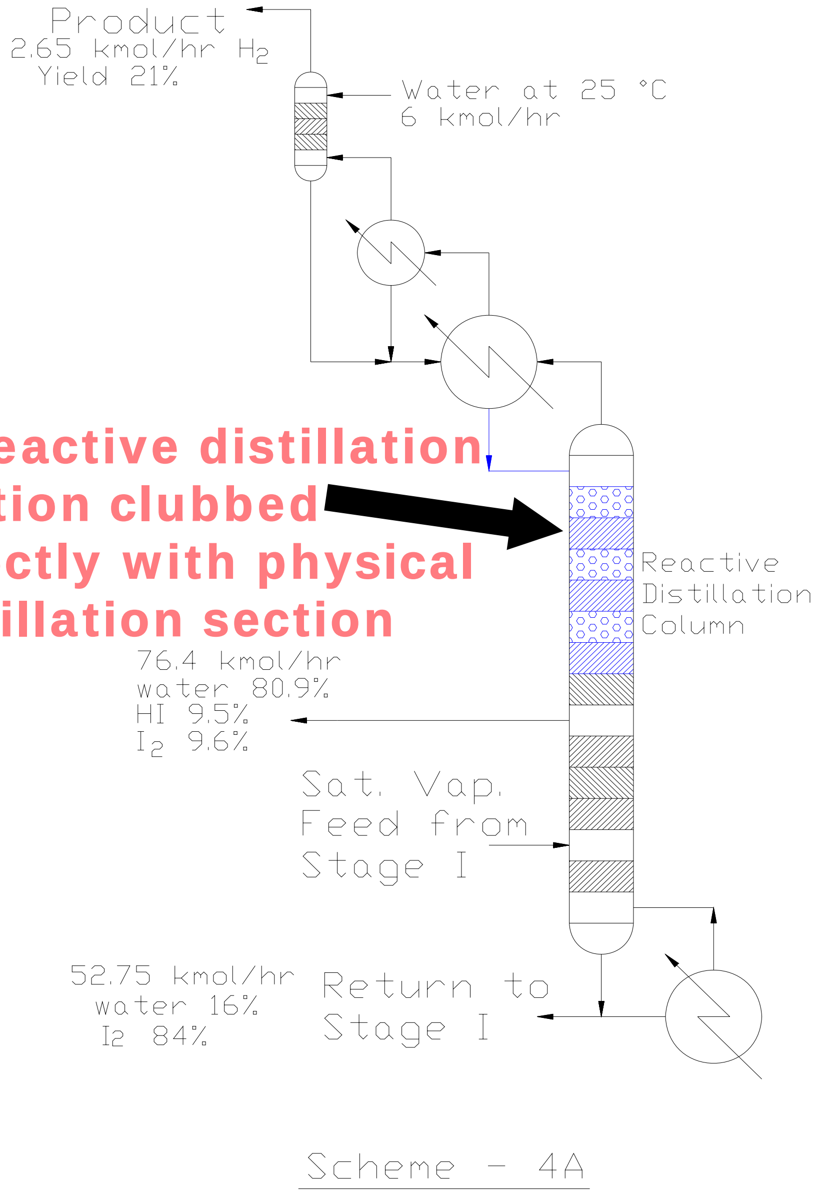
Effect of water on iodine flushing

Salient features of water flushing: Scheme-3

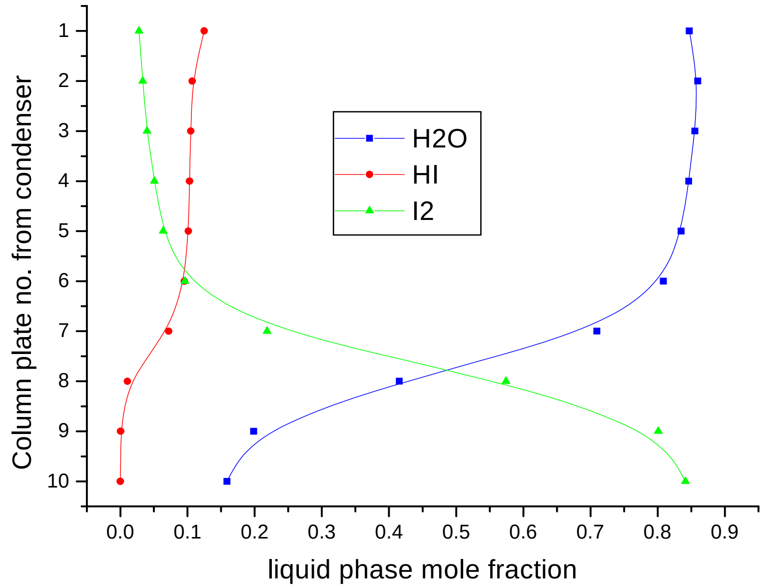
- Separate water scrubber is removed from the system
- Water is added as an additional reflux to the reactive distillation column
- This utilizes the scrubber waste stream HI content available for the reaction
- This modification led to increase in yield of hydrogen to 20%

