Monsanto

FROM (NAME & LOCATION) C. G. Hagberg (6440) - General Offices (Zone 270)

DATE April 27, 1971

SUBJECT Biphenyl Chlorination
CEA 2417

REFERENCE

TO A. J. Heinze

cc: D. K. Coval--Queeny
P. W. Gallier
R. McCutchan--Krummrich
S. I. Proctor
J. R. Savage
N. B. Wolk

At your request, I have analyzed the difference between batch and continuous stirred tank (CSTR) chlorination of biphenyl. The chlorination involves consecutive reactions of biphenyl to o,m,p-monochlorodiphenyl to dichlorodiphenyl to trichlorodiphenyl. Because of the consecutive nature of the reaction, one would always expect the batch (or plug flow if it were a continuous reactor) to give a higher yield of the intermediate product (monochlorodiphenyls) than a CSTR. References 1 to 3 give you illustrations and examples of this fact.

Reaction Kinetics

I have taken the plant batch data at 150°C for diphenyl chlorination and have developed a kinetic model to describe and quantify the several reaction rates. The kinetics were based on the formation of the various products with respect to diphenyl usage. The analysis is similar to that described in Reference 1. This method of analysis eliminated the need for specifying the Cl_2 concentration in the liquid. The kinetic model is detailed in the attachments.

Batch vs. CSTR Operation

To determine the product distribution from a CSTR reactor, the kinetic model was incorporated into equations for CSTR operation. These equations are also given in the attachments.

You have given me an analysis of the product distribution from a plant run using a single CSTR. The ability of the model to predict CSTR operation can be judged by comparing the model predictions with this data. The following table illustrates this comparison:

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Table 1. Biphenyl Chlorination in a Single CSTR

150°C

	Plant Data wt %	Model Predictions wt %
Biphenyl	48.8	48.9
o-monochlorodiphenyl	23.7	24.3
m-monochlorodiphenyl	2.0	2.2
p-monochlorodiphenyl	12.7	12.7
Dichlorodiphenyl	12.1	11.8
Trichlorodiphenyl	.7	.1
	100.0	100.0

The agreement of the CSTR model with the plant data is of sufficient accuracy that we can have confidence in its predictions. Trends in the operation of 1,2,3 and 4 CSTR's in series can be predicted using the model. I have done this using equal chlorine distribution to the reactors. The results are given in Table 2. The extent of biphenyl (54.85 mole percent in the exit stream) is common to all cases. From the results the conclusion is that as many as possible (4) CSTR's in series should be used to minimize the amount of dichloro's formed in a continuous operation. This is because many CSTR's in series approach the behavior of a batch or plug flow reactor.

Table 2. Biphenyl Chlorination in a Series of CSTR's
-- Model Predictions --

150°C

No. of CSTR's in series	1	2	3	4	15
Composition of Last Reactor Effluent (wt %)					~ Batch
Biphenyl	48.90	49.14	49.23	49.27	49.35
o-monochloro ϕ_2	24.35	26.13	26.72	27.02	27.68
m-monochloro ϕ_2	2.20	2.36	2.41	2.44	2.50
p-monochloro ϕ_2	21.66	13.58	13.89	14.05	14.39
dichloro ϕ_2	11.78	8.74	7.72	7.19	6.06
trichloro ϕ_2	.11	.05	.03	.03	.02
	100.00	100.00	100.00	100.00	100.00

The results indicate that about 18.6% more dichloro's would be made in a 4 CSTR Series of reactors than in a batch reactor operated to the same biphenyl extent. A single CSTR at the same

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biphenyl extent gives 94% more dichlorodiphenyl than a batch reactor. The difference in CSTR and batch operation becomes less as the biphenyl usage is decreased. Thus less dichloro could also be made by decreasing the extent of the biphenyl reaction.

Summary

I have shown through the use of a kinetic model the differences in batch and CSTR operation for biphenyl chlorination. CSTR operation can be simulated using the model to quantify the penalty (extra dichloro's) paid by operating in this manner. The conclusion is to use as many as possible (4) CSTR's in series for the continuous process.

Optimization of the 4 CSTR reactor train may be possible through use of the kinetic model or through actual plant testing. Variables of interest to examine are (1) the temperature of each reactor, (2) the Cl_2 distribution to each reactor, and (3) the total amount of Cl_2 added. To use the model to study the temperature effect, more kinetic data are needed at temperatures above and below 150°C. The effect of temperature on the rate constants must be evaluated.

I would be glad to do this optimization study in the future if you so desire and can get the data. I hope the results reported here give you the information you desire now and illustrate what can be done with reaction kinetic models to save time and expense in optimizing processes. A total of 20 hours was charged toward your CEA for this study.

Carl G. Hagberg

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References

1. Smith, J. M., "Chemical Engineering Kinetics," McGraw-Hill, New York, 1st Ed., pp 62 (1956), 2nd Ed., pp 79 and 200, (1970).

