

**OTTO-VON-GUERICKE-UNIVERSITÄT
MAGDEBURG**

Faculty of Process & Systems Engineering

Simulation Lab WS 2019/20

Supported by:

Elizabeth Richter

elizabeth.richter@ovgu.de

„NEOPENTYL GLYCOL PRODUCTION“

Date: 31-01-2020

Group member:	Course of study:	Matriculation No.:
Mahesh Kumar Ganesan	Process Safety and Environmental Engineering	221201
Angshuman Buragohain	Chemical and Energy Engineering	221552

TABLE OF CONTENTS

1. INTRODUCTION	3
1.1 ASPEN plus for process simulation	3
1.2 The manufacturing process	4
2. METHODS AND MATERIALS	5
2.1 Aldol condensation and separation of products	5
2.2 Hydrogenation	6
2.3 Purification	7
3. RESULTS AND DISCUSSION	8
3.1 Neopentyl glycol purity	8
3.2 Neopentyl glycol yield	9
3.3 Hydrogen economy	10
3.4 Analysis of distillation columns	11
4. CONCLUSION	12
5. SCOPE FOR FUTURE WORK	12

LIST OF FIGURES

Figure 1: Structure of Neopentyl glycol	3
Figure 2: Modelling of molecule of hydroxypivaldehyde	5
Figure 3: Aldol reactor	6
Figure 4: Operating inputs for DIST1 (DSTWU)	6
Figure 5: Operating inputs for RSTOIC hydrogenation reactor	7
Figure 6: Reaction addition to RSTOIC	7
Figure 7: Operating inputs of NPG purification distillation DSTWU	8
Figure 8: Error message for the process modification attempted	10
Figure 9: Fresh hydrogen and recycle hydrogen	10
Figure 10: Relux ratio vs theoritical number of stages	11
Figure I: Distillation results, DIST1 (left), NPG-PUR (right)	12
Figure II: Process model with attempted recycle	13

LIST OF TABLES

Table 1: Mole and mass fractions of products	8
Table 2: Mass and mole flow rates of feed and product	9

1. INTRODUCTION

Neopentyl glycol is an organic compound which is used in as a raw material in the synthesis of polymer type chemical compounds such as polyesters, as additives for specific purpose polymers such as plasticizer in the manufacture of PVC and other chemical products such as lubricants and paints. The IUPAC name of neopentyl glycol is 2,2-dimethylpropane-1,3-diol and its structure is as shown in Fig 1.

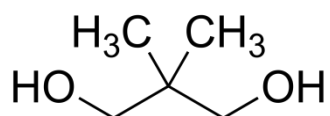
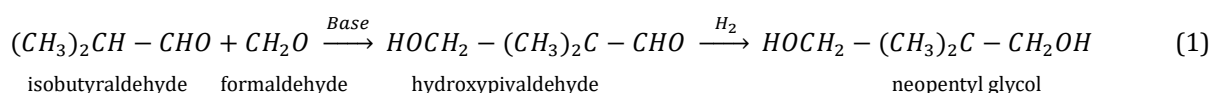


Figure 1: Structure of Neopentyl glycol

Not many processes for the manufacture of Neopentyl glycol exists. The main synthesis process involves aldol condensation of isobutyraldehyde and formaldehyde to produce hydroxypivaldehyde in presence of a basic catalyst. Hydroxypivaldehyde is further hydrogenated to produce neopentyl glycol. The reaction sequence is given in Eq. 1.



Heat of reaction for this aldol condensation reaction was estimated and found to be -60.4 kJ/mol, at 298 K [1]. There are by products formed in this reaction sequence due to the Cannizzaro reaction but use of adequate operating temperature and pressure in the reactors along with catalysts can effectively reduce the yield of by products and increase selectivity of the desired product. Furthermore, appropriate separation processes such as distillation and flash separation can be employed to get a high purity of the desired product.

