

SEPARATION OF FISCHER-TROPSCH WAX FROM CATALYST BY SUPERCRITICAL  
EXTRACTION

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## **Executive Summary**

The proposed process of using supercritical fluid extraction in conjunction with the Fischer-Tropsch slurry bubble column reactor has been examined using the ASPEN Plus<sup>®</sup> simulator by the research group at North Carolina State University. Qualitative results have been obtained for varying the following process parameters: solvent-to-wax ratio, solvent type (pentane or hexane), extraction temperature and pressure, and recovery unit temperature and pressure. The region of retrograde behavior was determined for pentane and hexane. Initial results show hexane to be the superior solvent; compared to pentane, hexane requires lower quantities of solvent makeup (the amount of solvent which needs to be added to account for solvent that cannot be recycled), and also results in a lower average molecular weight of slurry in the reactor. Studies indicate that increasing the extraction temperature, extraction pressure, recovery temperature, or solvent to wax ratio decreases the amount solvent makeup required. Decreasing the recovery pressure was found to decrease the makeup flowrate.

## Technical Objectives

The objective of this research project is to evaluate the potential of SCF extraction for separating the catalyst slurry of a Fischer-Tropsch (F-T) slurry bubble column (SBC) reactor into two fractions: (1) a catalyst-free wax containing less than 10 ppm particulate matter and (2) a concentrated catalyst slurry that is ready for recycle or regeneration. The wax will be extracted with a hydrocarbon solvent that has a critical temperature near the operating temperature of the SBC reactor, i.e., 200-300 °C. Initial work is being performed using n-hexane as the solvent. The success of the project depends on two major factors. First, the supercritical solvent must be able to dissolve the F-T wax; furthermore, this must be accomplished without entraining the solid catalyst. Second, the extraction must be controlled so as not to favor the removal of the low molecular weight wax compounds, i.e., a constant carbon-number distribution of the alkanes in the wax slurry must be maintained at steady-state column operation.

To implement our objectives, the following task structure is being implemented:

### Task 1: Equilibrium Solubility Measurements

- a. apparatus modification and construction.
- b. experimental measurement of selected model systems.
- c. catalyst/wax separation studies.

### Task 2: Thermodynamic Modeling

- a. programming and testing of SAFT equation for nonassociating systems.
- b. programming and testing of SAFT equation for associating systems.
- c. modeling measured results with the SAFT equation.
- d. pure component and mixture SAFT parameter determination for selected model systems.

### Task 3: Process Design Studies

- a. integration of our SAFT program into a process simulation package.
- b. process configuration studies using above simulation package.

## **Detailed Description of Technical Progress**

### Task 1a. Apparatus Modification and Construction

No effort planned this quarter.

### Task 1b. Experimental Measurements for n-Hexane/Hexadecanol System

Experiments on the n-hexane/hexadecanol binary are nearly complete. Results will be reported upon completion of experiments.

### Task 1c. Catalyst/Wax Separation Studies

No effort planned for this quarter.

### Task 2a and 2b. Programming and Testing SAFT for Nonassociating and Associating Systems

No effort planned for this quarter.

### Task 2c and 2d. Modeling VLE Data

Modeling of hexane/hexadecanol will commence upon completion of experiments.

### Task 3. Process Design Studies

Several parameters for the supercritical Fischer-Tropsch (F-T) extraction were studied using the Aspen Plus<sup>®</sup> simulation program. Parameters studied included solvent-to-wax ratio, solvent type (n-hexane and n-pentane), extraction temperature and pressure, and recovery temperature and pressure. The solvent n-octane was also studied. However, not enough data was collected to make a comparison because difficulties were encountered in converging the runs. Steady state solutions for n-hexane and n-pentane were converged with both recycle of wax to the reactor and solvent to the extraction unit. Figure 1 shows a simplified schematic of the Aspen Plus flowsheet.

