CHAPTER 6

SIMULATION STUDY AND DISCUSSION

6.1 Simulation Study

The simulation of the new model of the catalytic reforming of C_6 and C_7 hydrocarbons in a fixed-bed reactor is carried out using feedstocks and operating condition, such as temperature, pressure, and hydrogen/hydrocarbon ratio from experiments of the catalytic reforming on a $Pt-Al_2O_3$ catalyst. The simulation results are compared with those experimental data under isothermal and adiabatic mode of operation. Input data for the simulation are grouped as follows:

(1) The feed components into the catalytic reforming reactor are C_6 hydrocarbons. The operating conditions from experimental data for case 1 and 2 of Marin et al., (1982), case 3 and 4 of Van Trimpont et al., (1988), and for case 5 of Selman, (1975) are shown in Table 6-1.

(2) The feed components into the catalytic reforming reactor are C_7 hydrocarbons. The operating conditions from experimental data for case 6, 7, 8, and 9 (Hettinger et al., (1955)), case 10, 11, 12, 13, 14, and 15 (Van Trimpont et al., (1986)), case 16, 17, 18, 19, 20, and 21 of Heinemann, (1951) are shown in Table 6-1.

(3) The feed components, methylcyclopentane, methylcyclohexane, and n-heptane into the catalytic reactor and operating

condition for case 22 (Meerbott et al., (1954)) are shown in Table 6-2.

(4) The feed, East-West Texas C_6 to C_7 hydrocarbons, n-hexane, n-heptane, methylcyclopentane (MCP), ethylcyclopentane, methylcyclohexane (MCH), benzene, and toluene, and operating condition for case 23 and 24 of Meerbott et al., (1954) are shown in Table 6-3. The flow sheet for case 23 and 24 of reforming process using two reactors is shown in Figure 6-1.

The simulations were made on a 386 microcomputer using a C programming. The optimal step size (h) is carried out at 0.01 as shown in Figure 6-19.

6.2 Comparison of Simulation and Experimental Results

The simulated results of computed concentration profiles against W/F_{HC} (kg catalyst hr/kmol feed) under adiabatic mode of operation are compared with experimental data under isothermal operation and pilot plant data under adiabatic mode of operation. The percent error of the simulation results compared with experimental data is shown in Table 6-4.

Figure 6-2 and 6-3 show the concentration profiles of n-hexane, 2-methylpentane(2MP), 3-methylpentane(3MP), benzene, and methylcyclopentane(MCP) in the reactor against methylcyclopentane(MCP) for case 1 and case 2 under isothermal mode of operation. The catalyst used in those case is 0.59 wt% Pt, 0.67 wt% Cl on alumina type of catalyst. The computed results of case 1 and case 2 agree fairly with experimental data of Marin et al., (1982).

Figure 6-4 and 6-5 show the concentration profiles of n-hexane, 2-methylpentane, 3-methylpentane, and 2,2-dimethylbu-

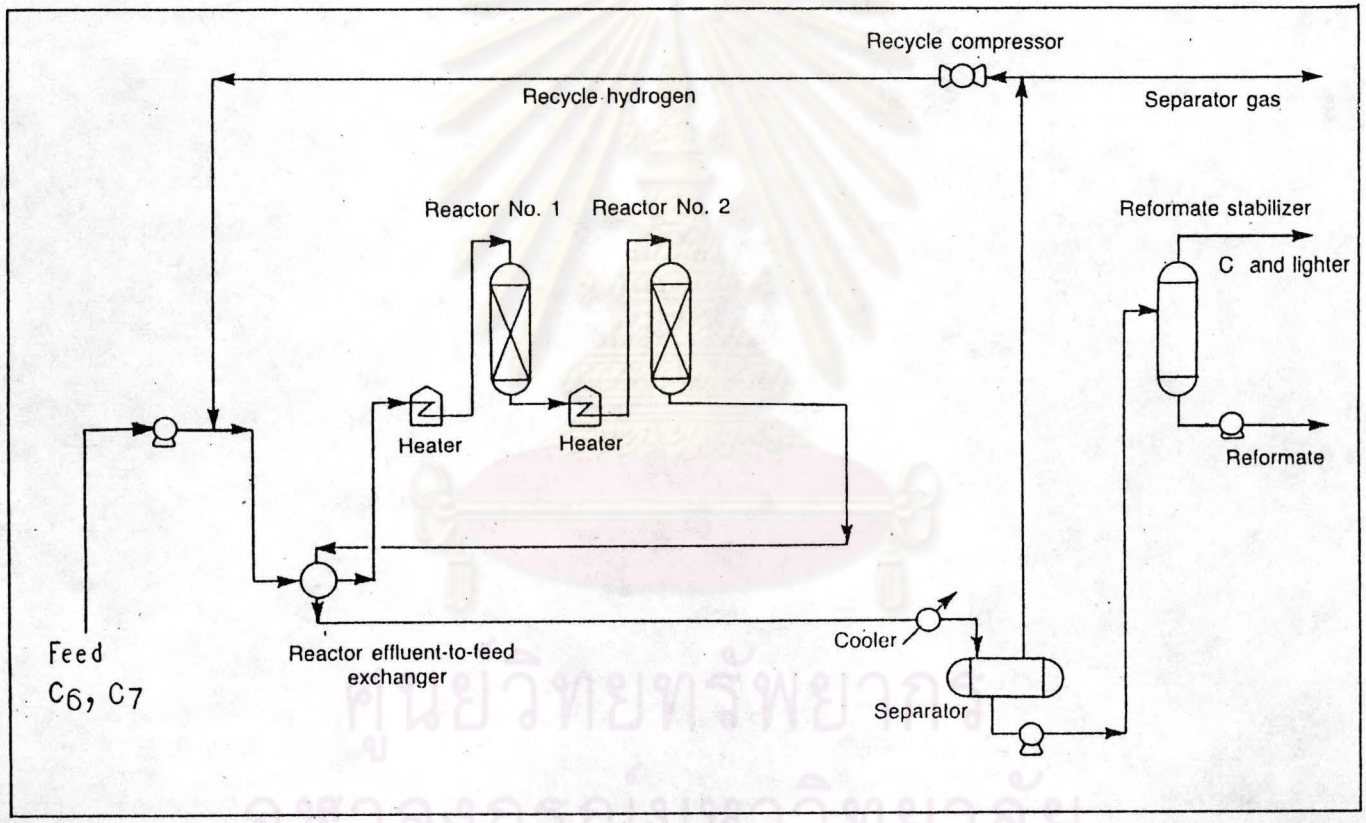

Figure 6-1 Flow sheet of two-reactor reforming of case 23 and 24 of Table 6-3

Table 6-1 Input data used in the simulation

Case	Feed	Tempeature °C	Pressure bar	H_2/Hydrocarbon mol/mol
1	n-Hexane	460.9	16.0	9.9
2	23DMB	419.1	10.0	10.01
3	n-Hexane,3MP,22DMB (40,30,30)	435.0	10.5	20.0
4	n-Hexane,2MP,3MP,22DMB (10,10,70,10)	435.0	10.5	20.0
5	MCP	454.4	13.7	10.0
6	n-Heptane	420.0	20.5	40.0
7	n-Heptane	496.1	13.7	5.0
8	n-Heptane	496.1	34.5	5.0
9	n-Heptane	496.1	24.1	5.0
10	MCH	350.0	15.5	30.0
11	MCH	350.0	5.0	9.0
12	MCH	350.0	20.5	40.0
13	MCH	400.0	8.1	53.0
14	MCH	400.0	8.5	16.0
15	MCH	400.0	9.0	8.0
16	MCH	452.0	48.2	6.6
17	Tol+MCH (41.5,58.5)	452.0	48.2	6.6
18	Tol+MCH (41.5,58.5)	439.0	48.2	6.6
19	MCH	426.6	20.7	4.0
20	MCH	482.2	20.7	4.0
21	MCH	426.6	41.3	4.0

