



DESIGN AND CONTROL OF REACTIVE DISTILLATION FOR ISOPROPYL ACETATES PRODUCTION

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ABSTRACT: The rectifying section and reactive zone in the first column, and the stripper in the next section, are used in the type-II process known as reactive distillations to create isopropyl acetate (IPAc). When acetic acid is esterified with different alcohols without implementing pure alcohols and acetic acid as reactants, the reactive distillation design and control are affected by this analysis of reactant purity. Given that ethanol at a concentration of 68% generates an isopropanol/water azeotrope, this generates considerable financial benefits. (by lowering the cost of raw materials). The acid's purity is fixed at 95% for industrial-grade acetic acid, 65% for isopropanol and 87% for ethanol. The results indicate that the manufacturing of IPAc through reactive distillation leads in an 8% increase in Total Annual Costs (TAC). After that, it is investigated whenever reactive distillations with azeotrope resources are operable. The alcohol feed composition, feed flow, and acid feed purity are three disturbances that are created in order to compare the effectiveness of one-temperature-one-composition control and dual temperature control. According to the results of the simulation, reactive distillation with azeotropic feeds may be controlled successfully.

Keywords: Azeotrope, Design, Control, Reactive Distillation (RD), isopropyl acetate,

I. INTRODUCTION

Reactive distillation is frequently used in order to esterification acetic acid (HOAc), which is efficient because it removes one or more products from the reaction region to avoid the reaction equilibrium limit [8]. Acetic acid is esterified with a number of alcohols ranging from C1 to C5 is accomplished continuously by reactive distillation techniques [6].

They suggested a systematic design approach to optimize potential designs for the lowest possible Total Annual Cost (TAC) developed qualitative links between potential process flowsheets and phase equilibria. Regarding these acetate esters, the results offer great conceptual design guidance for continuous reactive distillation methods.

liquid phases in the Isopropyl acetate (IPOAc), n-butyl acetate (BuOAc), and Amyl acetate (AmOAc) systems are binary mixtures of water and the acetate product separate into two phases, respectively, extremely high water purity might be used to generate the aqueous phase (For IPOAc, BuOAc, and AmOAc systems, respectively, 99.9 mol% at 91 °C, 99.6 mol% at 50 °C, and 99.9 mol% at 25 °C were measured at 1 atm).

isopropyl alcohol (IPOH) + acetic acid (HOAc) \leftrightarrow isopropyl acetate (IPOAc) + water (H₂O) (1)

n-butanol (BuOH) + acetic acid (HOAc) \leftrightarrow n-butyl acetate (BuOAc) + water (H₂O) (2)

amyl alcohol (AmOH) + acetic acid (HOAc) \leftrightarrow amy acetate (AmOAc) + water (H₂O) (3)

There is a heterogeneous ternary minimum-boiling azeotrope with various contents in each of these three systems including ester, water, and alcohol. All of

these azeotropes can be extracted from rectification sections due to the lowest boiling temperatures of their quaternary mixtures, they are known as distillate products. Due to a liquid-liquid split, the ternary azeotropes automatically create water in the aqueous phases with a high purity (>99.5 mol%^{4,5}), similar to the binary mixtures of acetate and water observed in BuOAc and AmOAc systems. The Batch reactive distillation (BRD) for the BuOAc and AmOAc models well if the H₂O is decanted from the distillates. Accordingly, the response is changed in the ideal course, and acetic acid derivation items might be gotten by totally refluxing the natural distillates and gathering them in the bottoms. By using a BRD approach, H₂O and BuOAc of high purity can be produced without the need for additional separation steps, as represented and implementing the results, they were able to forecast equivalent outcomes for the AmOAc system [10]. That was mentioned, the ternary azeotrope for the IPOAc framework doesn't give a high purity of H₂O in the watery stage, like a twofold blending of IPOAc and H₂O, which makes it considerably more testing to involve a BRD strategy for the IPOAc combination.

In the chemical industry, IsoPropyl Acetate (IPOAc) is a significant substance with several production applications. According to reports, it works well as a solvent for a number of synthetic resins, containing epoxy resins, methacrylic resin, nitrocellulose, and ethyl cellulose, as well as a number of natural resins, including manila gums, kauri, dammar and rosin [2]. Because it evaporates quickly and is not very hygroscopic, it is also a crucial component of printing inks, particularly gravure inks [3]. Additionally, it serves as a solvent in the creation of fragrances, flavourings, and adhesives.