1.1 ASPEN plus for process simulation

ASPEN plus is a software package designed to model and solve complex chemical processes and reduce human efforts on analytical solving methods. Lab scale modelling and pilot plant establishment before scaling up of a chemical process to a commercial level involves a lot of capital investment and operating costs. Such costs can be avoided by simulation models that can replicate real life chemical processes in practice. ASPEN plus software package is equipped with various libraries and solution methods to model and simulate a wide variety of chemical processes. Various unit operations and

processes such as distillation, vapor liquid separation, chemical reaction and available types can be modelled based on available parameters for the target process.

1.2 The manufacturing process

The first step of the manufacturing process involves aldol condensation of isobutyraldehyde and formaldehyde in presence of a base. Astle et al. [2] mentioned that weak basic anion exchange resins, with tertiary amines as active groups are best suited for catalysing the aldol condensation reaction. In this project work, triethyl amine has been considered as the catalyst. The resultant aldol product contains un-reacted isobutyraldehyde[3] which can be separated by distillation. The bottom product contains hydroxypivaldehyde in a relatively larger fraction and is forwarded for hydrogenation reaction which is the next step.

Hydrogenation of hydroxypivaldehyde has been studied in various scientific research works and noteworthy is the work of Mikio et al. [4] who studied the hydrogenation of hydroxypivaldehyde using bimetallic Ru-Pd on carbon catalyst at 373K and elevated hydrogen pressure. In the considered Aspen model, hydrogenation was carried out in a stoichiometric reactor with known conversion of hydroxypivaldehyde. The un-reacted hydrogen is separated from the products of hydrogenation using a vapor liquid separator. This hydrogen can be vented out to maintain fresh hydrogen feed in the catalyst bed of the reactor[5] or it can be reintroduced along with the fresh feed into the reactor [6].

The final step of manufacture involves purification of the hydrogenation products through a distillation column for getting a higher purity of neopentyl glycol in the bottom product. The midpoint of the column is fed product from the hydrogenation and a 10 percent sodium hydroxide solution which provides caustic to saponify the esters present in the hydrogenated product and to liberate triethylamine from its carboxylic acid salts [5]. This step is omitted in the model considered as the Cannizzaro side reaction during aldol condensation and the esterification side reaction during hydrogenation of hydroxypivaldehyde are assumed to have very low yields and are hence neglected. Top product of the column contains methanol, isobutanol, triethylamine, and water. Further purification of neopentyl glycol can be done by drying and further separation processes to get higher purity of neopentyl glycol but given the assumptions in the considered model, that is beyond the scope of this project work.

2. METHODS AND MATERIALS

The entire process of manufacture of neopentyl glycol can be divided into three sections:

1. Aldol condensation and separation of products.
2. Hydrogenation
3. Purification

These sections consists of reactors, distillation columns and vapor-liquid separators which will be discussed in detail section 2.1 2.2 and 2.3. The overall process flow diagram as modelled in ASPEN plus is shown in Appendix 1.

One of the vital intermediate products in the process is hydroxypivaldehyde (IUPAC: 3-Hydroxy-2,2-dimethylpropanal) which is not found in the databases of ASPEN plus. This molecule was modelled manually after referring to source [7] and is shown in Figure 2, the molecular weight, boiling point, specific gravity data was entered and ASPEN software was used to estimate the remaining relevant properties of the molecule.

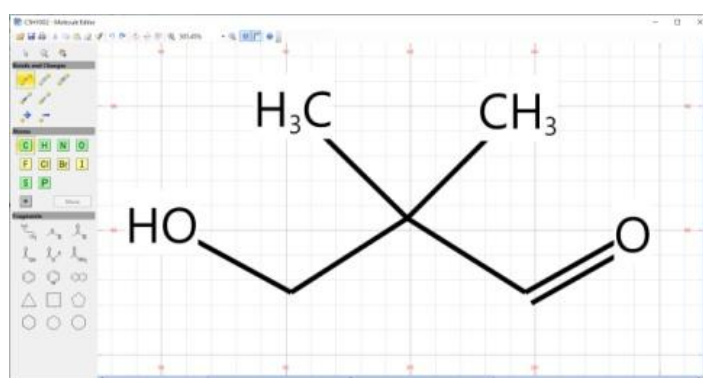


Figure 2: Modelling of molecule of hydroxypivaldehyde

Method assistant was used to determine the appropriate method for the model. The property method used in this project is SRK method as it involves hydrocarbons without any petroleum products. The feed to this process are 1 kmol/h of isobutyraldehyde (ISB), 1kmol/h 44% aqueous solution of formaldehyde and the catalyst is fed at 0.1 kmol/h.

