Appendix II: Thermodynamic Calculations

Memorandum

AIR PRODUCTS

To: T. H. Hsiung Dept./Loc PSG RES/Iron Run

From: H. C. Klotz Dept./Ext. MIS-RES/4638

Date: 6 November 1991

Subject: Equilibrium Calculations for Isobutylene/Alcohol Reactions

As you requested, I have estimated equilibrium compositions for two reactions involving conversion of isobutanol (IBOH) or tert-butanol (TBOH) to isobutylene (IBUE) and water. These calculations are based on ideal gas properties obtained from the JANF thermodynamic system. The calculations indicate that the isobutanol reaction essentially goes to completion, whereas the tert-butanol reaction goes to a lesser extent. If you have any questions, please contact me.

Rxn 1: IBOH = IBUE + H2O

Condition	Mol% IBOH	Mol% IBUE	Mol% H2O
T=100 C, P=1 atm	.0026	50.00	50.00
T=200 C, P=1 atm	.0004	50.00	50.00
T=300 C, P=1atm	.0001	50.00	50.00
T=100 C, P=52 atm	.135	49.93	49.93
T=200 C, P=52 atm	.022	49.99	49.99
T=300 C, P=52 atm	.003	50.00	50.00

Rxn 2: TBOH = IBUE + H2O

Condition	Mol% TBOH	Mol% IBUE	Mol% H2O
T=100 C, P=1 atm	54.84	22.58	22.58
T=200 C, P=1 atm	2.62	48.69	48.69
T=300 C, P=1atm	0.14	49.93	49.93
T=100 C, P=52 atm	91.90	4.05	4.05
T=200 C, P=52 atm	44.48	27.76	27.76
T=300 C, P=52 atm	6.50	46.75	46.75

Hub Klotz

H. C. Klotz

Memorandum

AIR PRODUCTS

To: B. E. Latshaw — Dept./Loc PG&E Res/Iron Run

From: H. C. Klotz — Dept./Ext. MIS-RES/4638

Date: 30 January 1992

Subject: Isobutanol Dehydration Heats of Reaction

cc: T. H. Hsiung
P. M. Mathias

As you requested, heats of reaction and adiabatic temperature drops for the isobutanol dehydration reaction have been estimated for a variety of conditions. The calculations are based on the LC Peng-Robinson model (ITHRMO=17) in the CAPP thermodynamic system. The heat of reaction to form isobutylene and water from isobutanol is 6.4 kcal/gmol in the gas phase over the range of conditions you specified.

I've also calculated the temperature decrease in an adiabatic reactor as a function of isobutanol conversion from two initial conditions (T=200 C, P=1 atm; T=300C, P=1 atm) which are summarized below:

	Initial Condition 1 T=200 C, P=1atm x(IBOH) = 1.0		Initial Condition 2 T=300 C, P=1atm x(IBOH) = 1.0	
%IBOH Conversion	Final T(C)	Liq Phase ?	Final T (C)	Liq Phase ?
0	200	N	300	N
10	182	N	284	N
20	164	N	269	N
30	145	N	252	N
40	126	N	236	N
50	107	N	219	N
60	87	N	202	N
70	77	Y	185	N
80	77	Y	167	N
90	77	Y	149	N
100	77	Y	130	N

As you know, equilibrium calculations indicate that this reaction should essentially go to completion at both conditions (1). Since the reaction is endothermic, there is the potential for a liquid phase to form as the reaction proceeds. As illustrated above, a liquid phase forms at the T=200 C initial condition between 60 and 70 % IBOH conversion, but no liquid phase forms for T=300 C case.

A series of calculations were also made for the T=300 C case at various pressures to determine the maximum reactor pressure which avoids forming a liquid phase during the reaction. The maximum pressure based on this criteria is 5.4 atm, and the temperature profile as a function of conversion is essentially identical to that shown for the T=300 C and P=1 atm case.

If you have any questions, please contact me.

Herb Klotz

H. C. Klotz

References

1. APCI memo, H. C. Klotz to T. H. Hsiung, "Equilibrium Calculations for Isobutylene/Alcohol Reactions", 6 November 1991