Esters play a significant role in the chemical processing industries. The manufacturing of varnishes, ink, synthetic

resins, and adhesives all utilize acetate esters, which are significant organic solvents. They are created when alcohols and acids combine in a condition is acidic. The reaction's less conversion rate is a major problem in the manufacture of these esters. Therefore, significant construction expenditures and high energy expenses are unavoidable. A highly alluring method, to lower these investments and energy costs is reactive distillation.

in particular, evaluated to the design of typical reactor/distillation systems, simulation has become a crucial part of the design of catalytic distillation processes. Compared to other systems use distillation systems after traditional reactor systems, because simultaneous reaction and distillation processes interact, Column Distillation (CD) systems are more complex. When there is no adequate shortcut or empirical approach for determining crucial parameters, modeling techniques become more crucial (Pilavachi, 1997). A new CD process may be modelled using well-known thermodynamic and kinetic data due to reliable modelling tools. It is possible to determine crucial design parameter values with a high degree of confidence. Additionally, simulation may be used to examine the important parameters would affect an already-running process and offer recommendations for future process improvement.

In this analysis, it is produced a substitute for chloroform or another entrainer that is not naturally found in the mixture. They suggested utilizing HOAc as an entrainer to remove IPOH from distillate compared to implementing the extract IPOAc. They show that the amounts of IPOH in the distillate may be greatly reduced using an RD system with a constant HOAc feed, which produces an exceptionally split between liquid-liquid split, as well as a byproduct of relatively high purity H₂O. Therefore, the distillate's organic phases

mostly transforms into a binary combination of IPOAc and water, consider the practically complete recovery of IPOAc using a stripper and a decanter.

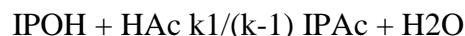
II. LITERATURE SURVEY

Y.T. Tang, H.P. Huang, Chen, Y.W., S.B., C.C., Yu, Huang, Lee, M.J et al., [7] presented the conventional layout of a reactive column and created a novel method that uses two columns (the RD column, which is a column that has a stripper, rectifying section, and reactive zone) to generate higher Ethyl ethanoate (EtAc) that matches the complete Acetic acid (HAc) criteria to the greatest requirements. Later, it was discovered that when reactive distillation is involved, similar difficulties develop with IsoPropyl Acetate (IPAc) production. Therefore, based on their research, on acetic acid esterifications with various alcohols, it provides a generalization. The reactive distillation column used to produce IPAc and EtAc was categorized as a type II arrangement. This sort of reactive distillation column has a considerably different process arrangement than a standard reactive distillation columns. A downstream stripper is instead of having different columns for reactive, repairing, and stripping, and in order to further purify acetate, the organics with a ternary azeotrope-like composition are recycled back to the decanter.

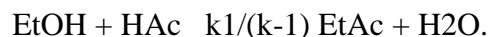
Hayden, O'Connell, J.G., J.P et.al [18] Non-Random Two-Liquid (NRTL) model parameter sets are described. The non-ideal dimerization of the vapor phase by acetic acid is also considered. With trimerization and dimerization sustaining the acetic acid vapour phase interaction, utilized are the second virial coefficients.. The fugacity coefficients are calculated using the built-in association parameters of Aspen Plus. In this study, the results of the alcohols ethanol (EtOH) and isopropyl alcohol (IPOH) are EtAc and IPAc,

respectively. Reversible processes are starting to develop:

This is the IPAc framework:



This is the EtAc framework:



The amberlyst 15 (Hass and Rohm) and CT179 purolite (Rohm), are the acidic ion-exchange resins being used as solid catalysts. In the Langmuir-Hinshelwood system or the pseudohomogeneous approach, the reaction rates are expressed.

X.H. Tao,; B.L. Yang,; Hua, B. et.al [9] distillation reaction occur at the same time have intricate interplaying effects. Therefore, it is essential to maximize the equipment characteristics and operational circumstances while modelling and simulating the reactive distillation process using mathematical methods. Reactive distillation is commonly modelled using techniques like the tridiagonal matrix approach, simultaneous correction method (Newton-Raphson), homotopy method, and relaxation method.

R.S. Zhang,; Han, Y.U. Ho_mann et al. [14] The heterogeneous catalytic distillation procedure was described using a mathematical model. Utilizing the Newton-Raphson iteration and the multi-target shooting approach were used to solve the boundary value problem. The calculation's results agreed with the data from the experiment.