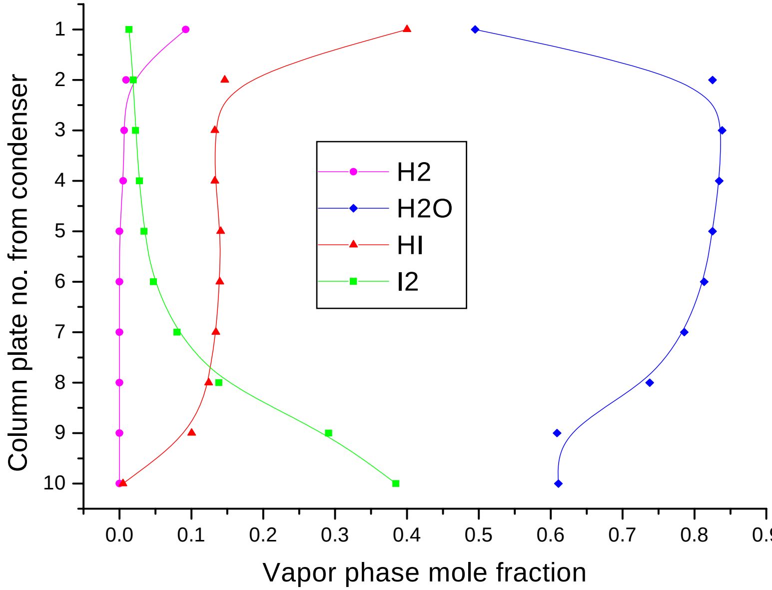
Observations from scheme-3 analysis

- Iodine composition in the bottom product stream reduces due to additional water in the system
- Higher HI content in the reactive distillation stages results in better yield of hydrogen in product stream
- Based on this observations scheme-4A is prepared to check the effect of high internal vapor-liquid flow rate



- **Reactive distillation section clubbed directly with physical distillation section**





Effect of high internal vapor-liquid flow rates

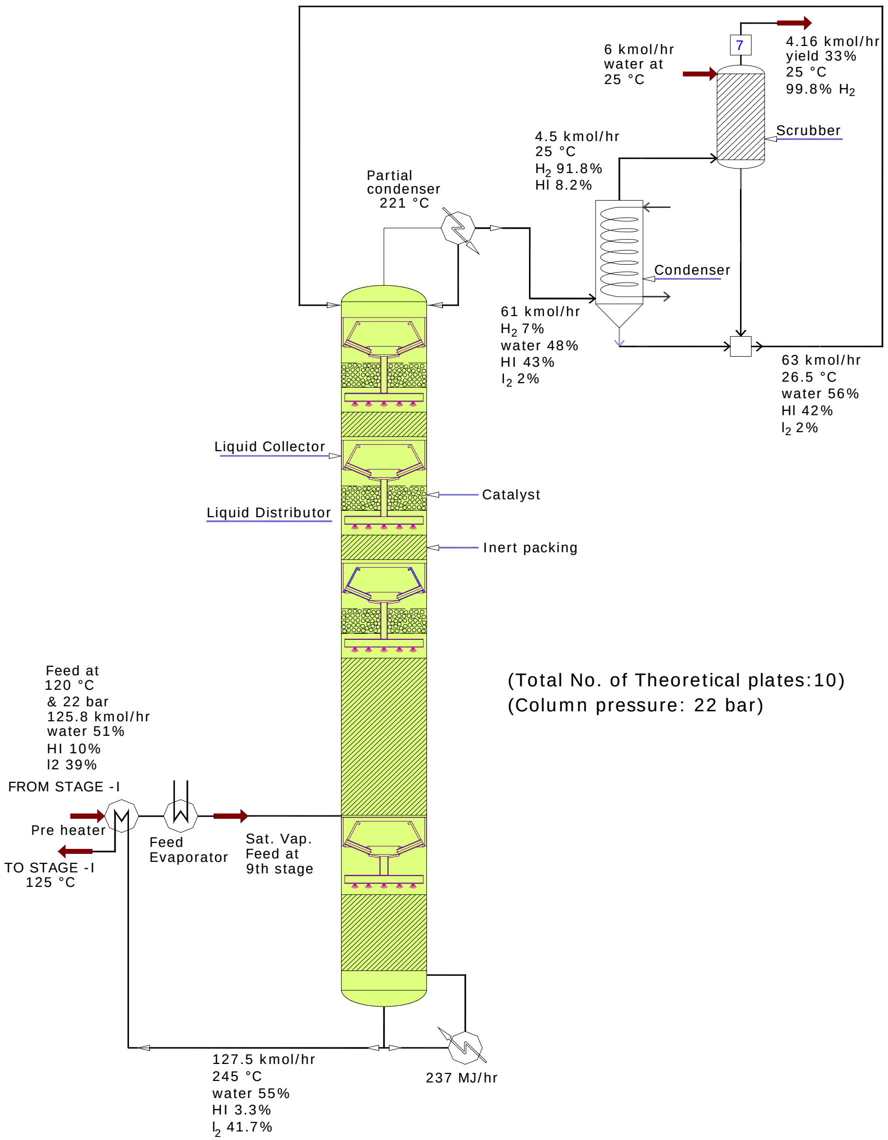
Salient features of high internal reflux: Scheme-4A