A mixing unit and a flash unit were used to model the reactor, which was held at a constant temperature and pressure of 230 °C and 10 atm, respectively. The mixing unit

combined a continuous Anderson-Schulz-Flory product distribution ( $\alpha=0.95$  for n-paraffins only) and the recycled product from the extraction unit. Two other flash units were used to model the extraction and the recovery of products. A makeup feed stream was required to maintain a constant solvent-to-wax ratio.

All simulations were modeled with the Redlich-Kwong-Soave (RKS) equation of state. The  $k_{ij}$  values used for the runs were set to zero. Future plans involve using  $k_{ij}$  values correlated to carbon number and temperature. Estimated critical constants (Tsonopoulos and Tan, 1993) were used for n-paraffins greater than C24. Antoine constants (Stephenson and Malanowski, 1987) were also added to the program.

The first series of studies involved finding the retrograde temperature region for the n-hexane and n-pentane solvents at a 20:1 solvent-to-wax ratio. This was done by selecting an extraction temperature and pressure and then raising the temperature in the recovery unit by increments of 5 °C. The pressure in the recovery unit was held at the same pressure as the extraction unit. If a retrograde region was observed, the extracted heavy waxes were selectively condensed in the recovery unit. The runs were compared by looking at the makeup flowrate required to maintain the 20:1 solvent-to-wax ratio. Figures 2 through 5 compare the makeup flowrates required for each run. The average molecular weight of the slurry leaving the reactor was also used as a standard of performance.

For n-hexane, retrograde regions are observed at temperatures and pressures between 535-575 K (262-302 °C) and 40-50 atm, respectively. For n-pentane, retrograde regions are observed at temperatures and pressures between 515-530 K (242-257 °C) and 50-60 atm, respectively. The results indicate that higher pressures, lower temperatures, and larger solvent size (n-hexane) require lower makeup flowrates.

Although the solvent makeup flowrate may be lowered by changing certain variables, the process still requires large quantities of solvent in comparison to product made (1000 kmol/hr basis) in the reactor. The makeup flowrate indicates how much solvent is lost in the process, either through the vapor stream from the reactor or the recovered liquid stream from the recovery unit. The solvent from these streams could ultimately be recovered and used for the makeup stream. However, any recovered solvent would require recompression and therefore increase energy requirements. The amount of

solvent circulated in the recycle loop also gives a qualitative indication of sizing requirements. As the amount of makeup feed increases, the amount circulating in the recycle loop increases, leading to larger sizing requirements and costs.

Average molecular weights of the slurry leaving the reactor are also compared for the retrograde runs. For n-pentane and n-hexane runs, the average molecular weights (AMW) range from 375 to 546 and 316 to 438, respectively. Higher carbon number solvents (n-hexane) and higher extraction pressures for each solvent lower the AMWs. For n-pentane, the average AMWs are 540.28 and 436.61 at extraction pressures of 50 atm and 60 atm, respectively. For n-hexane, the average AMWs are 426.41 and 353.92 at extraction pressures of 40 atm and 50 atm, respectively.

In addition to the retrograde runs, several other conditions were simulated using n-hexane as the solvent. These included runs where the pressure was decreased in the recovery unit. The lowest amount of makeup solvent found in initial tests (17,702 kmol/hr) was observed for n-hexane with the following conditions: 20:1 ratio, extraction temperature and pressure of 585 K (312 °C) and 50 atm, and recovery temperature and pressure of 565 K (292 °C) and 40 atm. Using this run as a base set, we systematically changed each of the variables in five sensitivity studies. Tables 1-5 summarize the results for each of these studies. In each table the bold type depicts the base set. Three runs of the sensitivity analysis were found to give lower flow rates than the base set.

The results of the sensitivity studies indicate that increasing extraction temperature, extraction pressure, recovery temperature, or solvent-to-wax ratio results in a decrease of makeup flowrate. Decreasing recovery pressure also decreases solvent makeup flowrate. In the retrograde runs, similar results are observed for the effect of separation pressure but opposite results are observed for the separation temperature. These differences may be attributed to the differences in the combination of extraction and recovery conditions.

