EM-63-21 QUINACRIDONES - ENGINEERING STUDIES: Solvent recovery; p-Toluidine handling; TFA process; Py
Filtration; Drying By: A. M. Auster 1961 - 1963

1/79 (1)

N40659

E. I. DU PONT DE NEMOURS & COMPANY

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TECHNICAL SECTION - COLORS

NEWPORT PLANT

PIGMENTS COLORS PROGRESS REPORT

SUBJECT: QUINACRIDONES - ENGINEERING STUDIES
Solvent Recovery
Para-toluidine Handling
TFA Process
Pyrolysis
"Sitol" Solution
Filtration
Drying

PERIOD COVERED: 1961 - 1963

DATE: MAY 20, 1965

P.T. KN-63-21

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SUBMITTED BY: A. M. AUSTER DATE SUBMITTED: 1963

APPROVED BY: H. H. GYORGY DATE ISSUED: 5/20/65

ABSTRACT

Status of QA engineering studies.

TABLE OF CONTENTS

Solvent Recovery

I. Wet Methanol Recovery

A. Capacity

The capacity, in terms of QA production, has not been determined recently. So far, 75 still has not limited production and is not a bottleneck at 36M lb. QA/month. A feed rate of 2,400 lb./yr. (approx. 300 gph) was measured prior to steam revisions (NB-5089-9). The filtrate tanks, H and J, hold a combined total of about 8,200 gallons. From the above, a 27 hour cycle results. Since the current maximum feed rate is higher than 300 gph, the unit is able to keep up with production.

Feed rate is limited by pressure drop and methanol bottoms concentration. Steam feed rate is not controlled, reflux is controlled by top temperature and feed is set to maintain between 10 and 12" H_2O P across the column as well as 102°C. minimum bottoms temperature. Normal feed valve setting is 1.4-1.5. Under these conditions, the still is operating at maximum capacity with incipient flooding. No more still capacity is possible without changing packings. If it is ever necessary, I suggest "Glitch Grid" Type E-25 in 304 S/S. Based on current sales forecast and a reduction of filtrate after the installation of the new filter, new capacity should not be required.

B. Methanol Purity

Current purity is in the neighborhood of 90+% methanol product. Dimethyl DQA oxidation requires 98+%. To achieve this degree of purity, take the following approach:

1. Cut feed rate to 1.0-1.2 on valve
2. Raise automatic reflux controller sensitivity to "High" for on-off control
3. Set top temperature pointer to 65°C
4. Check overhead purity and reset pointer as needed.

This system will cause the still to cycle badly, but when feeding only 250 gph of 15% methanol feed - 37.5 gph pure MeOH - a variation of only one gph in overhead takeoff will upset the purity. This sensitive control cannot be readily achieved in the steady state, so cyclic control is necessary.

II. Pyrolysis Dowtherm Recovery

Some Dowtherm from the bottom of the pyrolysis column is collected in "F" tank for reuse in subsequent pyrolyses. This type of recovery is "free" and should be exploited to its limit. Past attempts to increase recovery in this area showed suspicious affects on yield and were dropped. It a demister system is installed to reduce or eliminate non-volatile contaminants, and if the DPU removal system continues to operate properly, a further attempt to increase recovery should be tried. This will both increase available Dowtherm, reduce the load on 74 still, and further concentrate DPU in 65-58 tank. A controlled program should be started to stagewise reduce offtake to 65-58, while maintaining close watch on yield and quality. At least a 50% reduction in offtake to 65-58 tank (150-200 gallons) should be possible.

III. 74 Still Operation

A. DPU System Alcohols

A real effort should be made to dispose of cascade alcohols without redistillation in 74 still. Current Dowtherm concentration in this stream is about 10% in a 60-100 gallon stream. If the concentration can be reduced below 5% by reducing cascade top temperature set point, the stream should be thrown away. When this is done, the forecut from 74 still to the sewer should be eliminated. In its place, substitute a long intermediate cut - 140°C. at 240 mm to the intermediate tank.

B. Pyrolysis Distillate Recovery

Inasmuch as this is the most difficult distillation, first efforts should be made to minimize PD by redcuing 65-58 product and by throwing away cascade alcohols.

A normal charge will contain PT, intermediate tank material, and "A" tank Dowtherm. Our present procedure calls for starting up the still at 240 mm absolute pressure, automatic top temperature control set at 90°C. Product flows to the sewer until top temperature reaches 90°C. where still goes on total reflux. Top temperature is reset to 140°C. and alcohols and Dowtherm is stripped to the intermediate tank. This saves Dowtherm and also keeps alcohols out of 65-58. The still is then set on manual reflux control at 160 mm and a Dowtherm intermediate cut is taken to 65-58 until it is aniline free. Good Dowtherm is then stripped under very little reflux to "G" tank.

B. Pyrolysis Distillate Recovery (Continued)

The above procedure is satisfactory for the present but it would be helpful to investigate intermediate cut (65-58) specifications and procedure. It would shorten the intermediate cut considerably if the aniline specification could be raised.

Something to keep in mind - traces of basic nitrogen compounds can be removed from Dowtherm more efficiently with acid resins than by distillation. Possibly the intermediate cut could be purified this way, avoiding continued recycling.

Also, since 65-58 tank PD is now 99+% Dowtherm, check this first for reuse in pyrolyses after filtration only, and secondly after filtration and acid resin extraction. The 1% alcohols would be removed on heat-up of the pyrolysis vessel.