Table 6-2 Input data used in the simulation of mixed C_6 and C_7 hydrocarbons

Composition of mixed C_6 to C_7 hydrocarbons feed

Hydrocarbon Type	Volume %
MCP	22.2
MCH	22.3
n-Heptane	55.5
	100.0

Operating Conditions	case 22
Pressure, bar	16.5
Temperature, °C	482.2
$W/F_{HC}O$	20.0
Hydrogen/hydrocarbon	3.0

Table 6-3 Input data used in the simulation of mixed C_6 and C_7 hydrocarbons

Composition of East-West Texas C_6 to C_7 feed

Hydrocarbon Type	Volume %
n-Hexane	23.5
n-Heptane	30.3
MCP	7.4
ECP	10.9
MCH	15.9
Benzene	7.8
Toluene	4.2
	100.0

	Operating Conditions	
	case 23	case 24
Reactor No. 1		
Pressure, bar	23.4	19.9
Temperature, °C	482.2	482.2
$W/F_{HC}o$	20.0	20.0
Reactor No. 2		
Pressure, bar	19.9	16.5
Temperature, °C	482.2	482.2
$W/F_{HC}o$	20.0	20.0
Hydrogen/hydrocarbon	4.4	2.8

tane in the reactor against W/F_{HC} for case 3 and case 4. Experimental data of Christoffel (1979) are compared with the calculated results for case 3 and 4. The catalyst is 0.35 wt% Pt on alumina type of catalyst. The results are compared with pilot plant data. The agreement is good.

Figure 6-6 shows the concentration profiles of n-hexane, 2-methylpentane(2MP), 3-methylpentane(3MP), benzene in the reactor against methylcyclopentane(MCP) conversion for case 5. Experimental data of Selman (1975) are compared with the calculated results in this case. Feed is methylcyclopentane. The catalyst is 0.3 wt% Pt Rhenium and 0.61 wt% Cl on alumina type of catalyst. The agreement between experimental calculated data and the simulated results is in good agreement.

Figure 6-7 shows the concentration profiles of single-branched isoheptane(SBP7), multibranched isoheptane(MBP7), C_6-, toluene, methycyclohexane(MCH) , and the five-ring naphthenes with seven carbon atoms in the reactor against W/F_{HC} for case 6 under isothermal mode of operation. Experimental data of Van Trimpont (1988) is compared with the calculated results in this case. The catalyst is 0.59 wt% Pt, 0.67 wt% Cl on alumina type of catalyst. The agreement between experimental data and the calculated results is good.

Figure 6-8 shows the concentration profiles of C_6 hydrocarbons in the reactor against W/F_{HC} for case 7, 8, and 9 under isothermal mode of operation. Experimental data of Hettinger et al. (1955) are compared with the computed results of those case. The catalyst is 0.6%wt Pt on alumina type of catalyst. The agreement between experimental data and the calculated results are fairly good. The computed concentra-tion profiles of C_6- increase when pressure increases.

Figure 6-9 and 6-10 show the concentration profiles of toluene in the reactor against W/F_{HC} for case 10, 11, 12, 13, 14, and 15 under isothermal mode of operation. The catalyst containing 0.59 %wt Pt, 0.67%wt Cl on alumina is used for case 10, 11, and 12. The catalyst for case 13, 14, and 15 is 0.31 wt% Re, 0.30 wt% Pt, 0.95 wt% Cl type of catalyst. Experimental data of Van Trimpont (1986) are compared with the computed results of those case. The agreement for case 10, 11, and 12 as shown in Figure 6-9 is good. The agreement for case 13, 14, and 15 is not good when W/F_{HC} more than 1. Because the case 13, 14, and 15 used other catalyst. Thus, the limitation of the new model is type of catalyst.

Figure 6-11 and 6-12 show the concentration profiles of toluene in the reactor against W/F_{HC} for case 17, 18, 19 ,20, and 21. The catalyst of these case is platinum on alumina type of catalyst. The mode of operation is isothermal conditions. Experimental data of Heinemann (1951) are compared with the computed results. The agreement for case 17 and 18 as in Figure 6-11 is fairly good. The agreement for case 19, 20 and 20 as shown in Figure 6-12 is good. It is observed that the computed results of toluene increase when temperature increases. But toluene increase when pressure decreases.

Figure 6-13 shows the concentration profiles of benzene and toluene in the reactor against W/F_{HC} for case 22 with pilot plant data of Meerbott (1954) under adiabatic mode of operation. The catalyst is platinum on alumina type of catalyst. The results are compared with pilot plant data. The agreement is fairly good. Figure 6-14 shows the temperature profiles in the reactor against W/F_{HC} for the case 22. The agreement is good.

Figure 6-15 and 6-17 show the concentration profiles of benzene and toluene in the two reactors against W/F_{HC} for case 23 and 24. Pilot plant data of Meerbott (1954) are compared with the calculated results. The agreement for both case 23 and case 24 are good.