- Reactive and physical distillation columns are clubbed together so that the whole column observes increased internal vapor and liquid flow rates
- HI recovered by scrubber water is utilized by recycling
- Scrubbing water flow is reduced
- This modification led to increase in yield of hydrogen to 21%

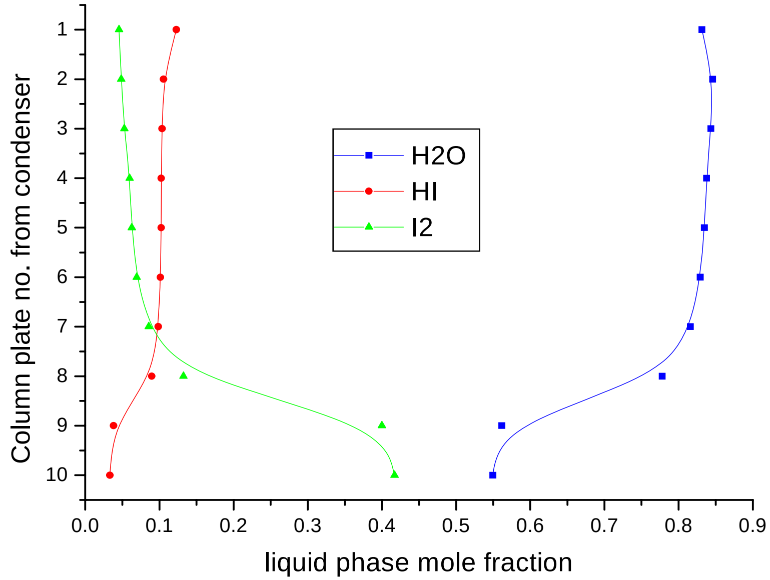
Observations from scheme-4A analysis

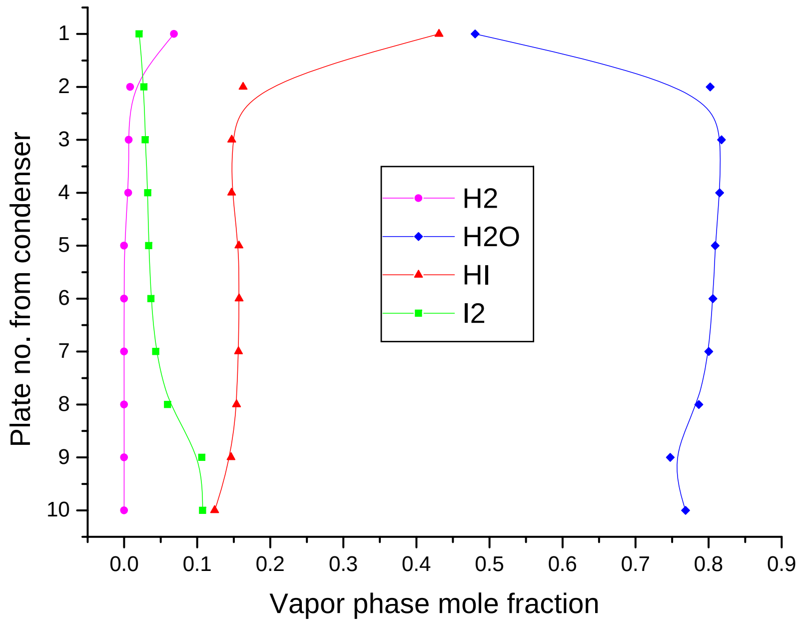
- Hydrogen production rate is not only function of HI concentration in the vapor phase but also concentration of iodine & HI in the liquid phase