C. "A" Tank Dowtherm Recovery

Occasionally, the still is charged with a full tank of Dowtherm contaminated only with heavy residues. This type of distillation is very fast and requires only a minimum controlled reflux of about 300-500 pph. This serves only for de-entrainment purposes. Even with a manually set signal on the product control valve, it is hard to maintain low constant reflux. I suspect the valve trim should be changed to linear rather than equal percentage type for better control in the low range.

D. Methanol Recovery

This operation is the least trouble of all since mid-column feed was started. Feeding the column provides rapid cool down and minimizes reflux requirements.

The plant wants this operation to be as completely automatic as possible. I have suggested, and the plant is going to install, the following control system:

a. Reflux will be controlled by temperature in the mid-upper section of the column. Top temperaturesis out since methanol purity cannot be controlled at its own boiling point. Set point should be only a fraction above the boiling point - 66°C.

b. Column feed will be automatically controlled by bottom column temperature. The optimum set point will have to be determined by trial and error with current temperatures used as a guide.

c. Boil-up, as as present, will be controlled by column $\triangle$ P.

D. Methanol Recovery (Continued)

This system is designed to control itself after start-up through its entire operation and finally shut itself down by going on total reflux. Occasionally, now, an operator is not present when feed runs out, allowing the MeOH storage tank to be contaminated with Dowtherm. The whole tank then has to be redistilled.

Magenta

I. Equipment

A. Cooling System

Paratoluidine distilled from 62 tank freezes at 45°C. when pure. This creates plugging problems in the overhead condenser. Water, even heated, is not usable as a cooling medium. Steam cannot be added to the recirculating cooling water without over-running the cooling tower and not enough purchased water is available. Cold Dowtherm, temperature-controlled by the Dowtherm cooler will be used. A set point will have to be determined but about 40°C. can be used to start.

Due to lower $\triangle T_{Lm}$ and lower film coefficient for Dowtherm, the capacity of the condenser will be reduced and distillation rate will have to be reduced accordingly. This should be determined in practice.

It would be helpful to raise the pressure in the column overhead vapors to 40 mm, increasing temperature, T_{Lm}, and condenser capacity. Laboratory studies at 40 mm distillation pressure showed little effect - N.B. 5090. Another method of raising vapor temperature and lowering freezing point is to operate initially at no reflux, reducing p-oluidine purity. Lower distillation rates also have the effect of raising top column pressure and temperature by lowering column pressure drop.

If TFA catalyses is used at 50% toluidine excess (versus current 300%), overhead purity will be too low to create a problem. Water can be used for cooling. Optimum distillation conditions will have to be determined. Use minimum distillation time as a criterion since time effects yield in the presence of TFA. Hint - use minimum reflux rate, maximum boil-up and about 350 gallons of distillate at end.

B. Paratoluidine Handling System

The "Tote" tanks used for handling p-toluidine are novel in that they are the first steam heated liquid tanks Tote has built. They are also the first to incorporate a flush bottom ball valve. Only one heating plate coil was used for ease of construction and maintenance. It should be sufficient to melt the contents in about eight hours. I am relying on the insulating effect of the solid on the walls to prevent heat escape. Temporary insulation may be required - asbestos blankets. The plate-coil is the heaviest available and will take our 150 psig steam. This should be tested prior to filling tanks. The tanks should also be tested full of water. The flush type ball valve design will minimize freeze-up tendencies, but in practice, it may have to be heated to start flow. All fill lines are steam jacketed.

The tanks will be unloaded into second floor storage tanks 62-9 and 12 by vacuum. Transportation to and from Orchem will be by company truck - contact N. Jedlicka and W. Sutton for arrangements. Also contact W. Huxtable, Orchem, Dyes and Chemicals Office, Telephone 8-172-388.

C. Centrifuge Bag

"Teflon" bags tear in this service and no other common fiber is usable. No explanation for "Teflon" failure is apparent. J. Flood and J. C. Chaney are looking at replacements. As a last resort, a solid bowl could be used but this presents a cleanout problem. Check manufacturers of fiberglass cloth, graphite or spun silicate fabrics. So far it appears that the TFA process requires no filtration.

D. Wet Methanol Recovery

The Magenta (2,9 dimethyl DQA) oxidation requires 99% methanol. Before producing this, 75 still should be adjusted to see if we can produce this purity. Especially determine capacity under these purity conditions.

E. TFA Process

Obviously, we should expedite development of the TFA process since it bypasses the disadvantages of the PTSA process and eliminates the capacity penalty. Laboratory development has yet to be taken through the quality evaluation stage. So far, the process looks good.

Aniline Condensation - Distillation

I. Standard Process

Little has been accomplished recently by modifying the existing process aside from installation of the DAT hold tank. A small distillation cycle reduction accrued from raising the maximum heating jacket Dowtherm from 50°C. to 70°C. Lowering the aniline:SSE mole ratio from 7:1 to 5:1 helped significantly (XOR-105) but was discontinued because it may have been causing lower yield. This XOR can be reopened if necessary.

Reflux control via top temperature was tried but showed no cycle advantage over hand control. I do not recommend any further work in this area.

Some help may be obtained by using the reboiler installed for continuous aniline distillation to boil up column bottoms. This increases boil-up to the limit of column capacity at 25 mm, aiding separation. The problem here is controlling boil-up to maintain 25 mm. It is easy to overrun this point with the reboiler since only hand control is available. Operation of this system is obvious by inspection. Start-up and shut-down procedures should be designed to keep the reboiler full of liquid to minimize operating effort.

II. Continuous Aniline Distillation

The purpose and test results of this system are described in attached XOR-77 and its Closing Report. Original calculations are contained in TS Notebook 2078. Test data is still in its original form in A-10 engineers' office file. Detail drawings NPD-10188, 10191, and 10190 describe the system. Copies are in the aniline distillation file.