For the sensitivity studies, AMWs do not change significantly (by more than 30) with changing extraction and recovery conditions. The largest increases in AMW are observed by decreasing the solvent-to-wax ratio. The lowest ratio (6:1) has an AMW of 473 while the highest ratio (20:1) has an AMW of 391.

Table 1. Results of varying the separation temperature for n-hexane.

<b>Tsep (K)</b>	<b>Psep (atm)</b>	<b>Tcond (K)</b>	<b>Pcond (atm)</b>	<b>Ratio Solvent:Wax</b>	<b>Makeup Flowrate (kmol/hr)</b>	<b>Average Molecular Weight</b>
570	50	565	40	20	21,616	371
575	50	565	40	20	22,610	383
580	50	565	40	20	21,038	389
<b>585</b>	<b>50</b>	<b>565</b>	<b>40</b>	<b>20</b>	<b>17,702</b>	<b>391</b>
590	50	565	40	20	12,501	385

Table 2. Results of varying the separation pressure for n-hexane.

<b>Tsep (K)</b>	<b>Psep (atm)</b>	<b>Tcond (K)</b>	<b>Pcond (atm)</b>	<b>Ratio Solvent:Wax</b>	<b>Makeup Flowrate (kmol/hr)</b>	<b>Average Molecular Weight</b>
585	38	565	40	20	946,000	410
585	40	565	40	20	307,000	415
585	42	565	40	20	156,000	421
585	44	565	40	20	89,117	423
585	46	565	40	20	53,304	420
585	48	565	40	20	32,097	411
<b>585</b>	<b>50</b>	<b>565</b>	<b>40</b>	<b>20</b>	<b>17,702</b>	<b>391</b>

Table 3. Results of varying the recovery temperature for n-hexane.

<b>Tsep (K)</b>	<b>Psep (atm)</b>	<b>Tcond (K)</b>	<b>Pcond (atm)</b>	<b>Ratio Solvent:Wax</b>	<b>Makeup Flowrate (kmol/hr)</b>	<b>Average Molecular Weight</b>
585	50	535	40	20	503,000	428
585	50	540	40	20	58,504	415
585	50	545	40	20	34,634	420
585	50	550	40	20	27,910	418
585	50	555	40	20	24,093	412
585	50	560	40	20	20,990	403
<b>585</b>	<b>50</b>	<b>565</b>	<b>40</b>	<b>20</b>	<b>17,702</b>	<b>391</b>

Table 4. Results of varying the recovery pressure for n-hexane.

<b>Tsep (K)</b>	<b>Psep (atm)</b>	<b>Tcond (K)</b>	<b>Pcond (atm)</b>	<b>Ratio</b>	<b>Makeup</b>	<b>Average</b>
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				<b>Solvent:Wax</b>	<b>Flowrate (kmol/hr)</b>	<b>Molecular Weight</b>
585	50	565	36	20	13,761	401
585	50	565	38	20	15,454	397
<b>585</b>	<b>50</b>	<b>565</b>	<b>40</b>	<b>20</b>	<b>17,702</b>	<b>391</b>
585	50	565	42	20	22,009	383
585	50	565	44	20	32,737	374
585	50	565	46	20	78,310	371
585	50	565	48	20	1,120,000	404

Table 5. Results of varying the solvent-to-wax ratio for n-hexane.