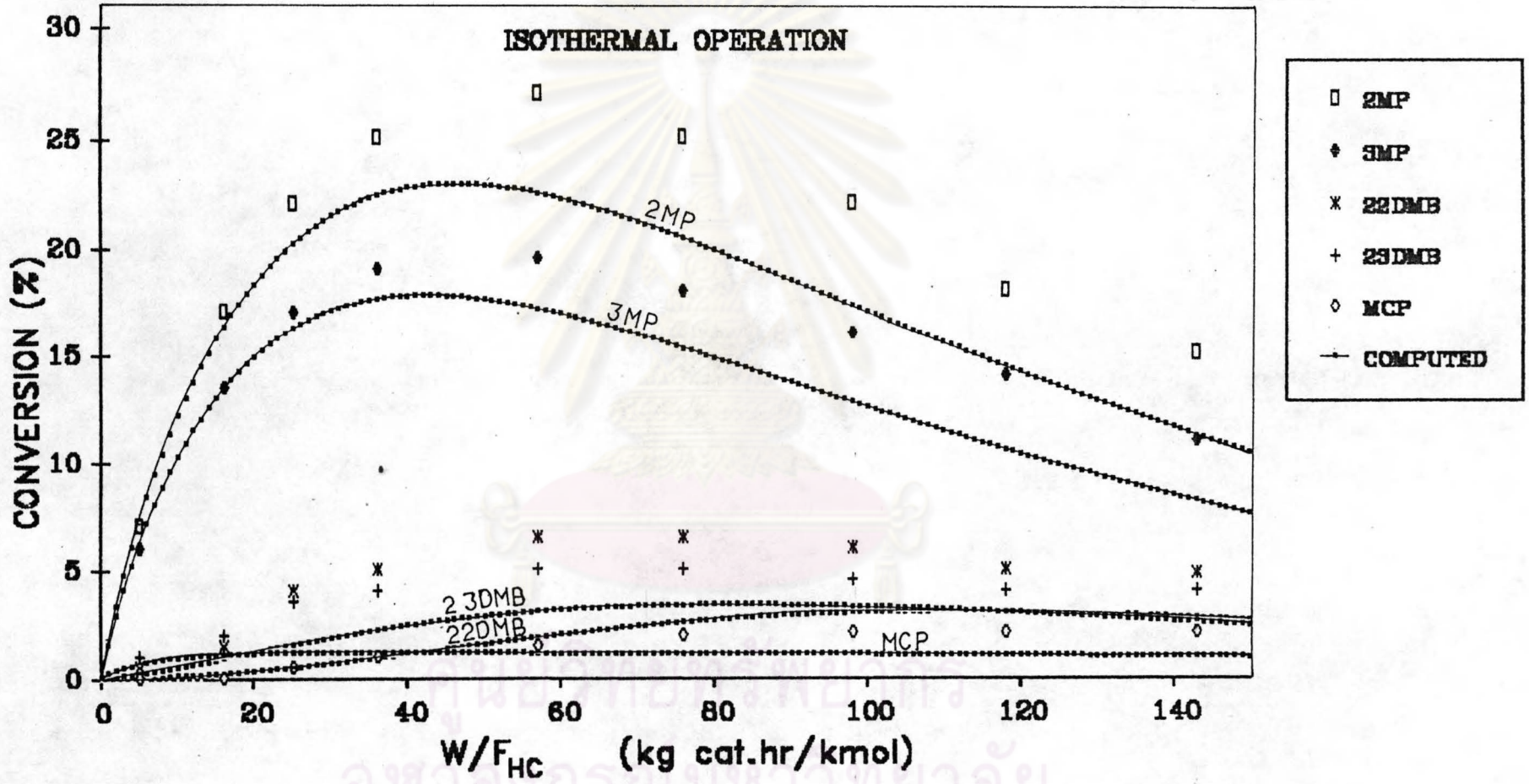

Figure 6-2 Conversion at 460.9 °C, 16 bar, H_2/hydrocarbon = 9.98, and n-Hexane feed. Experimental (Marin et al., (1982)): points. Catalyst: 0.59 %wt Pt, 0.67 %wt Cl on Al_2O_3 catalyst.

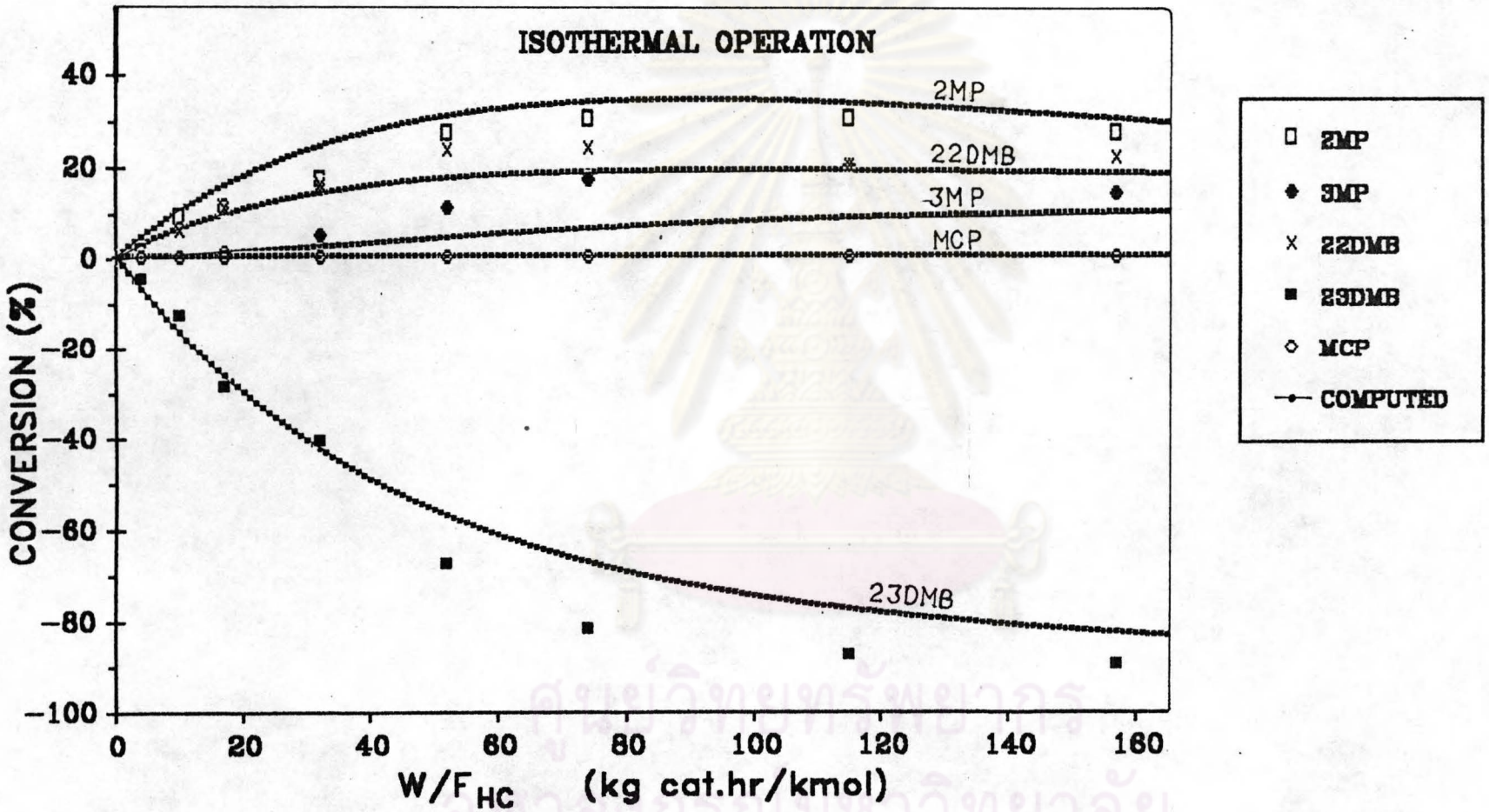

Figure 6-3 Conversion at 419 °C, 10 bar, H_2/hydrocarbon = 10.01, and 2,3-dimethylbuthane Experimental (Marint et al., (1982)): points. Catalyst: 0.59 %wt Pt, 0.67 %wt Cl on Al_2O