Since 62 tank capacity is no longer needed, it will be some time before the system is again operated, especially if TFA shortens the distillation cycle. However, since this type of distillation provides minimum DAT retention at distilling conditions, it is reasonable to expect increased yield. This is especially true if integrated into a continuous condensation, distillation, pyrolysis sytem.

I recommend that TFA development precede any further distillation study since it provides more immediate benefits and it increases probability of success of continuous aniline stripping by lowering aniline concentration. Further discussion is contained in the TFA section.

II. Continuous Aniline Distillation (Continued)

If continuous distillation follows TFA development, the only problem to be considered is separation of TFA from Dowtherm. Batch distillation shows that TFA distills after aniline in both standard and dimethyl DAT synthesis. TFA distills early from a DiCl DAT mass. Since no prediction methods are available, the extent of this problem can only be determined by laboratory or plant test. From observation, I expect that lower initial aniline concentration will more than compensate for TFA tails.

If continuous distillation is tried with catalyst neutralization, problems of DAT solution and carbonate filtration present themselves. DAT is difficult to solubulize after cooling, but this can be done by heating to 115-120°C. and holding about one-half hour. Overheating may cause yield loss. Carbonate filtration will require installation of the vertical tank, vertical leaf, sluicing filter stored in A-208. The complicated nature and operation of this filter is dictated by the hard filtering nature of the cake and by safety considerations in handling aniline-Dowtherm solution.

Operation is straightforward up to the point of unloading carbonates from the aniline - Dowtherm - DAT solution in the filter at the end of a distillation. At this point, there is DAT and aniline in the filter and DAT in 62 column which must be purged to the pyrolysis tank. This should be done first by blowing the filter down as far as possible with N_2, flushing with a 50-gallon flush, and repeating the cycle. The DAT - aniline - Dowtherm will be pushed into the column, stripping out the aniline. DAT will be purged from the bottom of the column by a stream of hot Dowtherm from 65 column bottoms. The 65 column bottoms stream will also be tied into the filter feed line where it can serve as an intermittent flush stream.

When aniline is purged from the filter, carbonates are unloaded to the centrifuge by flushing with Dowtherm through the sluicing nozzle. The centrifuge will send any remaining DAT and Dowtherm to the pyrolysis and retain solids to be unloaded manually as at present. The filter is somewhat oversize and should hold two batches before unloading. Valving during purging, sluicing, unloading operations is complicated and critical. A detailed operation procedure will have to be worked out.

II. Continuous Aniline Distillation (Continued)

The 65 column bottoms purge stream is necessary to both the distillation as discussed in XOR-77 and monthly reports and to flushing as above. This means that a system will have to be worked out to split this stream between "F" tank and 65-1 at atmospheric pressure and 62 column under vacuum. This can be handled with a pressure regulation valve going to 62 column and check valves to "F" and 65-1 for protection.

The bottoms reboiler circulation pump is not now hooked up. Even when reinstalled, the pump circulation rate is suction head limited due to low vacuum operation, however, it can be satisfactorily operated by throttling the reboiler dischage line valve. Before reinstalling, it is worthwhile to consider ways of increasing NPSH.

III. TFA Catalysis

Development of the TFA catalysis route is covered in monthly reports and in TS Notebook 5090. The attached tables list all experiments from inception to date and are taken from the monthly reports. Original laboratory sheets and further information can be found in the "DAT Catalyst Neutralization" file.

TFA catalysis has the following benefits:

1. Eliminates catalyst neutralization and watersremoval saving at least three hours cycle time.

2. Cuts distillation time from 6-8 hours to 2-3 hours by reducing excess aniline.

3. Eliminates tank cleanout after transfer saving 1/2 - 1 hour.

4. Eliminates centrifuge solids saving cleanout labor.

5. Increases DQA yield about 1% saving $8-10M/year ingredients.

6. Makes consistently good fluorescence DQA and should be less "accident-prone" than the present process.

In addition to the above, the standard reaction rate is fast enough with TFA (about 15 minutes to completion at 85°C.) to consider a small, continuous reactor in place of 62 tank.

A. Corrosion

Under certain conditions, TFA will attack steel, forming a black residue which will spontaneously ignite in air at about 130°C. This effect accounted for failure of the plant TFA - continuous aniline distillation test. Simple refluxing of a TFA - aniline - Dowtherm mixture through steel packing did not show this effect, but a complete distillation cycle showed a fast reaction forming black residue near the end of distillation. Corrosion of steel in aniline - TFA - Dowtherm at 100°C. is 7 mpy average with localized pitting (Notebook 5090-115). These phenomena may be explained by the chemical bonding of TFA by aniline as a neutral salt except when the salt is decomposed during distillation, leaving it free to attack the packing.

316 stainless steel, the tower lining material, hardly affected by either dry distillate vapors (vapor line conditions - see Notebook 5090-63) or refluxing conditions in aniline or substituted anilines service (Notebook 5090-116). 316 stainless steel then is an acceptable packing material. Hastelloy C and Inconel, materials in the reaction vessel and condenser tubes respectively, are also satisfactory in their services (Notebook 5090-115).

A storage test of aniline - Dowtherm - TFA was not done in the laboratory. However, weak aniline distillation from semi-works tests containing aniline, Dowtherm, TFA and o-cl aniline, Dowtherm, TFA have been stored on the dump since May, 1963. They should be emptied and inspected shortly.