2.1 Aldol condensation and separation of products

Referring to Appendix 1, this section consists of stream mixer (FEEDMIX), heat exchanger (HEATER), aldol condensation reactor (Gibb's reactor, ALDOLCON) and a distillation column (DISTL1). The feed is first mixed in a mixer at normal temperature

and pressure and then the mixture is preheated to a temperature of 90°C as the reaction gives optimised product yield at 90°C.

Figure 3: Aldol reactor

The reactor is modelled as Gibb's reactor with the known temperature and pressure of the reaction. The reactor specifications are referred from [5] and can be seen in Figure3.

Aldol product stream S3 consists of a mixture of hydroxypivaldehyde(HPA) and un-reacted isobutyraldehyde, formaldehyde and water from which HPA needs to be separated using distillation column (DIST1). Distillation recovers 90% of HPA at the bottom and the top product consisting of ISB and CH₂O can be recycled to the initial feed. The operating conditions of the distillation column is given in Figure 4.

Figure 4: Operating inputs for DIST1 (DSTWU)

2.2 Hydrogenation

This section involves hydrogenation of the bottom product of distillation column (DISTIL1) using 0.7kmol/h of fresh hydrogen gas at 500psig pressure. The aldol product taken from the base of the isobutyraldehyde recovery Column DISTIL1 is fed to

a two-stage trickle bed hydrogenation reactor which operates at 160° C to 170° C under 500 psig of H₂ [5]. For simplicity this is done in one stage for this project considering a stoichiometric reactor HYDROGNT. The hydrogenation reaction step was added to the reactor specification and a fractional conversion of 90% of hydroxypivaldehyde was considered. The operating temperature and pressure of the reactor can be seen in Figure 5.

Figure 5: Operating inputs for RSTOIC hydrogenation reactor

The reaction and the required conversion was added as shown in Figure 6.

Figure 6: Reaction addition to RSTOIC

The vapor liquid separator (FLASHSEP) separates all of the un-reacted hydrogen from the product stream, S6 of hydrogenation reactor and the remaining product mixture goes for distillation to increase the purity of the product neopentyl glycol.

2.3 Purification

The purification of hydrogenation products involves rigorous distillation and drying of the neopentyl glycol rich streams. Prior to purification, 10% NaOH is added to the product stream to remove esters and liberate triethyl amine from carboxylic salts but due to the negligence of Cannizzaro reaction and esterification reaction in this model as mentioned in section 1.2, this step is omitted. S7 consisting of product mixture of hydrogenation goes to the distillation column NPG-PUR modelled as a DSTWU with the operating parameters as shown in Figure 7.

The screenshot displays the 'Specifications' tab of an Aspen Plus distillation column model. The 'Column specifications' section includes 'Number of stages' set to 25. The 'Pressure' section shows both 'Condenser' and 'Reboiler' at 1 bar. Under 'Key component recoveries', the 'Light key' is ISOBU-01 with a recovery of 0.9, and the 'Heavy key' is NEOPE-01 with a recovery of 0.001. The 'Condenser specifications' section has 'Total condenser' selected.

Figure 7: Operating inputs of NPG purification distillation DSTWU

A mass fraction of 89.82% w/w and 88.51% mole fraction Neopentyl glycol is obtained at the bottom product considering this model.

3. RESULTS AND DISCUSSION

3.1 Neopentyl glycol purity

Table 1 below summarises the mole and mass fraction of final products for the model simulated.