<b>Tsep (K)</b>	<b>Psep (atm)</b>	<b>Tcond (K)</b>	<b>Pcond (atm)</b>	<b>Ratio Solvent:Wax</b>	<b>Makeup Flowrate (kmol/hr)</b>	<b>Average Molecular Weight</b>
585	50	565	40	6	430,000	473
585	50	565	40	8	184,000	458
585	50	565	40	10	110,000	446
585	50	565	40	12	73,891	435
585	50	565	40	14	52,370	426
585	50	565	40	16	38,049	416
585	50	565	40	18	27,295	406
<b>585</b>	<b>50</b>	<b>565</b>	<b>40</b>	<b>20</b>	<b>17,702</b>	<b>391</b>

### Plans for Next Quarter

Phase equilibrium experiments on the hexadecanol/hexane binary will be completed, and modeling of the hexadecanol/hexane data will commence. Further process design studies will include using n-heptane as the supercritical solvent. Retrograde condensation conditions in the recovery unit will be studied using both increases in temperature and decreases in pressure. Also, for next quarter, we plan to look at the effect of a second recovery unit.

## References

Stephenson, R.M.; Malanowski, S. Handbook of the Thermodynamics of Organic Compounds, Elsevier Science Publishing Company, New York **1987**.

Tsonopoulos, C.; Tan, Z. "The Critical Constants of Normal Alkanes From Methane to Polyethylene II. Application of the Flory Theory" *Fluid Phase Equilibria* **1993**, 83, 127-138.

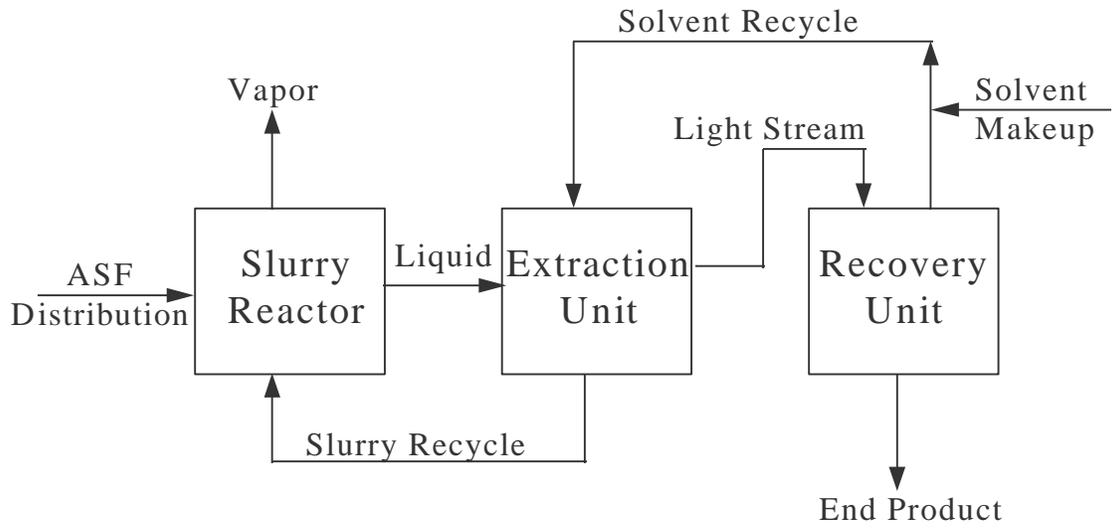


Figure 1. Aspen Plus Flowsheet for the Supercritical Fischer-Tropsch Separation.