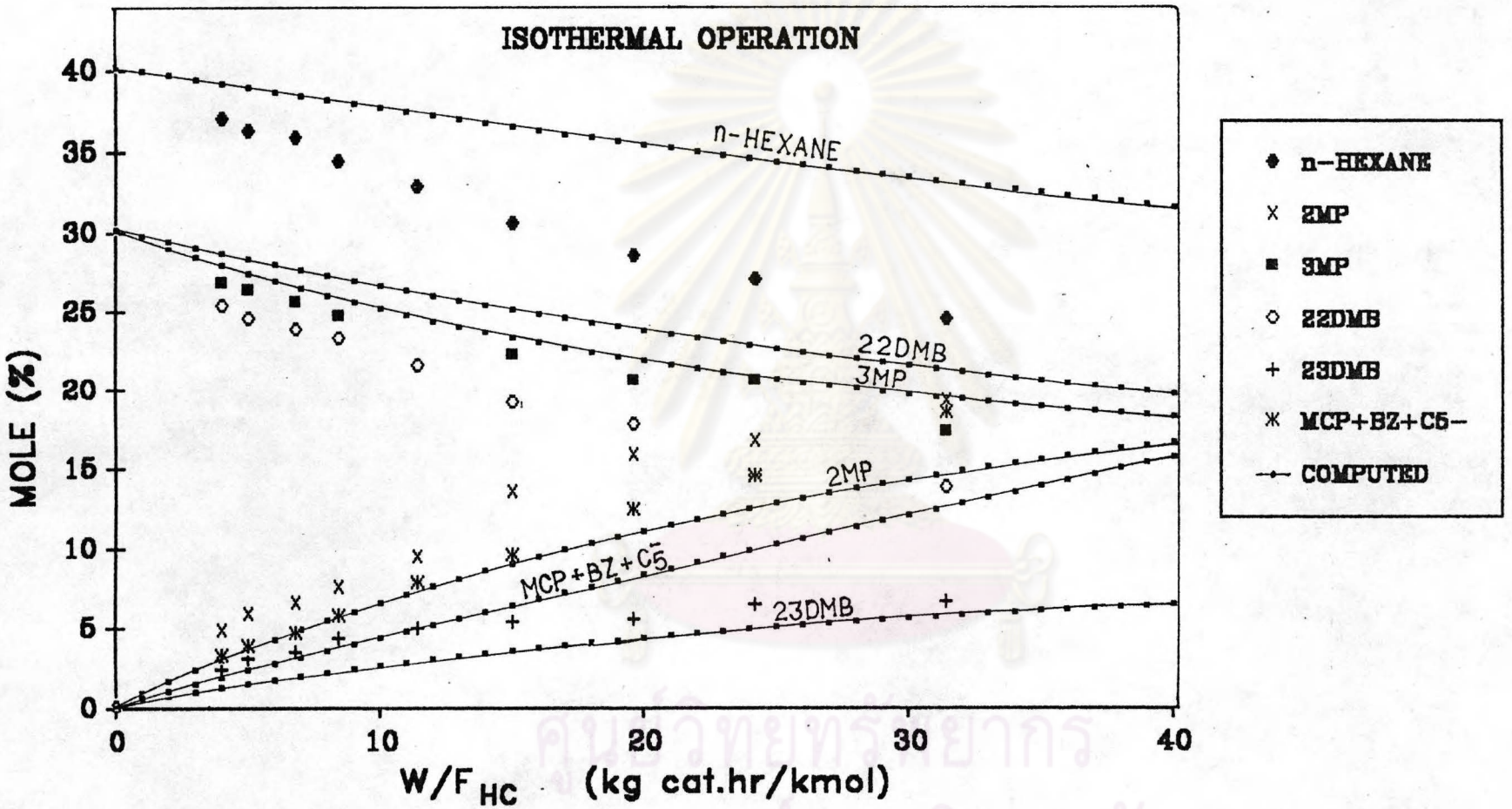

Figure 6-4 Conversion at 435 °C, 10.5 bar, H_2/hydrocarbon = 20, and n-Hexane, 2MP, 3MP, and 22DMB (0.4, 0, 0.3, 0.3) feed. Computed: ——. Experimental (Christoffel (1979)): points. Catalyst: 0.35% Pt on Alumina catalyst.

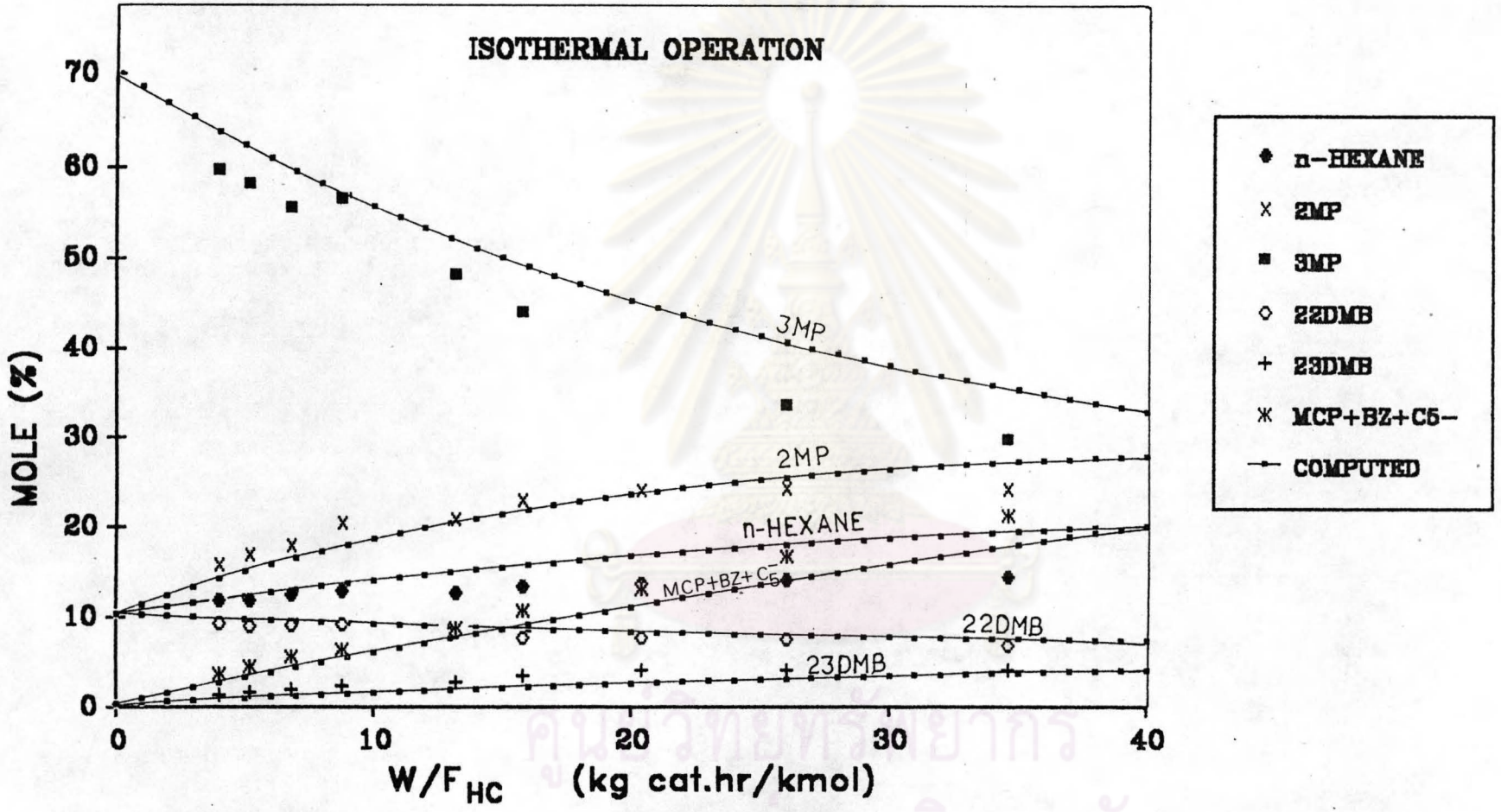

Figure 6-5 Conversion at 435 °C, 10.5 bar, H_2/hydrocarbon = 20, and n-Hexane, 2MP, 3MP, and 22DMB (0.1, 0.1, 0.7, 0.1) feed. Computed: ---- . Experimental (Christoffel (1979)):points. Catalyst: 0.35% Pt on Alumina catalyst.