Table 1: Mole and mass fractions of products

Mole Fractions	ISB+H2O	NPG	RECYCLE
ISOBU-01	0.458746	0.001372	0.45832
FORMA-01	0.000512	4.81E-08	0.013165
TRIET-01	0.097863	0.00043	0.079284
METHA-01	0	0	2.89E-09
ISOBU-02	0	0	1.87E-12
NEOPE-01	0.033377	0.897669	4.15E-12
WATER	0.404274	0.00083	0.445828
HYDRO-01	0	0	0
HPA	0.005228	0.0997	0.003402
Mass Fractions	ISB+H2O	NPG	RECYCLE
ISOBU-01	0.609294	0.000953	0.66301
FORMA-01	0.000283	1.39E-08	0.007931
TRIET-01	0.182407	0.000419	0.160955

METHA-01	0	0	9.31E-10
ISOBU-02	0	0	2.78E-12
NEOPE-01	0.064029	0.900415	8.68E-12
WATER	0.134151	0.000144	0.161132
HYDRO-01	0	0	0
HPA	0.009836	0.098069	0.006971

It can be observed that the product stream NPG has appreciable purity for neopentyl glycol, 89.76% on mole basis and 90.04% on mass basis. The streams RECYCLE and ISB+H₂O consists of considerable amount of isobutyraldehyde and water which can be recycled to the feed for process economy.

3.2 Neopentyl glycol yield

Table 2 below summarises the molar and mass flow rate of feed and final products for the model simulated.

Table 2: Mass and mole flow rates of feed and product

Component	Units	CH ₂ O	ISB	TE-AMINE	ISB+H ₂ O	NPG	RECYCLE
Mole Flows	kmol/hr	1.000	1.000	0.100	0.011	0.420	1.245
ISOBU-01	kmol/hr	0.000	1.000	0.000	0.005	0.001	0.571
FORMA-01	kmol/hr	0.440	0.000	0.000	0.000	0.000	0.016
TRIET-01	kmol/hr	0.000	0.000	0.100	0.001	0.000	0.099
METHA-01	kmol/hr	0.000	0.000	0.000	0.000	0.000	0.000
ISOBU-02	kmol/hr	0.000	0.000	0.000	0.000	0.000	0.000
NEOPE-01	kmol/hr	0.000	0.000	0.000	0.000	0.377	0.000
WATER	kmol/hr	0.560	0.000	0.000	0.005	0.000	0.555
HYDRO-01	kmol/hr	0.000	0.000	0.000	0.000	0.000	0.000
HPA	kmol/hr	0.000	0.000	0.000	0.000	0.042	0.004
Mass Flows	kg/hr	23.300	72.107	10.119	0.614	43.613	62.060
ISOBU-01	kg/hr	0.000	72.107	0.000	0.374	0.042	41.147
FORMA-01	kg/hr	13.212	0.000	0.000	0.000	0.000	0.492
TRIET-01	kg/hr	0.000	0.000	10.119	0.112	0.018	9.989
METHA-01	kg/hr	0.000	0.000	0.000	0.000	0.000	0.000
ISOBU-02	kg/hr	0.000	0.000	0.000	0.000	0.000	0.000
NEOPE-01	kg/hr	0.000	0.000	0.000	0.039	39.270	0.000
WATER	kg/hr	10.089	0.000	0.000	0.082	0.006	10.000

HYDRO-01	kg/hr	0.000	0.000	0.000	0.000	0.000	0.000
HPA	kg/hr	0.000	0.000	0.000	0.006	4.277	0.433

Total molar flow of feed is 2.1 kmol/hr compared to the total molar flow of main product Neopentyl glycol 0.425 kmol/hr. Most of the molar flow is lost at the top products (RECYCLE) in the distillation step (DIST1) after aldol condensation. Hence, the top product should be recycled for compensating the loss of material. This step was attempted as shown in Figure II in Appendix. However the simulation model showed error as there was mass difference in the input and output of the distillation column DIST1 as shown in Figure 8.

```

** ERROR
BLOCK DIST1 IS NOT IN MASS BALANCE:
MASS INLET FLOW = 0.13774013E+01, MASS OUTLET FLOW = 0.137
RELATIVE DIFFERENCE = 0.21257534E-03
MAY BE DUE TO A TEAR STREAM OR A STREAM FLOW MAY HAVE BEEN
CHANGED BY A CALCULATOR, TRANSFER, BALANCE, OR CONVERGENCE
AFTER THE BLOCK HAD BEEN EXECUTED.