C.G. Zhou; S.Q Zheng. et.al [13] Chemical reaction rate, enthalpy balance, phase equilibrium, molar fraction summation, and material balance are all part of the MESH equation is solved using a partial Newton approach that is provided, utilizing the original iteration variable value obtained by repeated relaxation.

Qi, Z.W.; Shi, J.M.; Sun, H.J.; Zhang, R.; Yu, Z. et al. [12] To address the receptive refining process of distillation, the

Newton-Raphson technique was created and developed. To make the reactive distillation's mathematical model completely consistent with conventional distillation, the stage's composition was one of the real elements that changed, the enthalpy and the flow.

Juha, T.; Veikko, J.P. et.al [11] A homotopy model of receptive refining is developed by adding homotopy parameters to the equations for phase equilibrium, chemical reaction equilibrium, and enthalpy equilibrium. Using this model, a reactive distillation column for Methyl tert-Butyl Ether (MTBE) was successfully simulated.

Wang, C.X. et al. [5] presented the relaxation approach to determine the catalytic distillation column for the hydrolysis of methyl formate. When the simulated and experimental results were compared, a strong correlation was found.

Steven, V.; Silva, E.A. et.al [1] The reactive distillation model was broken up into a number of smaller equation sets, with a collection of linear and nonlinear equations, all are represented a chemical reaction. This was performed using the equation tearing approach.

Boston, J.F. et.al [17] To model a multi-component conventional distillation process, the Inside-Out technique has been proposed. There are two thermodynamic property models compared to other techniques. A rough thermodynamic model is used to often perform the MESH equation's inner loop solution (Enthalpy balance, molar fraction summation, material balance, and phase equilibrium). In the outer loop, the complex thermodynamic models are used to calculate the approximative model parameters and the constant K for phase equilibrium. The calculation of thermodynamic characteristics is greatly speed up in this method. In the inner loop, using an iterative variable known as the

Stripping factor (S_b), the impacts of the stage temperature on the vapour and liquid flow rates, the number of iterative variables is reduced and convergence stability is enhanced.

R.B Saeger.; P.R. Bishnoi, et.al [16] The latest version of the modified Inside-Out approach includes a liquid composition model with two parameters, which improved the convergence rate demonstrating the impact on the phase equilibrium constant, the stability of extremely non-ideal systems.

Jelinek, J. et.al [15] reduced the inside-out approach. The integrated approach that might address any operation's distillation process and reduced the complexity of the process by using an approximative enthalpy model in the inner loop.

J. Chin; J. W. Lee; J. Choe, et al.[4] a Batch reactive distillation procedure for the synthesis of IPOAc was studied. They demonstrated the distillate splits into an organic and an aqueous phase due to the mixture's heterogeneity, and that the reaction can be modified to continue in the desired manner by removing the aqueous phase. However, they did attention to a problem that was restored to light more quickly by a reactant's considerable aqueous phase solubility (IPOH). The constant IPOAc receptive refining process are the constant state criteria are acquired, this issue also has to be resolved.^{2,9} It is impossible to extract pure IPOAc using HOAc as an entrainer, contrast to the situation for the synthesis of methyl acetate¹⁰. To increase the purity of water and the aqueous phase's IPOH loss should be reduced.

III. METHODOLOGY

Most of the tie lines in the high-purity H₂O corner, which is a normal phase-equilibrium feature envelope of the EtAc and IPAc systems point. In the IPAc system, this phenomena is considerably

stronger. A significantly bigger holdup is predicted since it was discovered that in this sort of operation. The base of the first column, commonly known as the RD column, is within the reactive zone.

From a reaction perspective, the fact that they use a large reactor with a high temperature for the reaction. (due to the base of the column) provides this effective. Included is the holdup at the column base, in this analysis to be ten times the tray holdup. The requisite acetates are produced in the reactive portion, the ppm levels are maintained which is followed by a rectifying section where heavy acid (HAc).

The requirements identify as producing: preserving acid purity below 100 ppm while producing 99 mol% pure ester compounds at a rate of 50 kmol/h. EtOH's feed composition in this analysis is set at 87 mol% and IPOH's feed composition is set at 64.91 mol%, respectively.