B. Distillation

TFA - aluminum salts probably successively decompose and recombine during distillation depending on temperature and aniline concentration. Observations are that TFA begins to distill from aniline at about 120°C. and from o-cl aniline and p-toluidine about 100°C. In all cases, some TFA strings along behind after aniline has apparently distilled. This will slightly lengthen distillation cycles. In any case, since long hold times, especially in the presence of TFA, reduces yield, the shortest possible plant distillation cycle must be developed. A plant test using TFA, 3:1 ratio aniline:SSE and neutralizing catalyst would help (see reference letter AMA to AAB attached).

C. Catalyst Recovery and Re-use

This has been established in the laboratory for DAT, DiCl DAT and DiMe DAT syntheses. An acceptable procedure for analyzing and sampling plant distillates still has to be developed. The TFA salt will probably be crystalline in storage depending on distillate aniline concentration. Tank agitation with nitrogen may yield a representative sample. A laboratory procedure is available for analyzing TFA in aniline - Dowtherm but the accuracy of this test must be checked.

D. Laboratory TFA Process Development

This is geared first to meeting or surpassing standard PTSA process yields and secondly, taking advantage of increased TFA catalytic activity by reducing aniline excesses and/or hold times and/or catalyst amount. Also, the effect of fractional distillation times are checked. In all cases of longer than standard fractional distillation, yields are lowered but similar losses are true for the standard PTSA process. In Scarlet synthesis, a 6:1 mol ratio of o-cl aniline:SSE is apparently required versus 3:1 aniline:SSE in standard and Magenta syntheses. If this proves to be a true picture, it means only that the o-cl aniline condensation cycle will be longer than the others by added hold and distillation times. The process is still satisfactory. Experiments have not yet progressed into the distillation study (Notebook 5090-108 to 5090-114).

E. Semi-works Tests

These were run at 216% batch size DAT and DiCl DAT with TFA versus 216% DAT and 108% DiCl DAT with PTSA. Yield data is not available due to improper charging of the reaction vessels (SSE not dissolved). Operability was demonstrated (Colors Monthly Report 5-6/63).

Semi-works DQAs were laboratory oxidized to crudes showing little quality differences. Laboratory DQAs were also included in this evaluation. Laboratory millings of the above crudes showed very similar tints by rubout but TFA QAs showed light masstones, indicating undermilling (data sheets are attached). Obviously, these conclusions are preliminary and more oxidations with longer milling and rubouts against extended standards are required.

COPY

E. I. DU PONT DE NEMOURS & COMPANY

PIGMENTS DEPARTMENT

CC: A. A. Brizzolara
H. H. Gyorgy, Newport
A. M. Auster, "

NEWARK, NEW JERSEY
JULY 24, 1963

J. C. CHANEY
PIGMENTS
NEWPORT

TFA VERSUS PTSA QUALITY

Samples of laboratory oxidized β-QA and 4,11-dichlor-QA (from lab and semi-works TFA and PTSA catalyzed condensations) for dispersion milling in you 1-2/3 gallon mills were mailed to you last week. The oxidations of DQA to β-QA were all made on the high water formula. The "Higgins Oxidation" was used for making the 4,11-dichlo-QA. Below are listed the identification and rubouts of all samples:

Exp. No.	DQA Source	Yield (from 40g DQA)	Composite Sample for Milling
TSC-94-4A$_1$	TFA (Lab)	38.9g	TSC-94-4A
TSC-94-4A$_2$	TFA (Lab)	38.8g	TSC-94-4A
TSC-94-4B$_1$	PTSA (Lab)	39.1g	TSC-94-4B
TSC-94-4B$_2$	PTSA (Lab)	39.0g	TSC-94-4B
TSC-94-7A$_1$	PTSA (SW-00557)	38.9g	TSC-94-7A
TSC-94-7A$_2$	PTSA (SW-00557)	38.9g	TSC-94-7A
TSC-94-7B$_3$	TFA (SW-00558)	38.7g	TSC-94-7B
TSC-94-7B$_4$	TFA (SW-00558)	38.8g	TSC-94-7B
TSC-94-10A$_1$	PTSA (SW-00559)	39.2	TSC-94-10A
TSC-94-10A$_2$	PTSA (SW-00559)	39.4	TSC-94-10A
TSC-94-10B$_1$	TFA (4,11-Dichlor) (SW-00560)	39.4	TSC-94-10B
TSC-94-10B$_2$	TFA (4,11-Dichlor) (SW-00560)	39.3	TSC-94-10B

(Rubouts (Read by W. W. West)

TSC-94	Tint
$4A_1$ vs $4A_2$	99, B^2
$4B_1$ vs $4B_2$	=, B^2
$4B_1$ vs $4A_2$	96, B^5
$4A_2$ vs $4B_2$	105, Y^4
$4B_1$ vs $4A_1$	97, B^6
$4A_1$ vs $4B_2$	103, Y^4
$7A_1$ vs $7A_2$	98, =
$7B_3$ vs $7B_4$	108, D^4
$7A_1$ vs $7B_3$	112, D^6
$7A_1$ vs $7B_4$	110, D^6
A_1 vs A_2	99, I^4
B_1 vs B_2	99, =
A_2 vs B_1	104, B^9, D^4
A_2 vs B_2	103, B^7, D^8
B_2 vs A_1	98, Y^6, I^7
A_1 vs B_1	102, B^7, I^7

s/ W. A. WEST
TECHNICAL SECTION

WAW:mac/tmj

Date: September 12, 1963

WORK REQUEST

Special Instructions:

Rubouts - Beta Ext.