## Makeup Flowrates for Pentane Retrograde Runs - Separation and Recovery P = 50 atm

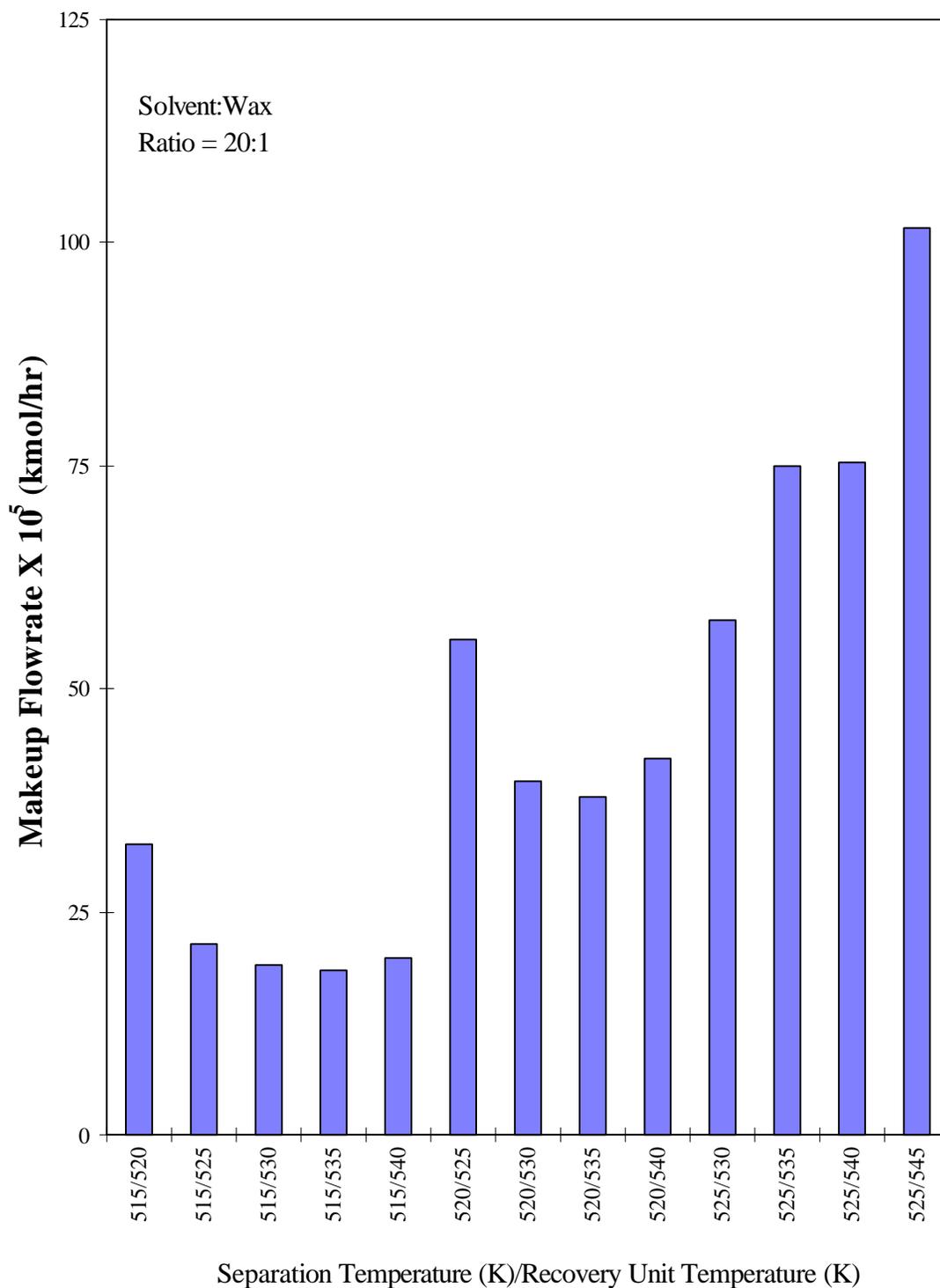


Figure 2. Makeup Flowrates for Pentane Retrograde Runs at 50 atm.