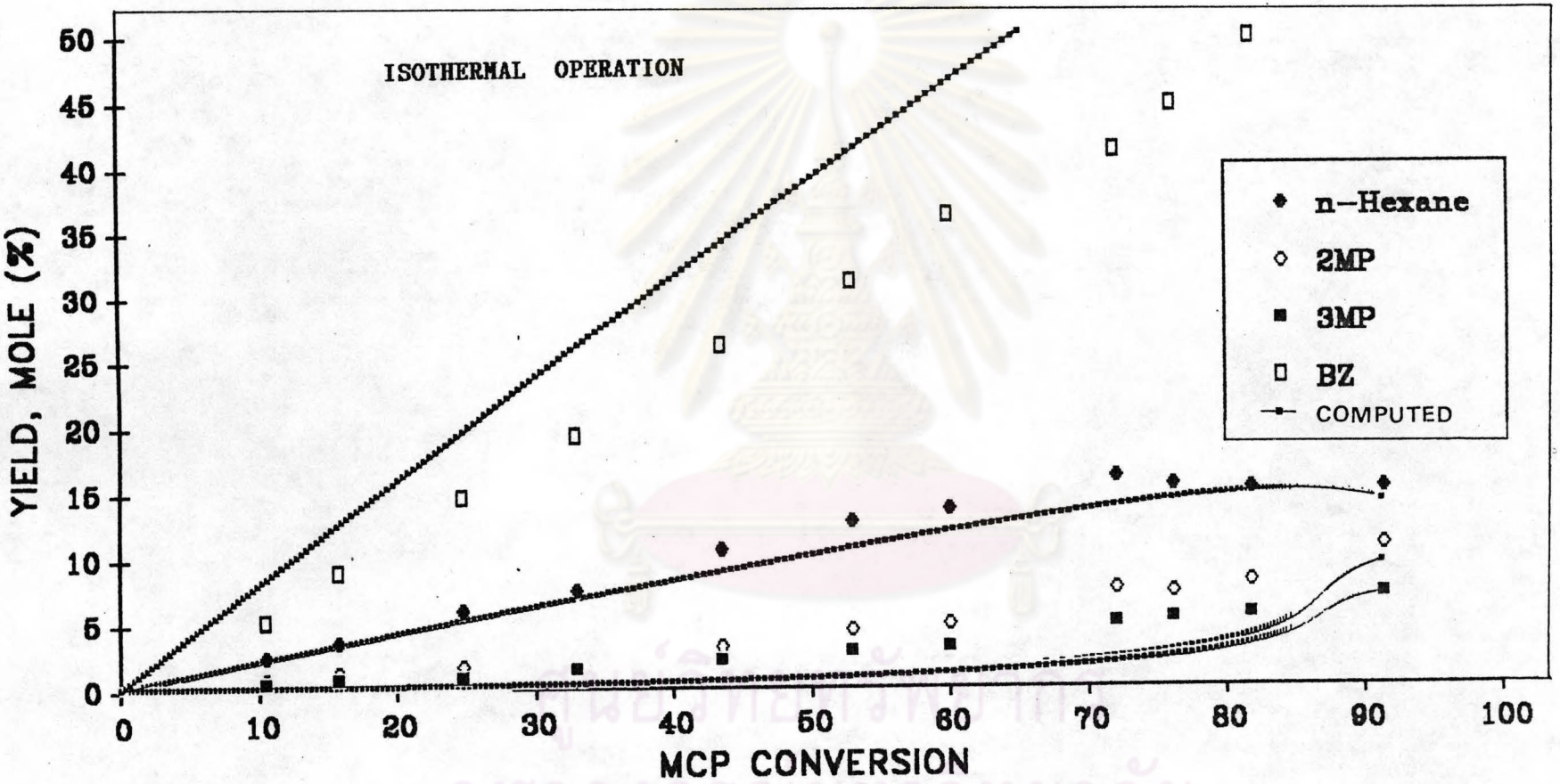

Figure 6-6 Conversion at 454 °C, 13.7 bar, H_2/hydrocarbon = 10, and MCP feed. Computed: ⟷ . Experimental (Selman, (1975)): points. Catalyst: 0.3 %pt, 0.3% Rhenium, and 0.6 %Cl on Alumina catalyst

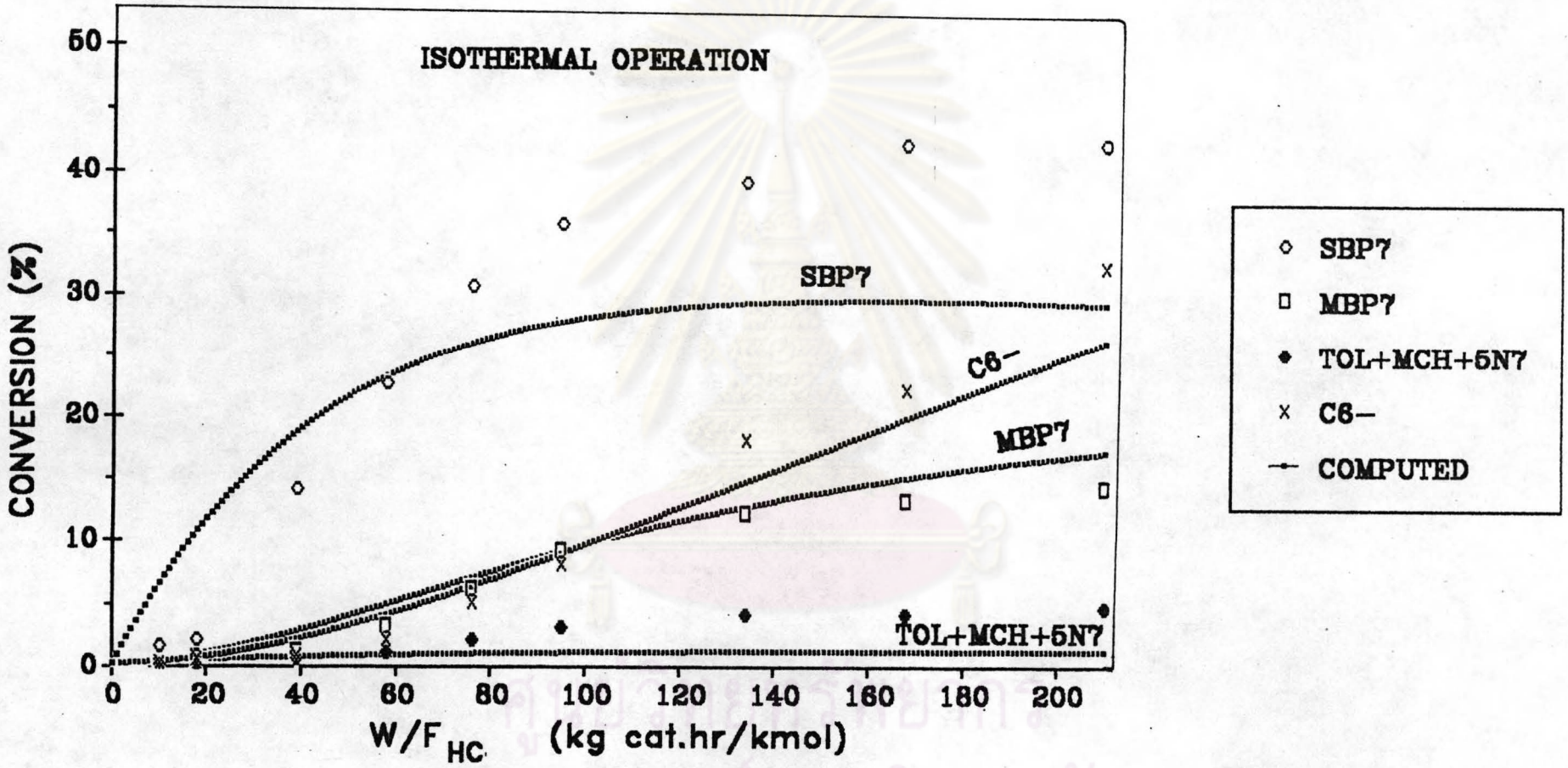

Figure 6-7 Conversion at 420 °C, 20.5 bar, H_2/hydrocarbon = 40, and n-Heptane feed. Experimental (Van Trimpont et al., (1988)): points. Catalyst: 0.59 %wt Pt, 0.67 %wt Cl on Al_2O_3 catalyst.