Sample**	Versus	*Rubout (Hoover-Muller, 5 x 50;150 lbs.) Masstone Value (Lt-Dk)	Masstone Hue R,Y,G,B	Masstone Chroma (Int-Dull)	Tint Str.	Tint Hue R,Y,G,B	Tint Chroma (Int.-Dull)	Analytical % Cl	Analytical % Sol.	Analytical % Ext. Sol.
94-4-A		v Lt (30)			98	SB 8	SD 7			
94-4-B	N-7003	v Lt (40)			98	v SB 4	v SD 4			
94-4-A	L-71452	v Dk (20)			95	SB 8	SD 7			
94-7-B		v Lt (40)			95	B 14	D 12			
94-4-A	94-4-B	Dk (10)			100	v SB 4	v SD 3			
94-7-A	94-7-B	v Dk (60)			100	s Y 7	VSI 5			

(*) If no difference in value, hue, or chroma perceptible, indicate as equal. Show difference by number, that is: vvs=1, vs=2-5, s=6-11, full=12-17, v full=18 and up.

(**) Combined samples A1 and A2 - See preceding letter WAW to JCC - July 24, 1963

Date: September 12, 1963

WORK REQUEST

Special Instructions: Use N-7003 - no extender to 94-4A, 94-4B, 94-7A, 94-7B.
For 94-10 samples, use 10% blanc fixe and rub against N-7010 dispersion mill scarlet std.

Sample	Versus	*Rubout (Hoover-Muller, 5 x 50;150 lbs.) Masstone Value (Lt-Dk)	Masstone Hue R,Y,G,B	Masstone Chroma (Int-Dull)	Tint Str.	Tint Hue R,Y,G,B	Tint Chroma (Int-Dull)	Analytical % Cl	Analytical % Sol.	Analytical % Ext. Sol.
94-4A	94-4B	Dk (10)								
94-4A	N-7003	v Lt (30)								
94-7A	94-7B	v Dk (20)								
94-7B	N-7003	v Lt (40)								
94-10A	94-10B									
94-10B	N-7010									

(*) If no difference in value, hue, or chroma perceptible, indicate as equal.
Show difference by number, that is: vvs=1, vs=2-5, s=6-11, full=12-17, v full=18 and up

TABLE AMA - II

Development of TFAA Catalyst in Aniline Condensation

Exp. No.	Acid Catalyst	Base	DQA Yield	DQA Fluor.	Hold Time	Comments
Control	0.5 g PTSA	0.45 g Na_2CO_3 + 5 ml H_2O	77.8 gm	98%	1 hr.	Control
KS-40	2.08 g TFAA	None	68.8	50	1 hr.	Batch distilled TFAA - poor technique - DPU
KS-41	3.08 g TFAA	2.0 g Na_2CO_3 + 5 ml H_2O	77.0	86	1 hr.	No DPU
KS-42	3.08 g TFAA	2.0 g Na_2CO_3 + 5 ml H_2O	78.5	100	2 hr.	No DPU
KS-43	3.08 g TFAA	None	71.6	73	2 hr.	batch distilled TFAA - poor technique or too much catalyst
KS-49	1.54 g TFAA	2.0 g Na_2CO_3 + 5 ml H_2O	79.0	90	2 hr.	
KS-50	1.54 g TFAA	2.0 g Na_2CO_3 + 5 ml H_2P	80.0	113	1 hr.	
KS-51	1.54 g TFAA	None	68.5	86	2 hr.	Continuously distilled TFAA - physical losses and DAT oxidation evident
KS-52	1.54 g TFAA	None	71.4	84	1 hr.	Same as KS-51
KS-53	1.54 g TFAA	None	77.8	101	2 hr.	Batch distilled TFAA - good technique
New Control	0.5 g PTSA	0.45 g Na_2CO_3 + 5 ml H_2O	69.0	107	1 hr.	New control
KS-54	0.77 g TFAA	1.0 g Na_2CO_3 + 5 ml H_2O	68.8	107	1 hr.	
KS-55	0.77 g TFAA	1.0 g Na_2CO_3 + 5 ml H_2O	69.0	107	2 hr.	
KS-56	1.08 g TFAA	None	69.0	108	2 hr.	Batch distilled TFAA

TABLE AMA - II (Continued)

Exp. No.	Acid Catalyst	Base	DQA Yield	DQA Fluor.	Hold Time	Comments
KS-57	KS-56 distillate	None	62.0	82	2 hr.	Re-used topped portion of KS-56 TFAA distillate - some catalyst probably lost.
KS-58	1.08 g TFAA	None	67.8	98	1 hr.	Batch distilled TFAA
KS-59	KS-58 distillate	None	69.0	105	1 hr.	Re-used KS-58 distillate as is

TABLE AMA - II

Development of TFA Catalyst in Aniline Condensation

Exp. No.	Catalyst	Base	Hold Time	Aniline Excess %	DQA Yield Grams	DQA Fluor. %	Comments
KS-55	0.77 g TFA	1.0 g Na_2CO_3 + 5 ml H_2O	2 hr.	230	69.0	107	Control - TFA
KS-60	"	"	20 min.	"	69.8	119	Reactants mixed hot and quenched after indicated time.
KS-61	"	"	15 min.	"	69.8	119	
KS-62	"	"	10 min.	"	69.5	110	
KS-63	"	"	5 min.	"	60.9	44	
3127-37	0.5 g PTSA	0.45 g Na_2CO_3 + 5 ml H_2O	1 hr.	"	78.0	87	Control - PTSA
KS-24	"	"	20 min.	"	68.0	-	Reactants mixed hot and quenched after indicated time.
KS-29	"	"	25 min.	"	75.2	-	
KS-39	"	"	30 min.	"	77.5	91	
5090-44	0.77 g TFA	None	1 hr.	"	69.8	117	Lowered reaction temp. to 85°C. and batch distilled.
5090-50	0.5 g PTSA	.45 g Na_2CO_3 + 5 ml H_2O	1 hr.	"	80.6	104	New PTSA control
5090-52	0.77 g TFA	None	30 min.	50	82.0	111	Reduced aniline excess
5090-53	"	None	30 min.	30	81.5	105	Batch distilled
5090-54	"	None	30 min.	15	81.2	103	
5090-60	0.3 g TFA	None	30 min.	63	82.0	104	Batch distilled