### Makeup Flowrates for Pentane Retrograde Runs - Separation and Recovery P = 60 atm

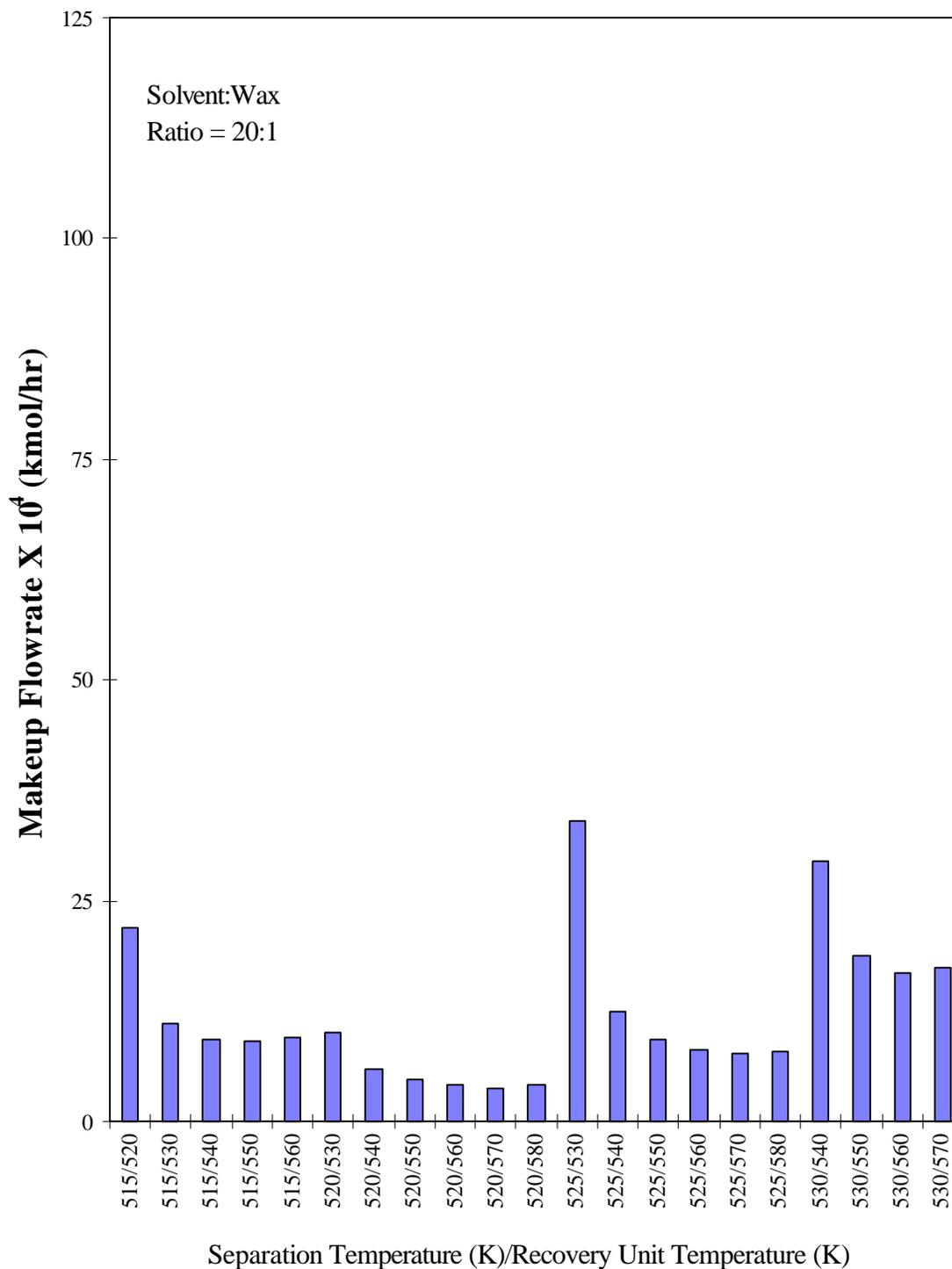


Figure 3. Makeup Flowrates for Pentane Retrograde Runs at 60 atm.