- Based on positive points of earlier schemes a new scheme is generated with the following features
  - Higher internal vapor-liquid flow rates are maintained
  - In place of separate side stream and bottom stream, a Single bottom product stream carrying lowest HI content is removed from the system
  - Scrubber water is recycled to recover HI



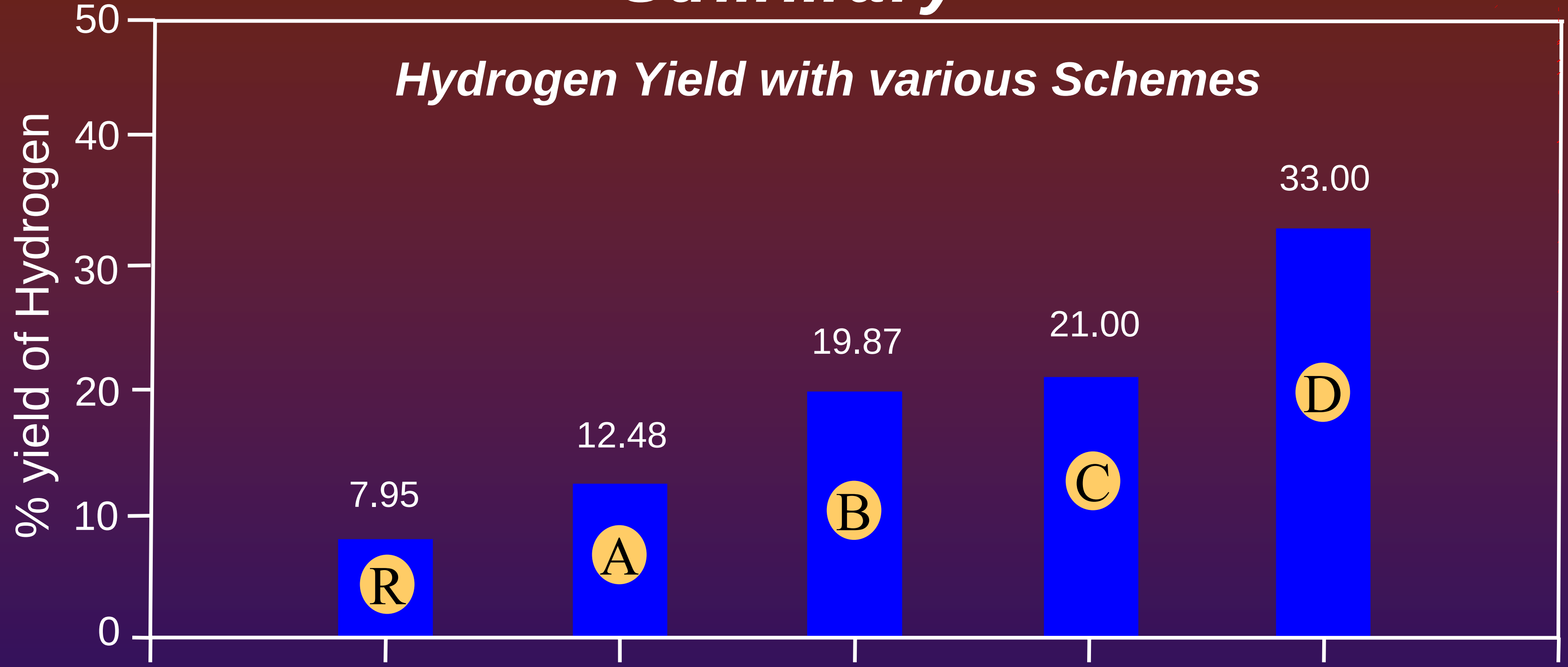
HIx REACTIVE DISTILLATION (STAGE III)





Proposed Scheme for HI_X Reactive Distillation

Summary



- R Modified Reference Scheme
- A Side stream withdrawal location shifted downwards
- B Effect of water scrubbing on iodine flushing
- C Effect of high internal reflux
- D Proposed scheme

Conclusion

In the absence of definite thermodynamic model available in the literature hydrogen yield may vary from the actual one. However, relative gains in various schemes cannot be ignored. Nevertheless we are initiating the efforts to conduct experiments and improve the model to reduce the uncertainties. It is concluded that increased hydrogen yield is obtained at the cost of lower iodine enrichment. We strongly feel that efforts to improve hydrogen yield are more desirable than iodine enrichment as iodine stream is any way going to mix with aqueous stream before it enters the Bunsen reactor. In the present study more focus is given to equilibrium yield. Total optimization will require energy considerations also.

Thank You!