Exp. #	Catalyst	DiCl DQA Yield	DiCl DQA Fluor.	Reaction Time	Reaction Temp.	Comments
PTSA Control		83.0g		2 hr.	110°C.	PTSA control
5090-38	1.4g TFA	81.6g	-	2 hr.	110°C.	Some catalyst lost
5090-39	1.4g TFA	83.5g	80	2 hr.	100°C.	Higher yields probably effect of lower temp.
5090-40	1.4g TFA	83.2g	80	2 hr.	100°C.	
5090-41	1.4g TFA	84.0g	77	2 hr.	90°C.	

TABLE AMA - II

Exp. No.	Catalyst	Base	Hold Time Hrs.	Distn. Time Hrs.	Aniline Excess %	DQA Yield Grams	DQA Fluor. %	Comments
5090-59	1.45 g.TFA	None	1	6	65	68.0	29	2 ft. column pack with steel Black residue
5090-52	0.77 g.TFA	None	1/2	~1	50	82.0	111	Control
5090-61	1.45 g. TFA	None	1	6	65	69.2	68	Ineonel packed column
5090-62	1.45 g. TFA	None	1	6	65	72.0	77	" " "
5090-64	1.45 g. TFA	None	1	6	65	73.6	80	No packing in column
5090-65	1.45 g. TFA	None	1	6	65	77.2	93	No packing and extra Dowtherm distilled
5090-66	1.45 g. TFA	2 g Na_2CO_3 + H_2O	1	6	65	78.2	96	No packing
5090-67	0.77 g. TFA	None	1/2	~1	50	84.0	108	New control
5090-68	0.45 g. TFA	None	1/2	4	50	82.0	103	No packing
5090-70	0.45 g. TFA	None	1/2	4	50	81.6	101	316 S.S. packing - reduced pressure

TABLE AMA-I

TFA CATALYSIS DEVELOPEMENT

Exp. No.	Catalyst	Base	Distillation Time, hrs.	Distillation Pressure, Mmtls.	Aniline Excess %	DQA Yield Gms.	Fluor, %	Comments
5090-67	.77g TFA	none	1	25	50	84.0	108	TFA control
5090-68	.45g TFA	none	4	25	50	82.0	103	No column packing
5090-70	.45g TFA	none	4	20	50	81.6	101	316 SS packing
5090-75	0.5g PTSA	.45g NA_2CO_3 5 ml. H_2O	1	25	230	83.4	113	PTSA control
5090-79	0.45g TFA	none	3	25	50	82.0	96	316 SS packing
5090-82	0.45g TFA	none	3	20	50	82.6	107	316 SS packing
5090-84	0.5g PTSA	.45 Na_2CO_3 5 ml. H_2O	3	20	230	82.0	98	316 SS packing
5090-90	0.45g TFA	none	3	20	50	82.4	97	berl saddle ceramic packing

TABLE I - AMA

Lab Data - Dimethyl DQA via TFA

Exp. No.	Catalyst	Base	Hold Time Hrs.	Distn. Time Hrs.	p-toluidine: SSE Mol Ratio	Reaction Temp. °C.	DQA Yld. Gms.	DQA Fl. %	Comments
5090-80	2.1 g PTSA	1.35 g Na_2CO_3	2	≈ 1	7:1	110	72.8	53	PTSA control
5090-81	1.45 g TFA	None	2	≈ 1	7:1	110	67.8	53	
5090-83	1.45 g TFA	None	2	≈1.5	7:1	110	71.5	53	Used exhaustive distillation procedure
5090-86	1.45 g TFA	1.4 g Na_2CO_3	2	≈ 1	7:1	110	69.2	41	Neutralized catalyst - no help
5090-95	1.45 g TFA	None	2	≈1.5	7:1	90	71.6	55	Low reaction temp. & exhaustive distn.
5090-96	2.9 g TFA	None	2	≈1.5	7:1	90	69.5	57	Double catalyst - no help
5090-97	2.1 g PTSA	1.35 g Na_2CO_3	2	≈1.5	7:1	110	70.5	50	PTSA control with exhaustive distn.
5090-98	1.45 g TFA	None	2	≈ 1	5:1	90	70.6	90	Lowered toluidine and total distillate
5090-99	1.45 g TFA	None	2	≈ 1	3:1	90	72.4	60	Further lowered catalyst & total distillate
5090-100	0.72 g TFA	None	2	≈ 1	3:1	90	72.4	60	Lowered catalyst
5090-101	0.30 g TFA	None	2	≈ 1	3:1	90	72.1	56	Further lowered catalyst
5090-104	0.30 g TFA	None	2	4	3:1	90	70.0	54	4-hr. fractionation, S/S packed column
5090-105	0.30 g TFA	None	2	4	3:1	90	70.5	54	Same as 5090-104

TABLE I - AMA - (Continued)