2. Levenspiel, O., "Chemical Reaction Engineering," John Wiley, New York, pp 169-193 (1962).

3. Peters, M. S., "Timmerhaus, K. D., "Plant Design and Economics for Chemical Engineers," McGraw-Hill, New York, pp 745 (1970).

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1. Reactions

$$BiP + Cl_2 \longrightarrow o\,MCP + HCl \qquad k_1$$
$$BiP + Cl_2 \longrightarrow m\,MCP + HCl \qquad k_2$$
$$BiP + Cl_2 \longrightarrow p\,MCP + HCl \qquad k_3$$
$$\sum_1^3 MCP + Cl_2 \longrightarrow DCP + HCl \qquad k_D$$
$$DCP + Cl_2 \longrightarrow TCP + HCl \qquad k_T$$

2. Batch Reaction Kinetic Equations

$$V_B \frac{d\,BiP}{dt} = -(k_1 + k_2 + k_3)\,BiP\,Cl_2 \qquad (1)$$

$$V_B \frac{d\,oMCP}{dt} = -k_D\,oMCP\,Cl_2 + k_1\,BiP\,Cl_2 \qquad (2)$$

$$V_B \frac{d\,mMCP}{dt} = -k_D\,mMCP\,Cl_2 + k_2\,BiP\,Cl_2 \qquad (3)$$

$$V_B \frac{d\,pMCP}{dt} = -k_D\,pMCP\,Cl_2 + k_3\,BiP\,Cl_2 \qquad (4)$$

$$V_B \frac{d\,DCP}{dt} = -k_T\,DCP\,Cl_2 + k_D \sum_1^3 MCP\,Cl_2 \qquad (5)$$

$$V_B \frac{d\,TCP}{dt} = +k_T\,DCP\,Cl_2 \qquad (6)$$

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3. Define: $X = \frac{k_1}{k_2}$ $R = \frac{k_1}{k_D}$

$Y = \frac{k_1}{k_3}$ $S = \frac{k_1}{k_T}$

4. Kinetic Model - Batch Reactor

Base the kinetics on B_iP usage (B_iP_u)

Divide by the first reaction equation and substitute the above definitions.

Let: $A = \frac{k_1}{(k_1+k_2+k_3)} = \frac{1}{\left(1+\frac{1}{X}+\frac{1}{Y}\right)}$

$$\frac{d\,oMCP}{dB_iP_u} = A - \frac{A}{R}\frac{oMCP}{B_iP}$$

$$\frac{d\,mMCP}{dB_iP_u} = \frac{A}{X} - \frac{A}{R}\frac{mMCP}{B_iP}$$

$$\frac{d\,pMCP}{dB_iP_u} = \frac{A}{Y} - \frac{A}{R}\frac{pMCP}{B_iP}$$

$$\frac{d\,DCP}{dB_iP_u} = \frac{A}{R}\frac{\left(\sum_1^3 MCP\right)}{B_iP} - \frac{A}{RS}\frac{DCP}{B_iP}$$

$$\frac{d\,TCP}{dB_iP_u} = \frac{A}{RS}\frac{DCP}{B_iP}$$

where: $B_iP = 100 - B_iP_u$

$$\frac{dB_iP}{dB_iP_u} = -1$$

Units are in mol percent.

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5. The above kinetic model was fit to data at 150°C from the plant reactor. CDP E0027 was used to determine values for the four unknown constants (X, Y, R, S). A copy of the computer output is attached. The results at 150°C were:

$X = 11.087$ $\quad R = 1.9952$

$Y = 1.9237$ $\quad S = 29.831$

These may vary with temperature.

6. CSTR Equations

$$\frac{\text{Moles in}}{\text{hr}} - \frac{\text{Moles out}}{\text{hr}} = \text{Vol} * \text{Rate}$$

$$BiP_I - BiP = V_R (k_1 + k_2 + k_3) BiP\ Cl_2$$

$$oMCP_I - oMCP = V_R k_D oMCP\ Cl_2 - V_R k_1 BiP\ Cl_2$$

$$mMCP_I - mMCP = V_R k_D mMCP\ Cl_2 - V_R k_2 BiP\ Cl_2$$

$$pMCP_I - pMCP = V_R k_D pMCP\ Cl_2 - V_R k_3 BiP\ Cl_2$$

$$DCP_I - DCP = V_R k_T DCP\ Cl_2 - V_R k_D \Sigma MCP\ Cl_2$$

$$TCP_I - TCP = -V_R k_T DCP\ Cl_2$$

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7. Final CSTR Equations

Using the above defined terms and $k_1' = V_R k_1 C_{l_2}$

$$BiP = \frac{BiP_I}{1 + k_1' A} \quad (1)$$

$$oMCP = \frac{oMCP_I + k_1' BiP}{1 + k_1'/R} \quad (2)$$

$$mMCP = \frac{mMCP_I + k_1' BiP/X}{1 + k_1'/R} \quad (3)$$

$$pMCP = \frac{pMCP_I + k_1' BiP/Y}{1 + k_1'/R} \quad (4)$$

$$DCP = \frac{DCP_I + k_1' \Sigma MCP/R}{1 + \frac{k_1'}{RS}} \quad (5)$$

$$TCP = TCP_I + k_1' DCP/(RS) \quad (6)$$

By defining the BiP^{exit} mole %, Eq'n (1) can be used to calculate k_1' given the inlet concentrations.