The purity level of alcohol is a little lower than the matching alcohol azeotropic composition. Water is an impurity in both systems, and the acetic acid utilised is of industrial quality, 95 mol%. Due to the minimal boiling point, users will see that the RD column's overhead composition resembles of a ternary azeotrope. Since the acid composition decreases as the column rises (hence, the alcohol-leaning capacity of the RCMs should be referred to RD column profile will approach the azeotrope (which will be confirmed in the distillation lines). This is used for liquid-liquid separation to eliminate water.

The provided's is comparable to the organic phase's. As a consequence, the water is removed using a decanter, and the organic phase is recycled and returned to the Reactive Distillation (RD) column. After that, a stripper is used to purify the organic distillate. Additionally recycled and reinserted into the decanter- is the

stripper's top. EtAc and IPAc of the highest purity are produced in the stripper's bottom (the top corner distillation zone in RCMs) through a simple separation of the alcohols and acetates. The feasibility of this flowsheet is demonstrated through steady-state modelling.

In the product stream is determined by the amount of acid that is allowed in the RD column's overhead the level of acid purity. A technique is used to develop a better design to lower the TAC based on the process flowsheet. The design process followed the same pattern. Because of the strict rules regarding the finished product's acid level, the reactants stoichiometric ratio is permitted.

As a result, the reactive zone's (N_{rxn}) and rectifying section's (N_r) tray counts are considered design variables. The placement of the feed trays for the heavy and light reactants (N_{fheavy} and N_{flight}), feed ratio of two reactants (FR), and the quantity of trays within the stripper (N_s). The reflux ratio of the RD column and reboiler duty of the strippers are two modifying variables taken into consideration. Aspen Plus RADFRAC module, which has a FORMula TRANslation (FORTRAN) function for response rates, is used to execute all simulations, in an effort to find better designs for these two processes.

The following procedures are used to create a design that is perfected by providing a manufacturing rate and product parameters:

- (1) At first, set the reactants feed ratio at one ($FR = F_{Acid}/F_{Alcohol} = 1$).
- (2) Repair several reactive trays (N_{rxn}).

(3) After adding the heavy reactant feed (NF_{Acid}) to the reactive zone's top, add the light reactant feed (NF_{Alcohol}) to the reactive zone's bottom tray.

(4) Assume that the rectifying section's (N_r) and the stripping section's (N_s) tray numbers are identical.

(5) Repeat step 5 organic reflux flow (R) and stripper heat input (Q_R, S) should be alternated until the product specification is met.

(6) However, get back to stage 4 and modify the N_r and N_s until the TAC is approximately in line with expectations.

(7) Until the TAC is reduced to a minimum, return to step three and locate the feed locations (NF_{Acid} and NF_{Alcohol}).

8) Proceed to step 2 and change N_{rxn} until the TAC is decreased.

(8) Change the Feed Ratio (FR) back to (1) until the Total Annual Cost (TAC) is at its lowest possible level.

When evaluating the resultant design, the TAC is stated as

$$TAC = \text{operating cost} + \frac{\text{capital cost}}{\text{payback year}}$$

Here, the column, trays, exchangers, and reboilers are included in the capital cost, the steam, cooling water, and catalyst are included in the operational cost. Here, three payback years are utilized.