```

Figure 8: Error message for the process modification attempted

3.3 Hydrogen economy

The following Figure 9 shows the molar and mass flow rates of fresh hydrogen fed to the hydrogenation reactor and the hydrogen removed from the hydrogenation product stream through a vapor liquid separator.

	Units	H2	RH2
— Mole Flows	kmol/hr	0,7	0,32257
ISOBU-01	kmol/hr	0	0
FORMA-01	kmol/hr	0	0
TRIET-01	kmol/hr	0	0
METHA-01	kmol/hr	0	0
ISOBU-02	kmol/hr	0	0
NEOPE-01	kmol/hr	0	0
WATER	kmol/hr	0	0
HYDRO-01	kmol/hr	0,7	0,32257
HPA	kmol/hr	0	0

Figure 9: Fresh hydrogen and recycle hydrogen

46.07% extracted hydrogen relative to the fresh hydrogen was recovered in the flash separator, which can be recycled back and mixed with the fresh hydrogen feed.

3.4 Analysis of distillation columns

The distillation columns for separating the aldol condensation products and the hydrogenation products have been analysed for reflux ratio vs. number of stages to understand the optimisation of number of stages and the reflux ratio. Increasing number of stages involves initial capital investment whereas it decreases the reflux ratio meaning increasing the flow of products meaning more revenue from products for the process. A compromise has to be made between the two parameters which is based on economic consideration. The dependence of reflux ratio on number of stages is shown in Figure 10 for both the distillation columns used in the model.