$$k_1' = \frac{BiP_I - BiP}{A \cdot BiP}$$

Then Eq'ns (2)-(6) can be used consecutively to calculate the product concentration from the CSTR in mol percent.

The mol percent concentrations are then converted to wt %.

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PROGRESS OF PARAMETER SEARCH
FIRST VALUES ARE THE INITIAL GUESSES
THEN INTERMEDIATE RESULTS ARE GIVEN
FINAL VALUES ARE THE BEST PARAMETER ESTIMATES

DIFF = DATA - CALC
PERC = DIFF / DATA * 100.
SSQ = SUM OF SQUARES OF DIFF
STD DEV = (SSQ / (DATA POINTS - 1))**.5

SSQ	X X(1)	Y X(2)	R X(3)	S X(4)	X(5)
0.57090E 01	0.10000E 02	0.20000E 01	0.20000E 01	0.35000E 02	
0.40176E 01	0.11197E 02	0.19243E 01	0.19920E 01	0.28480E 02	
0.40150E 01	0.11096E 02	0.19236E 01	0.19952E 01	0.26843E 02	
0.40146E 01	0.11095E 02	0.19236E 01	0.19953E 01	0.27101E 02	
0.40142E 01	0.11088E 02	0.19237E 01	0.19952E 01	0.29699E 02	
0.40136E 01	0.11087E 02	0.19237E 01	0.19952E 01	0.29831E 02	
0.40136E 01	0.11087E 02	0.19237E 01	0.19952E 01	0.29831E 02	

MEAN VALUE OF DATA = 12.87349 STD DEV = 0.459613 COMPUTER TIME REQUIRED = 78.8 SECS

COMPARISON OF MODEL PREDICTIONS WITH DATA USING THE BEST PARAMETER ESTIMATES IN THE MODEL

RUN 1 - 150 DEG C

COMP 1 oMCP	TIME(SAM)	TIME(ACT)	DATA	CALC	DIFF	PERC	WF
	0.0	0.0	0.0	0.0			
	27.460	27.460	15.7400	16.1878	-0.44784	-2.85	1.00
	33.220	33.220	18.7500	19.3077	-0.55771	-2.97	1.00
	50.000	50.000	26.8400	27.5893	-0.74928	-2.79	1.00
	66.000	66.000	33.5500	33.7963	-0.24635	-0.73	1.00
	80.760	80.760	37.8000	36.6377	1.16228	3.07	1.00

COMP 2 mMCP	TIME(SAM)	TIME(ACT)	DATA	CALC	DIFF	PERC	WF
	0.0	0.0	0.0	0.0			
	27.460	27.460	1.5600	1.4601	0.09986	6.40	1.00
	33.220	33.220	1.7600	1.7416	0.01844	1.05	1.00
	50.000	50.000	2.4800	2.4886	-0.00858	-0.35	1.00
	66.000	66.000	3.0000	3.0485	-0.04845	-1.62	1.00
	80.760	80.760	3.1300	3.3047	-0.17475	-5.58	1.00

COMP 3 pMCP	TIME(SAM)	TIME(ACT)	DATA	CALC	DIFF	PERC	WF
	0.0	0.0	0.0	0.0			
	27.460	27.460	8.7000	8.4151	0.28487	3.27	1.00
	33.220	33.220	10.4800	10.0371	0.44286	4.23	1.00
	50.000	50.000	14.8000	14.3424	0.45756	3.09	1.00
	66.000	66.000	17.3000	17.5691	-0.26909	-1.56	1.00
	80.760	80.760	18.4500	19.0460	-0.59601	-3.23	1.00

COMP 4 DCP	TIME(SAM)	TIME(ACT)	DATA	CALC	DIFF	PERC	WF
	0.0	0.0	0.0	0.0			
	27.460	27.460	1.4700	1.3956	0.07436	5.06	1.00
	33.220	33.220	2.2300	2.1315	0.09852	4.42	1.00
	50.000	50.000	5.8300	5.5666	0.26339	4.52	1.00
	66.000	66.000	12.2000	11.5389	0.66105	5.42	1.00
	80.760	80.760	21.4000	21.6260	-0.22604	-1.06	1.00

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