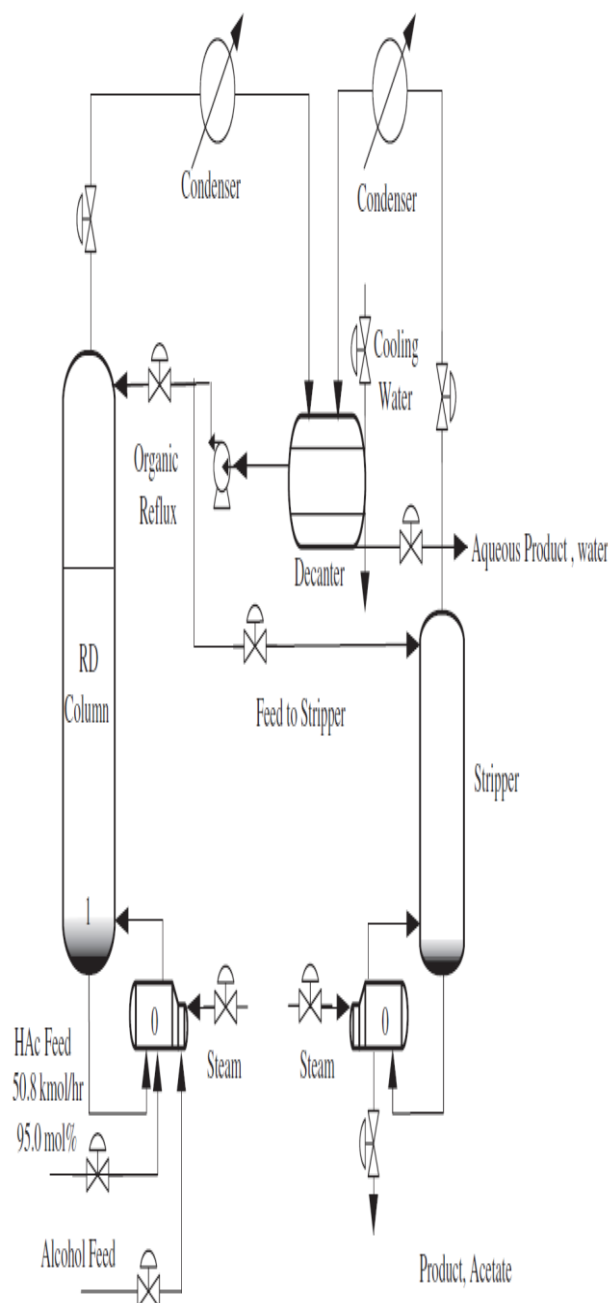
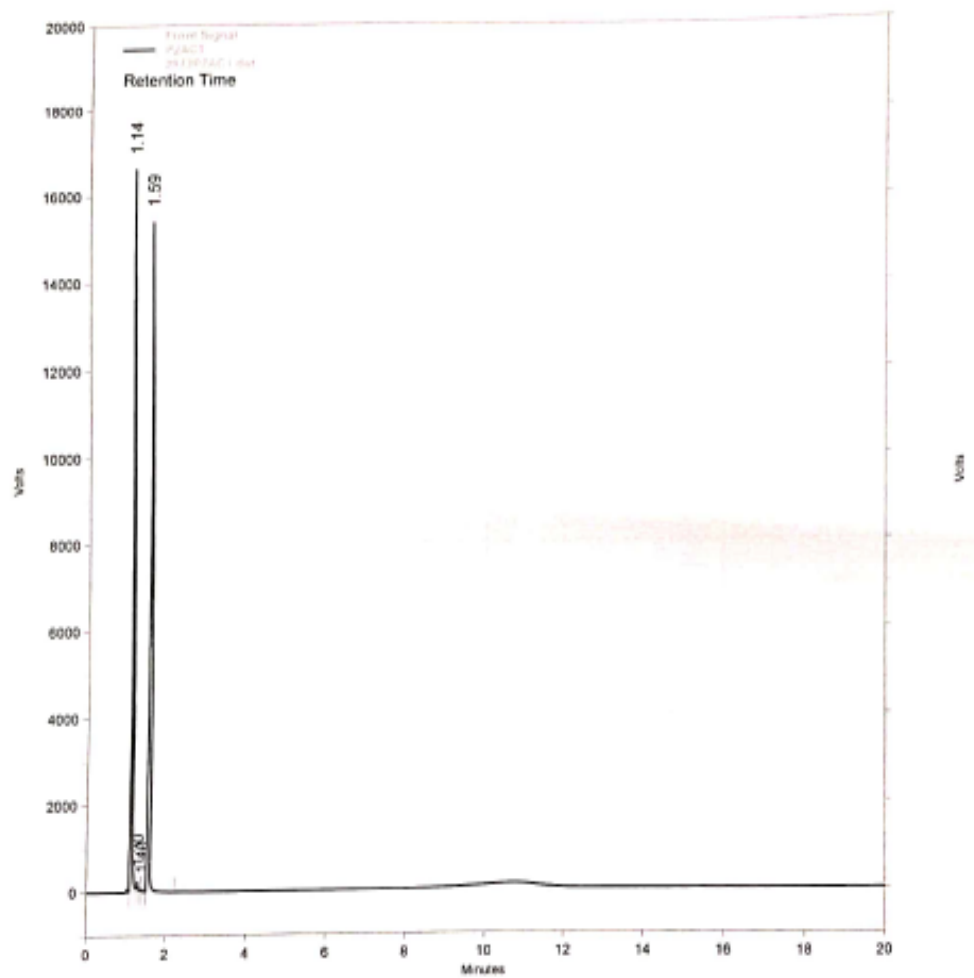