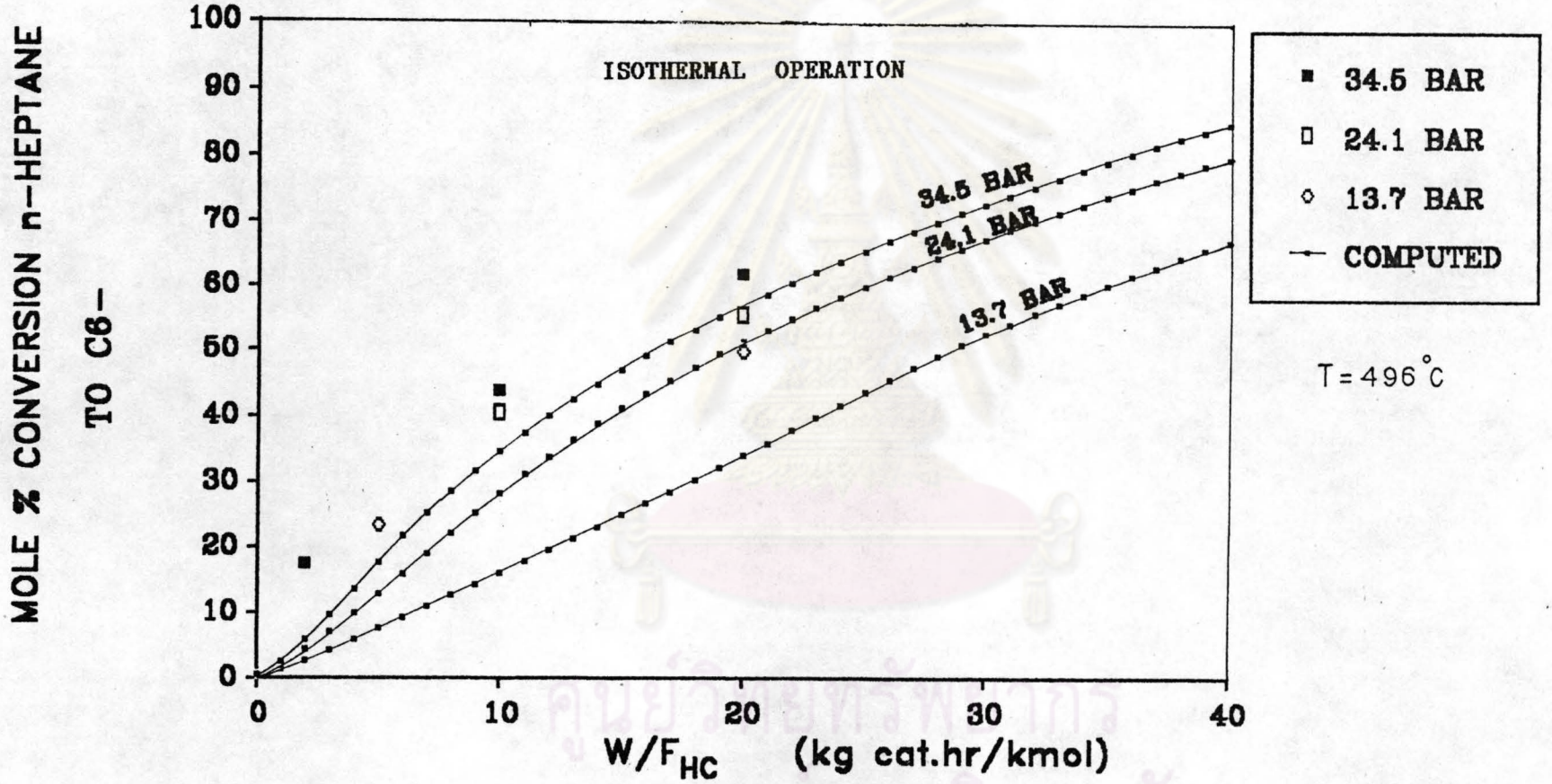

Figure 6-8 Effect of Pressure on yield of hydrocracking. Experimental (Hettinger et al. (1955)): points. Catalyst: 0.6 %wt Pt on Al_2O_3 catalyst.

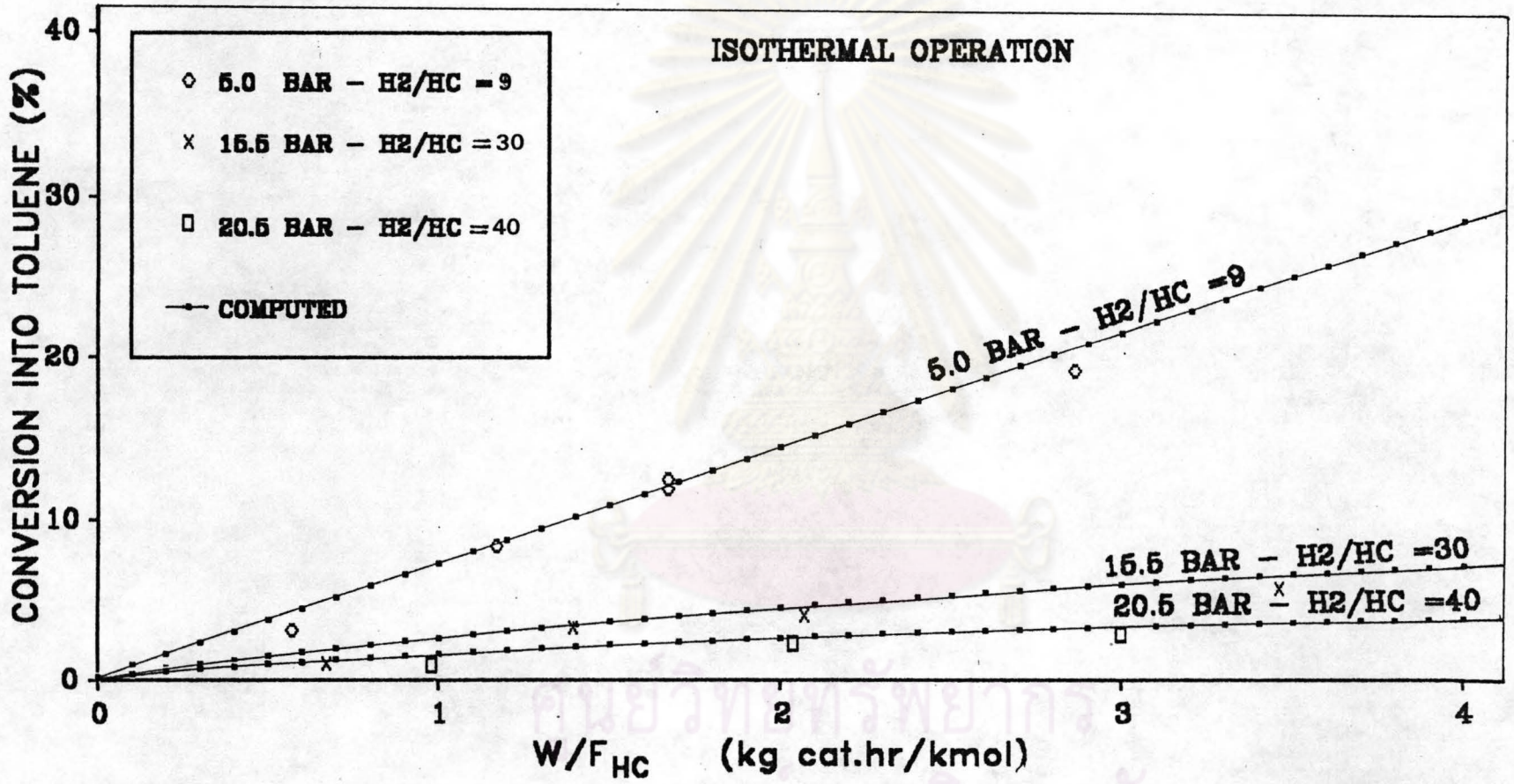

Figure 6-9 Dehydrogenation of methylcyclohexane at temperature 350 °C. Effect of pressure and hydrogen/hydrocarbon ratio on yield of toluene. Experimental (Van Trimpont et al. (1986)): points. Catalyst: 0.59 %wt Pt, 0.67 %wt Cl on Al_2O_3 catalyst.