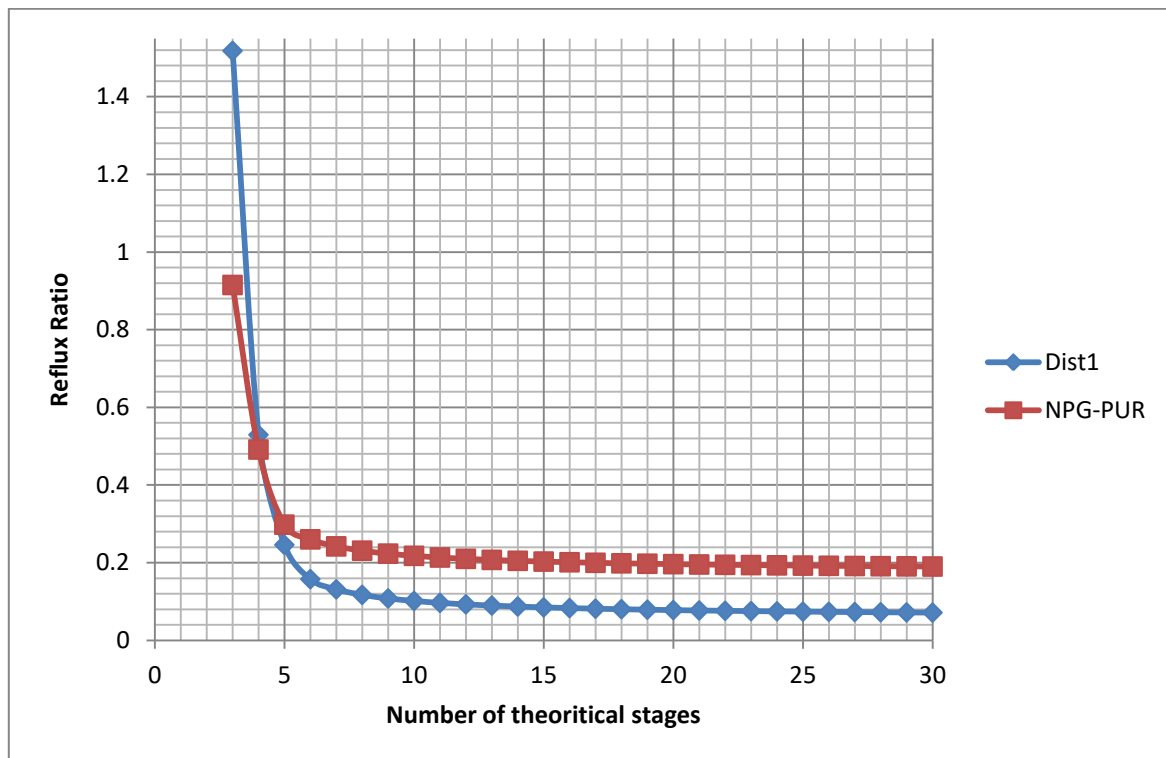


Figure 10: Reflux ratio vs. theoretical number of stages

The results of distillation for both the columns assumed as DSTWU are shown in the Figure 11 below.

▶ Minimum reflux ratio	0,18123		▶ Minimum reflux ratio	0,0619897	
▶ Actual reflux ratio	0,196119		▶ Actual reflux ratio	0,0738372	
▶ Minimum number of stages	1,89637		▶ Minimum number of stages	2,27475	
▶ Number of actual stages	20		▶ Number of actual stages	25	
▶ Feed stage	18,287		▶ Feed stage	18,2287	
▶ Number of actual stages above feed	17,287		▶ Number of actual stages above feed	17,2287	
▶ Reboiler heating required	850,582	cal/sec	▶ Reboiler heating required	309,142	cal/sec
▶ Condenser cooling required	3100,6	cal/sec	▶ Condenser cooling required	26,1888	cal/sec
▶ Distillate temperature	50,9179	C	▶ Distillate temperature	55,5614	C
▶ Bottom temperature	180,833	C	▶ Bottom temperature	206,014	C
▶ Distillate to feed fraction	0,742696		▶ Distillate to feed fraction	0,0262162	
▶ HETP	0,5	meter	▶ HETP	0,4	meter

Figure 11: Distillation results, DIST1 (left), NPG-PUR (right)

4. CONCLUSION

The model simulated yields a sufficiently pure neopentyl glycol: 89.76% on mole basis and 90.04% on mass basis. The product flow rate is low as compared to the feed flow rate but the loss of material is identified to happen at the distillation stage and the stream RECYCLE can be recycled to mix with the initial feed for reducing loss of material.

The top product of final purification by distillation (NPG-PUR) has a high content of isobutyraldehyde and water which can be recycled back to the feed as well. Furthermore, the un-reacted hydrogen extracted using a flash separator can be recycled to mix with the fresh hydrogen feed as well.

5. SCOPE FOR FUTURE WORK

The recycle of top products of distillation of the aldol condensation products which contains significant mass flow of un-reacted materials was attempted as shown in Figure II in Appendix. Error in the mass balance occurred during simulation which can be investigated further and rectified for a more efficient model.

Cannizzaro reactions during aldol condensation has been neglected in this model which yields salts. Similarly, esterification reaction occurring during hydrogenation of hydroxypivaldehyde due to self condensation is also neglected in this model. Such side reactions can be considered for further investigation on their effect on the process.

Subsequently, saponification, salt removal and drying units can be added to the purification process of neopentyl glycol.

Economic analysis on distillation columns based on number of stages, height of the column and reflux ratio optimisation can be carried out.

5. REFERENCES

- [1] R.C. Reid, J.M. Prausnitz, B.E. Poling. "The Properties of Gases and Liquids, McGraw-Hill: New York", 1986.
- [2] M.J. Astle, J.A. Zaslowsky. *Ind. Eng. Chem.*, 1952; 44, 2867–2871.
- [3] M. A. Tike, A. M. Gharde and V. V. Mahajani, "Studies to aid process development for the manufacture of neopentyl glycol from isobutyraldehyde: aldol condensation followed by hydrogenation" *Asia-Pac. J. Chem. Eng.* 2008; 3: 333–346.
- [4] Y. Mikio, M. Gen, W. Kumiko. JP Patent, 3193738, 1991.
- [5] Don L. Morris; Billy W. Palmer; Thomas W. McAninch, all of Longview, Tex. "Process for the production of neopentyl glycol" *Eastman Kodak Company, Rochester, N.Y.* 4,855,515.
- [6] Roger L. Wright Longview, Tex. "Process for the purification of Neopentyl Glycol" 4021496.
- [7] Koivusalmi, E., Hakanpää-Laitinen, H., Haatainen, E., Saarela, T., & Kilpeläinen, I. (2000). "Quantitative analysis of the compounds in synthesis mixtures of 2,2-dimethyl-3-hydroxypropionaldehyde by RP-HPLC and GC. *Chromatographia*", 52(1-2), 22–26.