Exp. No.	Catalyst	Base	Hold Time Hrs.	Distn. Time Hrs.	p-toluidine: SSE Mol Ratio	Reaction Temp. °C.	DQA Yld. Gms.	DQA Fl. %	Comments
5090-106	Distillate from 5090-105	None	2	4	3:1	90	69.2	53	Re-used catalyst in distillate
5090-107	Distillate from 5090-106	None	2	4	3:1	90	70.5	56	Re-used catalyst second time

ENGINEERING COMPUTATION SHEET

SHEET NO

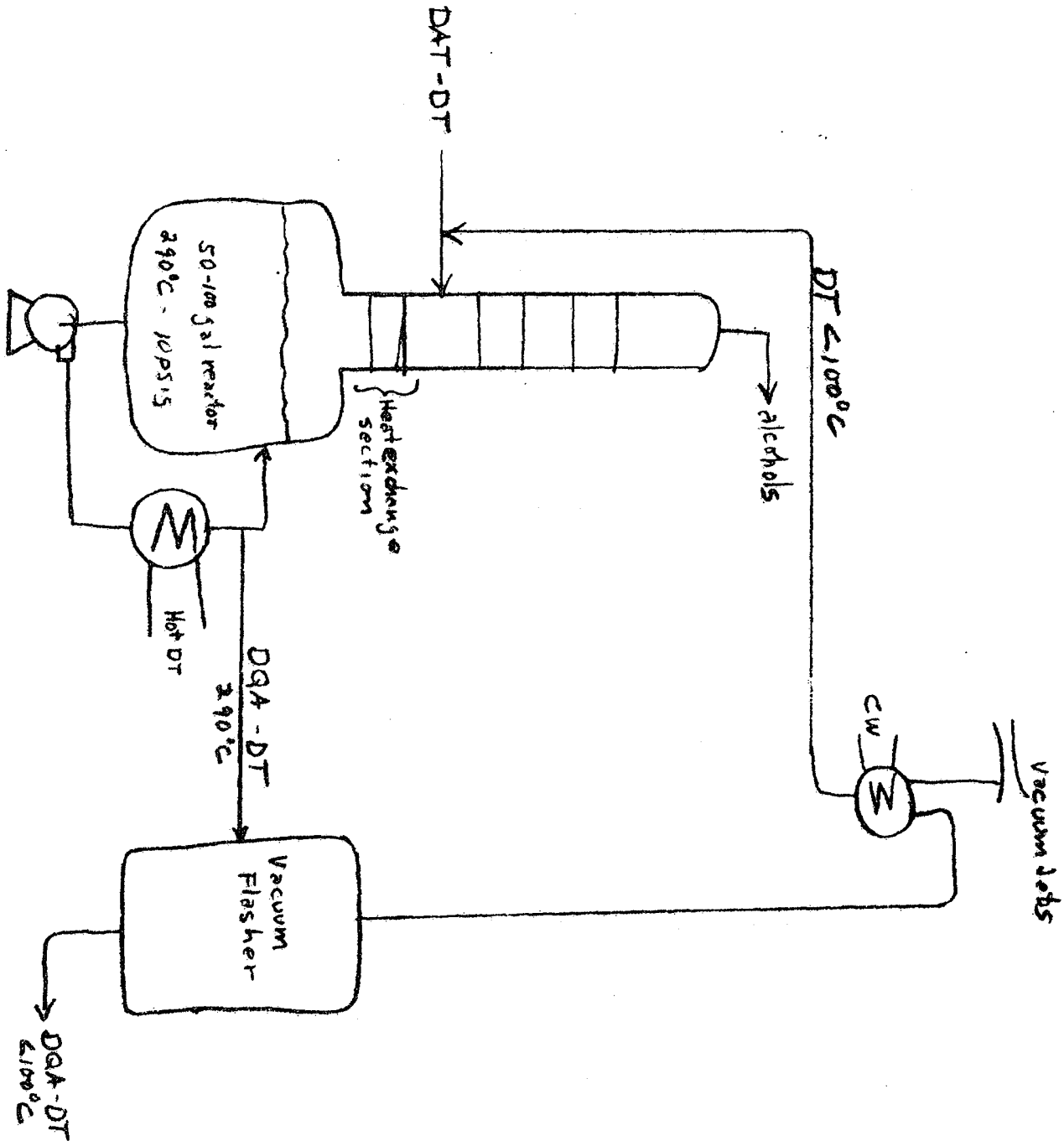
TITLE OF PROJ. OR STUDY

PROJ. OR STUDY NO.

SUBJECT Continuous Pyrolysis System

WORKS Newport

COMPUTER Cuter DATE 10/9 19 63



Pyrolysis

I. Pressure Pyrolysis

As would be expected, temperature affects the rate of pyrolysis reaction. The extent of this effect was reported in the 3-4/63 Monthly Report. Apparent reaction time was reduced from 45 minutes at 250°C. to 5-10 minutes at 278°C. These rates permit consideration of a continuous reaction system using Dowtherm under pressure or a higher boiling solvent. The rate data contained in NB-3127 may be enough to determine rate constants for the two step pyrolysis reaction as well as an Arrenius relationship.

With this data, a satisfactory mathematical model of a continuous reactor can be established for computer evaluation. A feed to pyrolysis vapors heat exchanger should be included in the system for heat economy and a DQA - Dowtherm vacuum flasher after the reaction should be included to both recover Dowtherm and cool the stream. Attached is a sketch of a possible system.

II. DAT Column Feed

Aside from its use in a continuous system, the concept of using latent heat in vapors to preheat feed can be useful in the present equipment. Laboratory experiments (NB-5090-20-24) showed that this approach increased pyrolysis yield. This was tried in XOR-95 but showed no advantage. I suspect this was due to too much hold-up in the bottom of 65 column, allowing DAT to partially pyrolyze under unfavorable conditions (see Monthly Report 3-4/63, page 36). This equipment should be tried again as soon as the vapor line demister is installed.