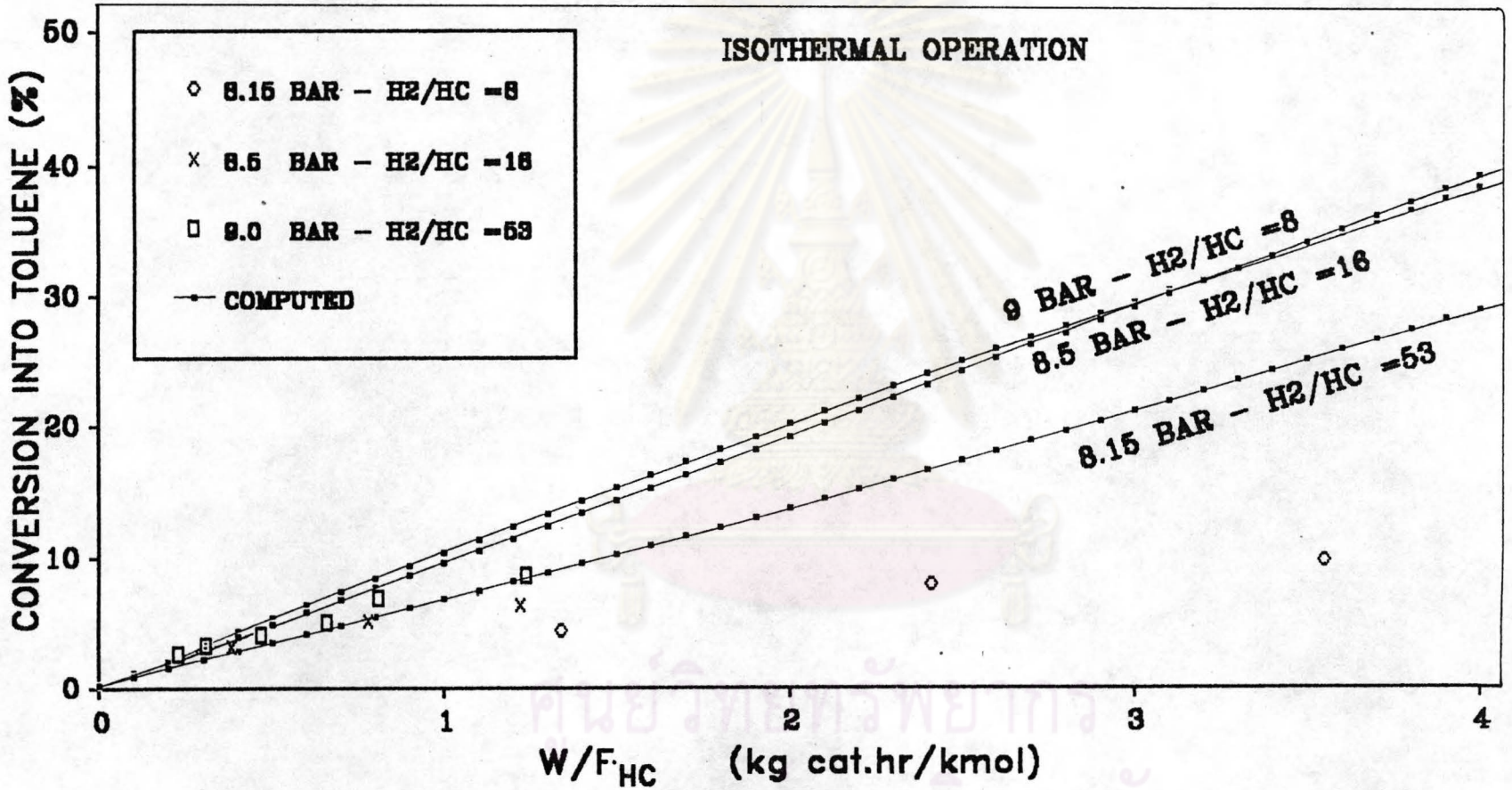

Figure 6-10 Dehydrogenation of methylcyclohexane at temperature 400 °C. Effect of pressure and hydrogen/hydrocarbon ratio on yield of toluene. Experimental (Froment et al. (1988)): points. Catalyst: 0.3 %wt Pt, 0.31 wt % Re, 0.95 wt % Cl on Al_2O_3 catalyst.

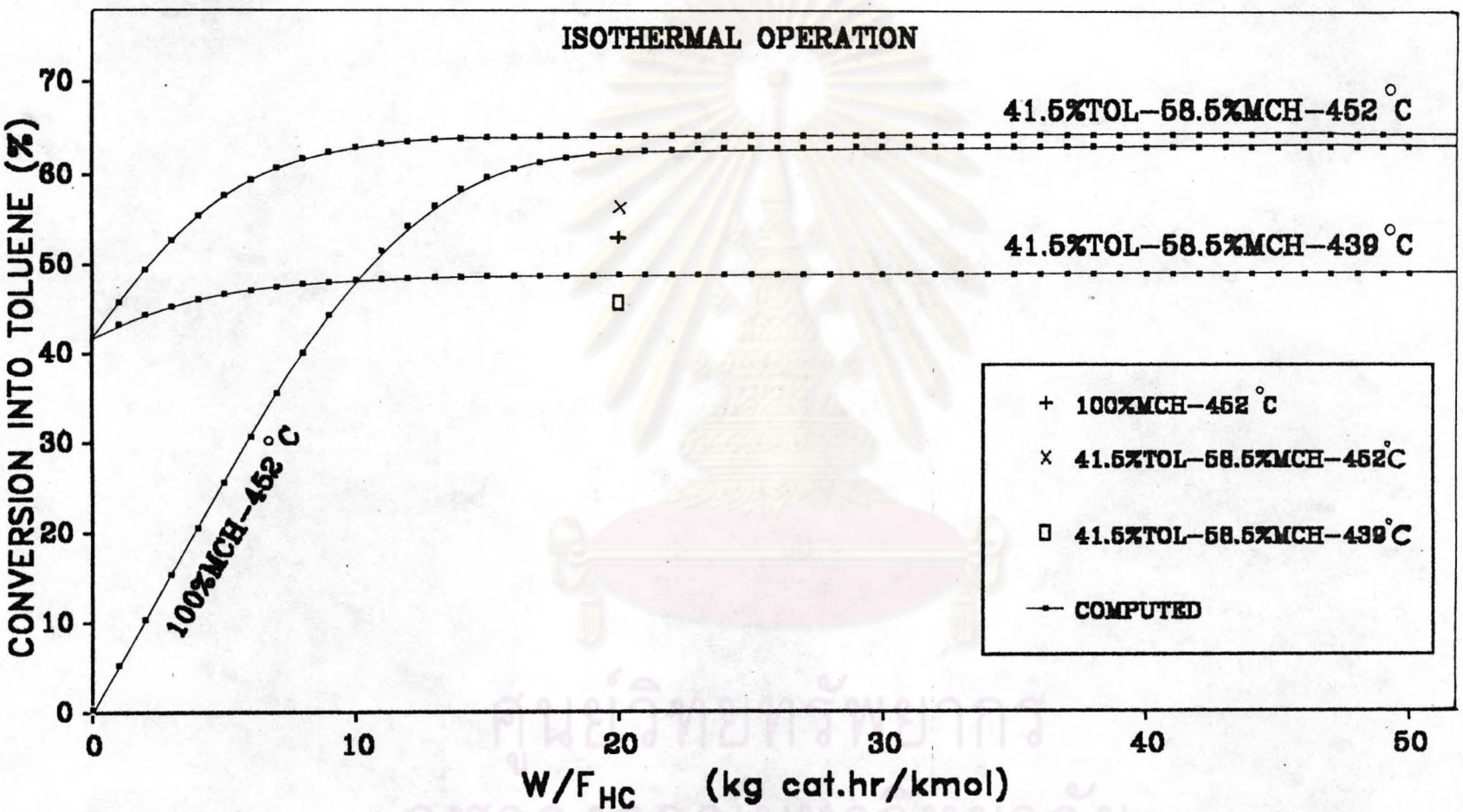

Figure 6-11 Dehydrogenation of methylcyclohexane at pressure 48.2 bar and H_2/hydrocarbon ratio =6.6. Effect of temperature and feed composition on yield of toluene. Experimental (Heinemann, (1951)):points. Catalyst: platinum on Al_2O_3 catalyst.