APPENDIX

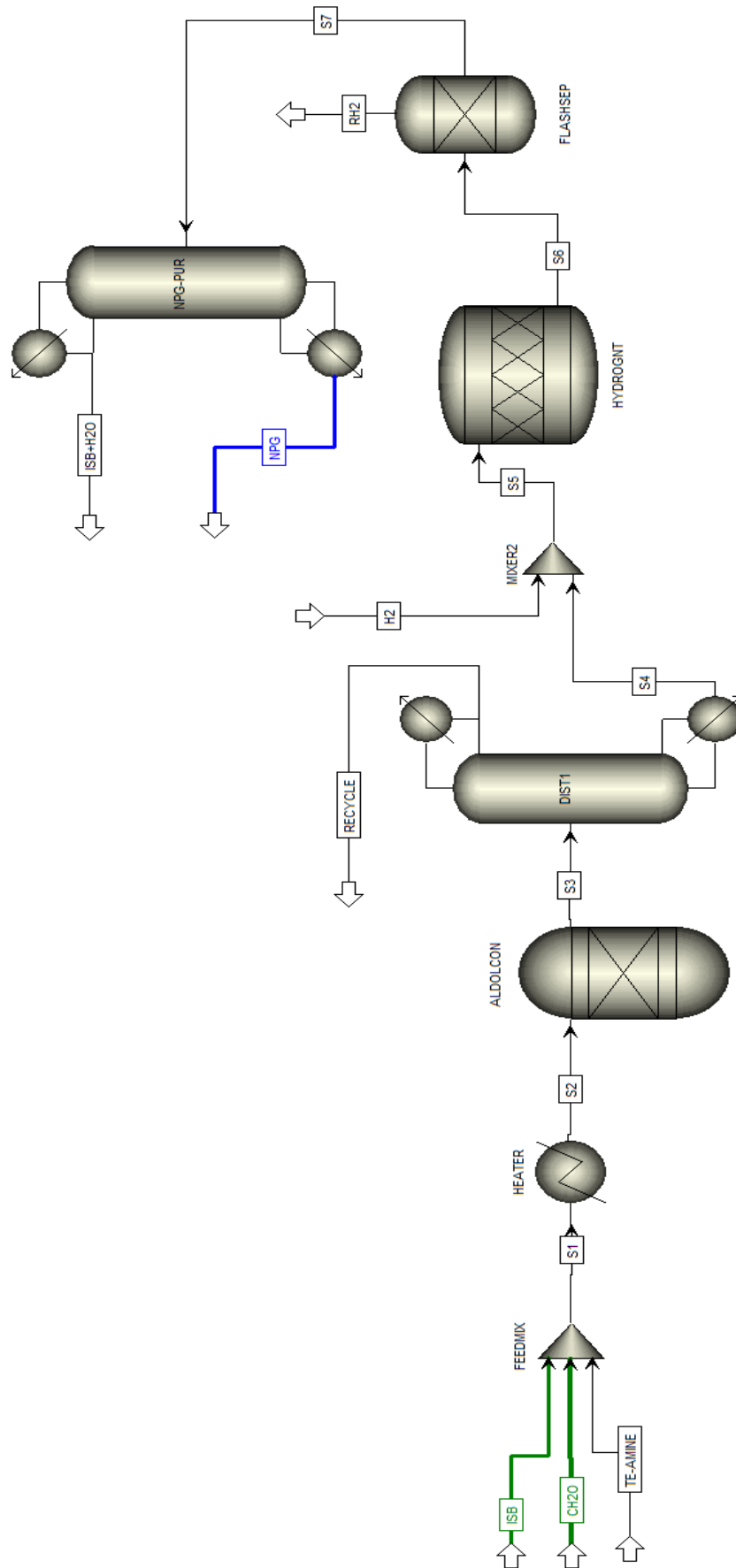


Figure I: Process Model for manufacture of Neopentyl glycol