QA Filtration

The filter system design can be completed only if the projected drying route is known, since the presscake handling system affects both. The dryer - handling system study then, must be considered top priority. Keep in mind that the handling system must also be adaptable to the present drying system for the short term. Some alternatives are a simple press pan with manual presscake handling, a ribbon mixer with repulping and subsequent pump discharge, a steam heated mixer for partial drying, granulating and dry discharge, or direct drop into the dryer (that is, heated flight or rotary vacuum).

The initial installation calls for use of the present leaf filters as scavengers, one each for beta and gamma. Maroon has little tendency to bleed and will not need scavenging. Either initially or as they wear out, the type FFF-19N woven "Nylon" cloths on the leaf filters should be replaced with eggshell "Nylon" felt type 61NY18B. This type provides more positive retention of fines. TheFFF-19N to be

used on the recessed plate filter will be pre-shrunk to prevent dislodging cloth. The heat treatment and porosity should be specified and standardized. See J. Flood, Louviers, for recommendations.

If the dryer type calls for high feed solids, steam blowing - 90 psig through the wash port should be used. This will displace imbound water. Excess filter cycle time can possibly be used for hot air blowing to further i increase solids. This is not in the project.

Installation design details, such as pan arrangment and isolation of filter from unloading, remain to be completed. A filtrate measuring device and steam pressure regulator must be specified.

QA Drying

The choice of a dryer is mostly dependent on economics and handling difficulty. Assuming that spray drying is too expensive, and heat screw drying is not much better economically, I suggest we reconsider rotary conical vacuum dryers. It offers no more difficulties than either of the above choices and is decidedly less expensive - $25M equipment if one dryer is sufficient for the short term. The tests conducted at Patterson Foundry in April, 1962 indicated a probable cycle of 15-20 hours with 1500 lbs. (dry) loading - 35% solids. Current status of drying studies is covered in attached letter

Nutsche Filtration

The Nutsche automation system is covered in the letter on the subject - AMA to FJS - 8/63 and in Monthly Report 7-8/63. Orientation and specification of new nozzles should be directed toward sealing of cake cracks as well as mixing to prevent solvent bypassing.

For future expansion, I suggest the recessed plate filter be considered. To minimize cake compressibility effects, the filter may be used in conjunction with the Nutsche which would filter off Dowtherm and reslurry in methanol for transfer to the recessed plate.

Solution "Sitol" Facilities

The installation and operation of this system is straighforward. Aside from its project stated advantage, this system can be used to increase Maroon oxidation capacity by titrating the "Sitol" itself with acid to remove carbonates prior to oxidation. This will prevent foaming on acidification of Maroon.

List of Contacts

Vendors

F. W. Glitsch Co. - Valve trays and Glitsch Grid
Mr. Butterworth
New York, N.Y.
YU-6-6357

Jordan Pressure Regulators
Fred Weldsford
Philadelphia, Penna.
MOhawk 4-8026

Sparkler Mfg. Company - Horizontal plate filters
J. C. Sharbaugh
11 Park Road
Havertown, Penna.

Briggs Filtration Company - Cartridge filters and coalescer
J. L. Beatty
919 E. Darby Rd.
Havertown, Penna.
JA-8-5613 or Hilltop 7-1180

Bowser, Inc. - Leaf and cartridge filters (DPU and carbonates)
James A. Parente
3639 N. Broad St.
Philadelphia 40, Penna.
Baldwin 8-2582

Fairbanks, Morse and Co. - C.M. Pumps
D. P. Caldwell
1005 Baylor Drive
Newark, Delaware
368-8862

Warner-Lewis Co. - Coalescers
Roger Sanborn
545 Fifth Ave.
New York 17, N.Y.
Oxford 7-2769 and Oxford 7-6175

Pittsburg Brass Mfg. Co. - Ball valves
Richard H. Bill
2409 Chatham Drive
Wilmington, Delaware
PO-2-3665

Tote System, Inc. - Tote Tanks
Vincent B. Janson
181 Warrior Rd.
Drexel Hill, Penna.
215 Hilltop 6-2134

List of Contacts (Continued)

Vendors

Patterson Foundry Co. - Conical vacuum dryers
P. L. Dolon
298 Levering Mill Rd.
Bala-Cynwyd, Pa.
Mohawk 4-5522

R. B. Mack or Juliane
East Liverpool, Ohio
385-2400

Western Precipitation - Screw dryer
E. F. Ewing, Inc.
Board St. Trust Bldg.
Glenside, Pa.
Hancock 4-2074

Robbins and Meyers, Inc. - Moyno Pump
D. F. McCulloch
8418 West Chester Pk.
Upper Darby, Pa.
Sunset 9-2523

Rietz Mfg. Co. - Thermoscrew
Robson B. Dunwoody
P.O. Box 690
West Chester, Pa.
Owen 6-6313

Bowen Engineering Co. - Spray Dryers
R. W. Bayless
R. DeHoff
North Branch, N.J.
Randolph 5-3232

T. E. Grimac
P.O. Box 7
Cherry Hill, N.J.
(609) Normandy 3-4900

Consultants

R. B. Akell - Distillation
F. T. Wyman - Corrosion
F. J. Sercelj - Instrumentation
J. E. Flood and J. Chalmers - Filtration
R. Leedom - Agitation
L. DeFrate - Dowtherm Power System
H. Jacobs - Waste Disposal
J. Folsom - Dowtherm Heater