### Makeup Flowrates for Hexane Retrograde Runs - Separation and Recovery P = 40 atm

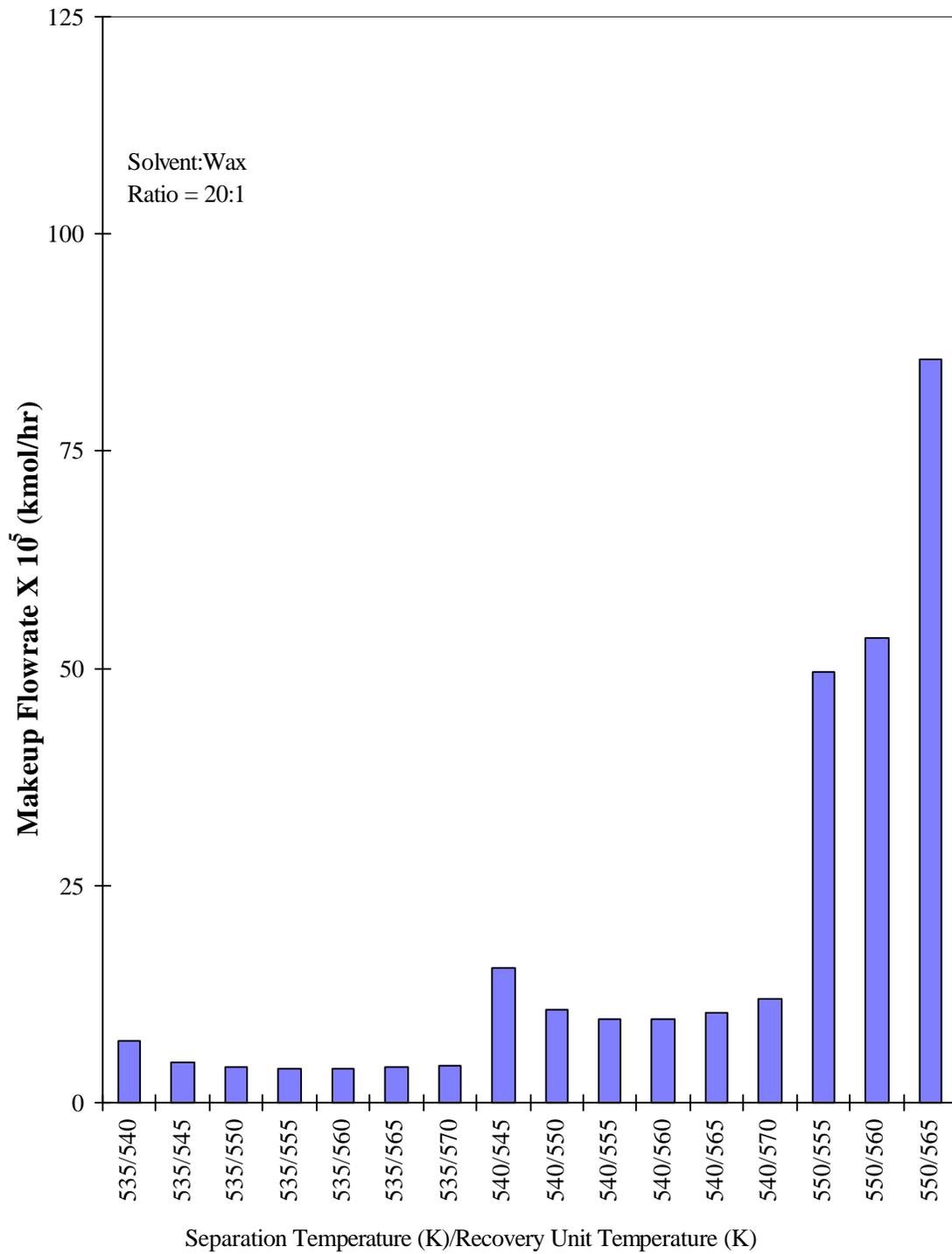


Figure 4. Makeup Flowrates for Hexane Retrograde Runs at 40 atm.