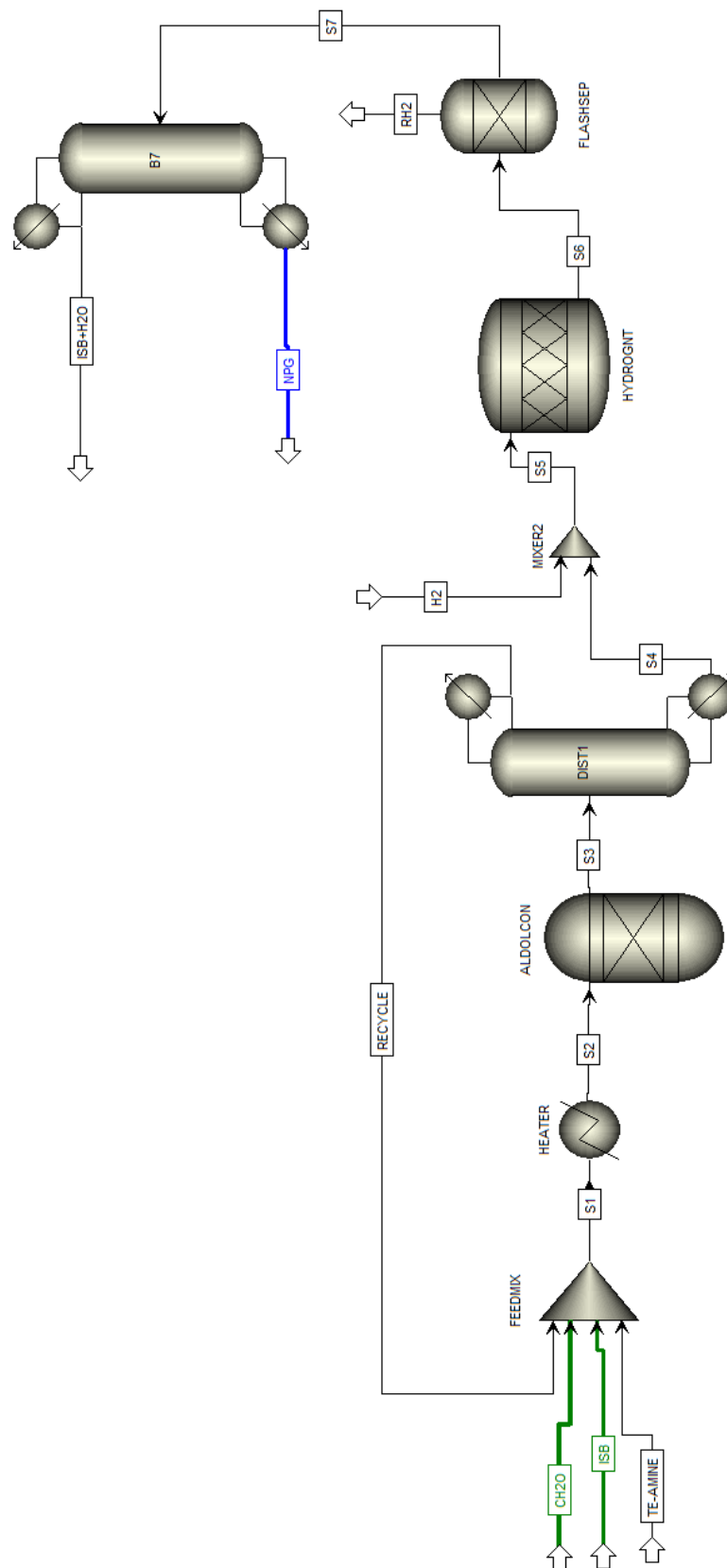


Figure II: Process model with attempted recycle