Fig.1: Block Diagram

CSIR-IICT CPC DIVISION

Data File: E:\ISOPROPYL ACETATE\P2AC13172.rst\2973P2AC1.dat
Method: D:\Method\IPA.met
Acquired: 14-03-2023 14:16:01 (GMT +05:30)
P2AC1



Front Signal Results		
Retention Time	Area	Area %
1.140	330730668	45.93
1.590	6173561	0.77

Fig.2: CSIR-IICT CPC DIVISION

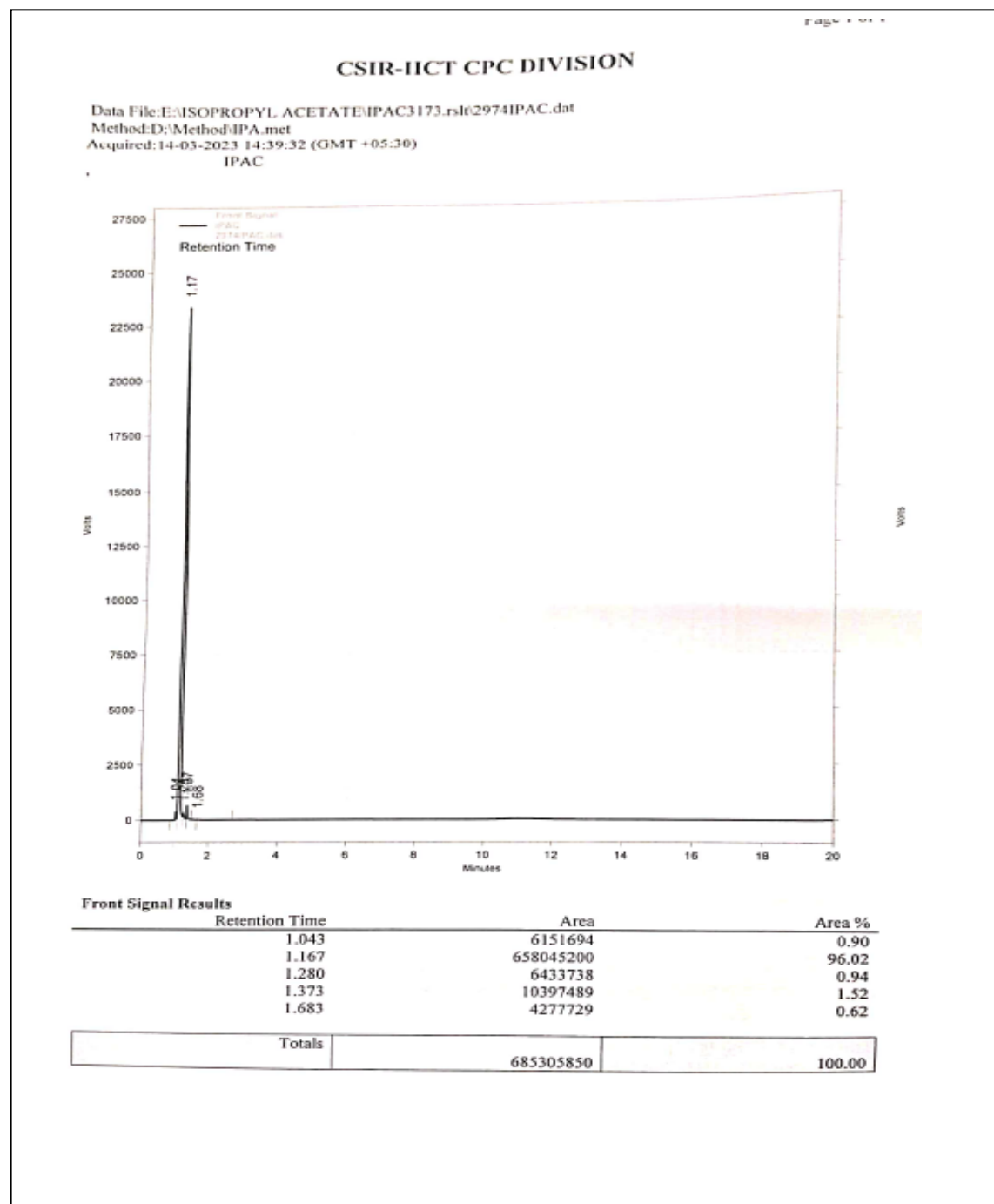


Fig.3: CSIR-IICT CPC DIVISION

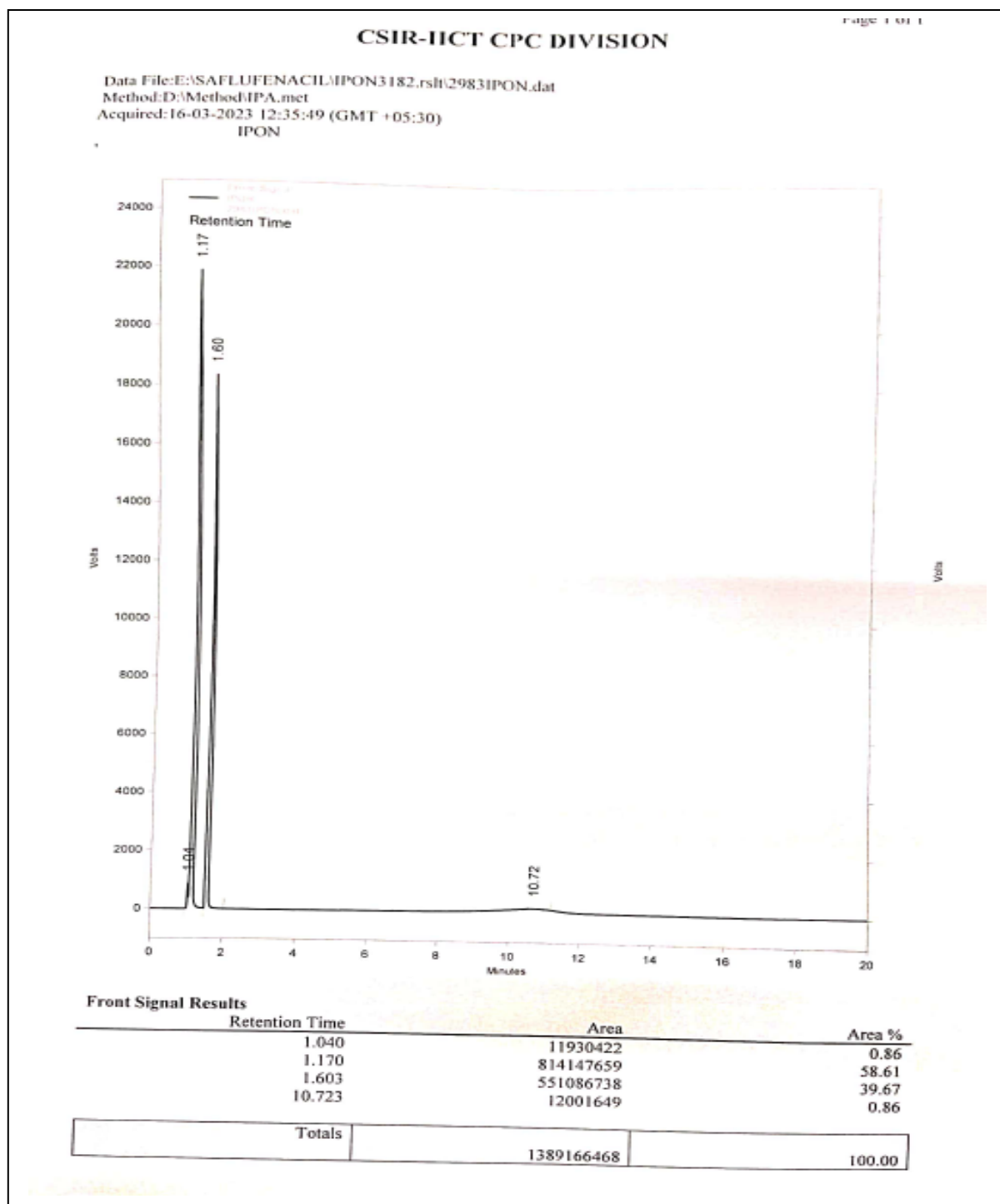


Fig.4: CSIR-IICT CPC DIVISION

IV. CONCLUSION

This analysis provides conceptual concepts for two azeotropic reactive distillation processes. IsoPropyl Acetate (IPAc) is using the reactive distillations that are being researched. The quantitative design is improved through a systematic design process that is provided. An area, a retention time, and a reactive zone in a column used for reactive distillation, the type II reactive distillation arrangement consists of a rectifying portion and a stripper. This provides IPAc productions with attractive alternatives.

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