## Makeup Flowrates for Hexane Retrograde Runs - Separation and Recovery P = 50 atm

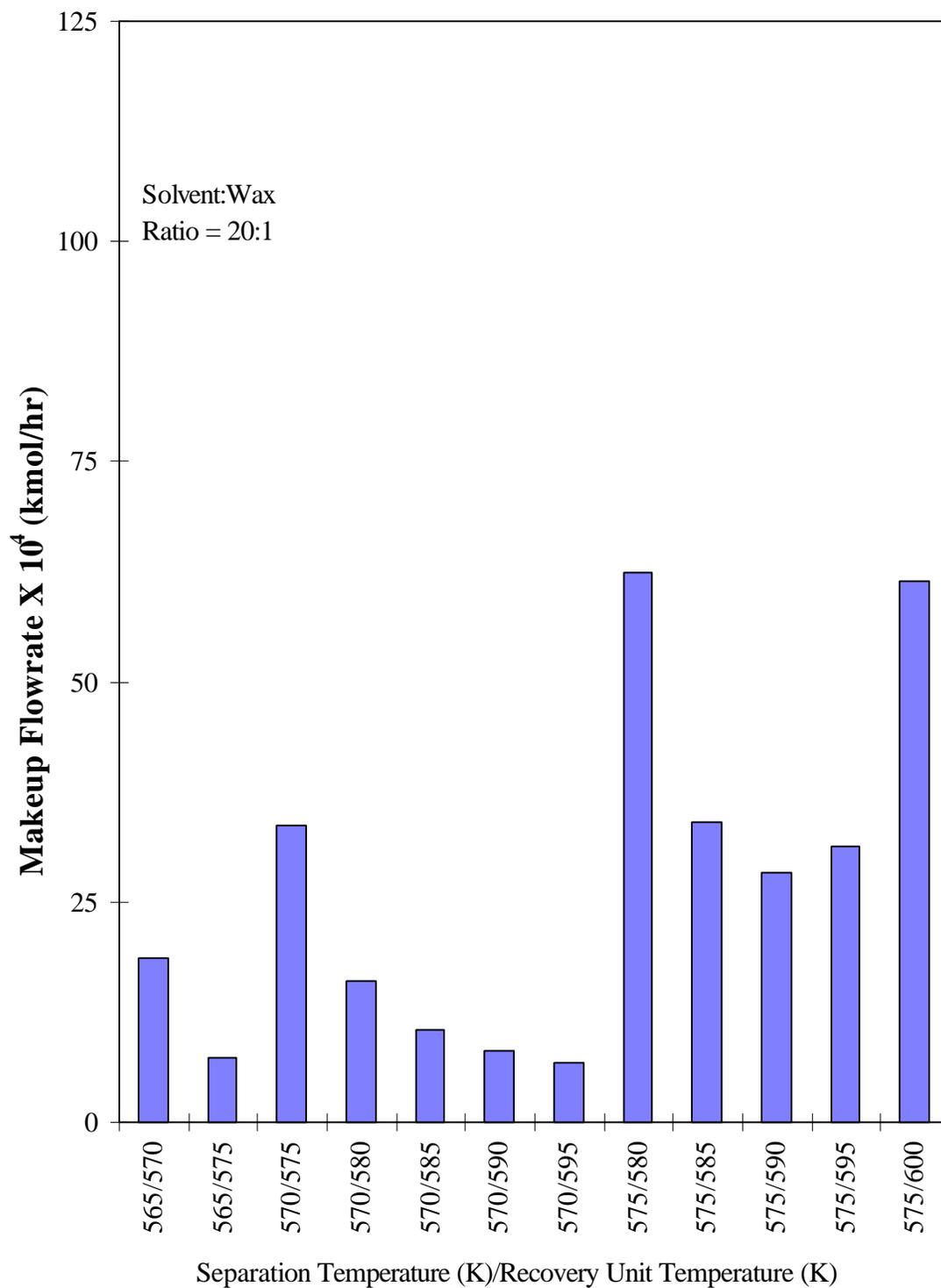


Figure 5. Makeup Flowrates for Hexane Retrograde Runs at 50 atm.