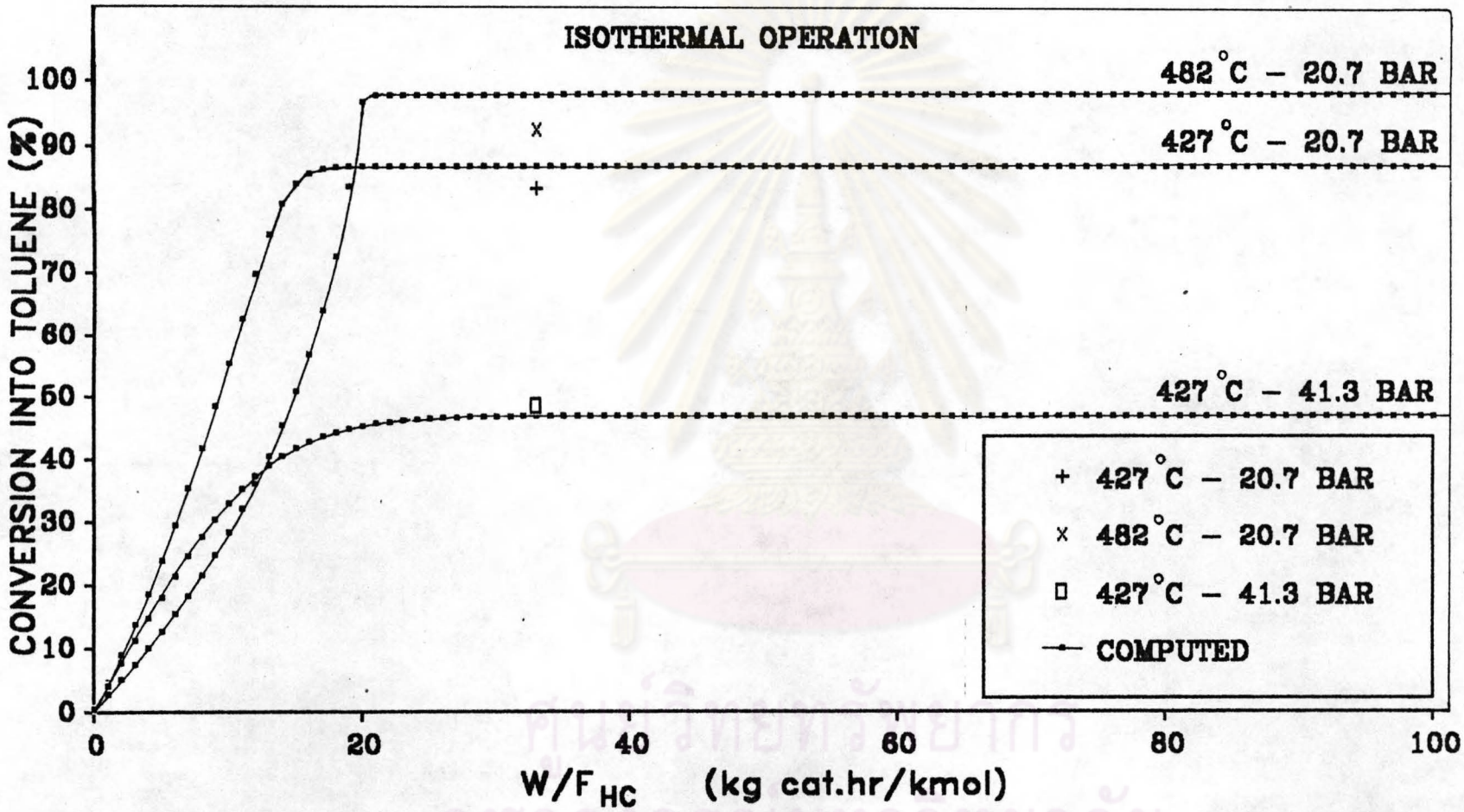

Figure 6-12 Dehydrogenation of methylcyclohexane at H_2/hydrocarbon ratio =4. Effect of temperature and pressure on yield of toluene. Experimental(Heinemann (1951)):points. Catalyst: platinum on Al_2O_3 catalyst.

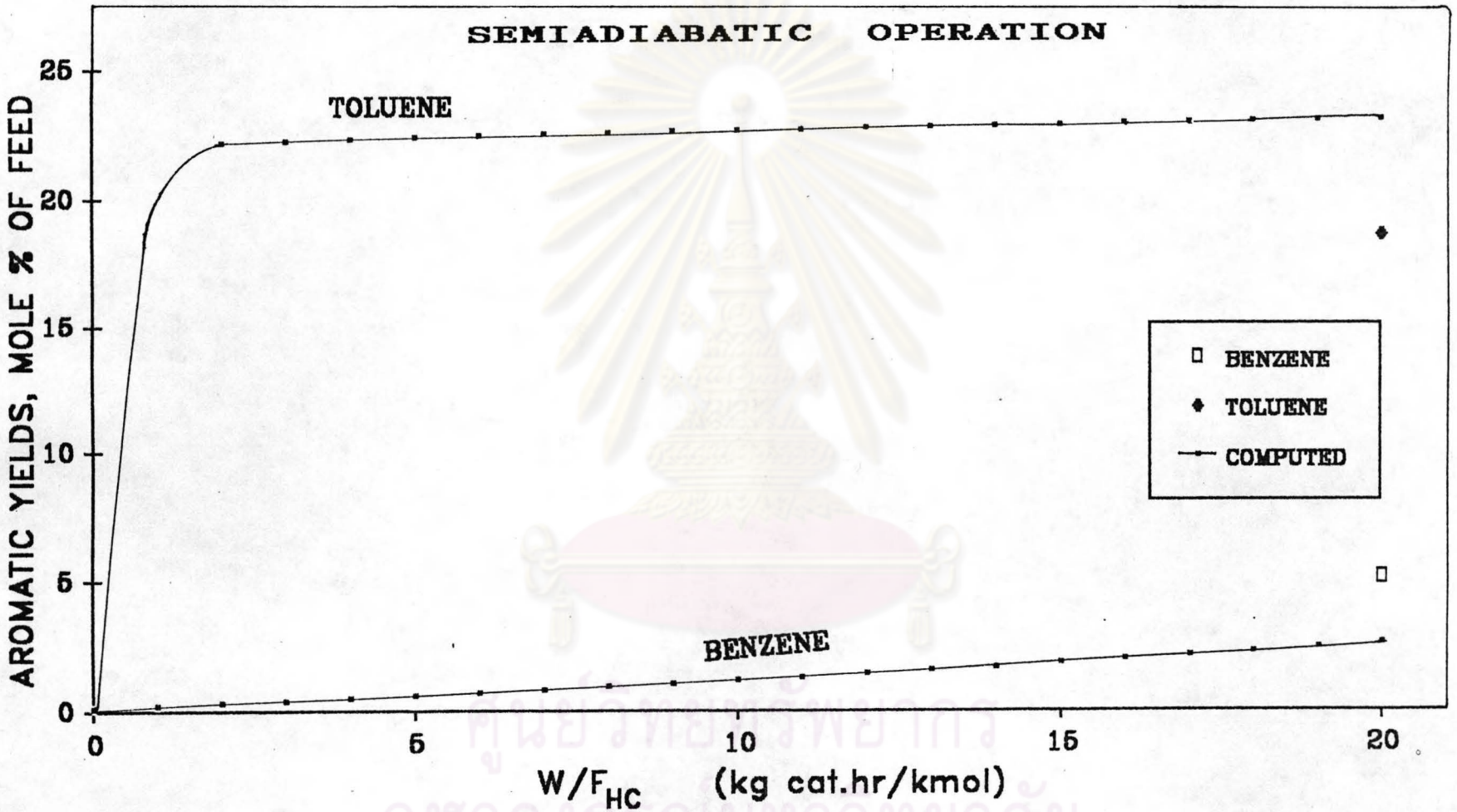

Figure 6-13 Comparison of aromatic yields between computed and experimental data (Meerbott, (1954)). Feeds are methylcyclopentane, methylcyclohexane, and n-heptane [0.222, 0.223, 0.555]. Operating condition is case 22. Catalyst: Platinum on alumina.

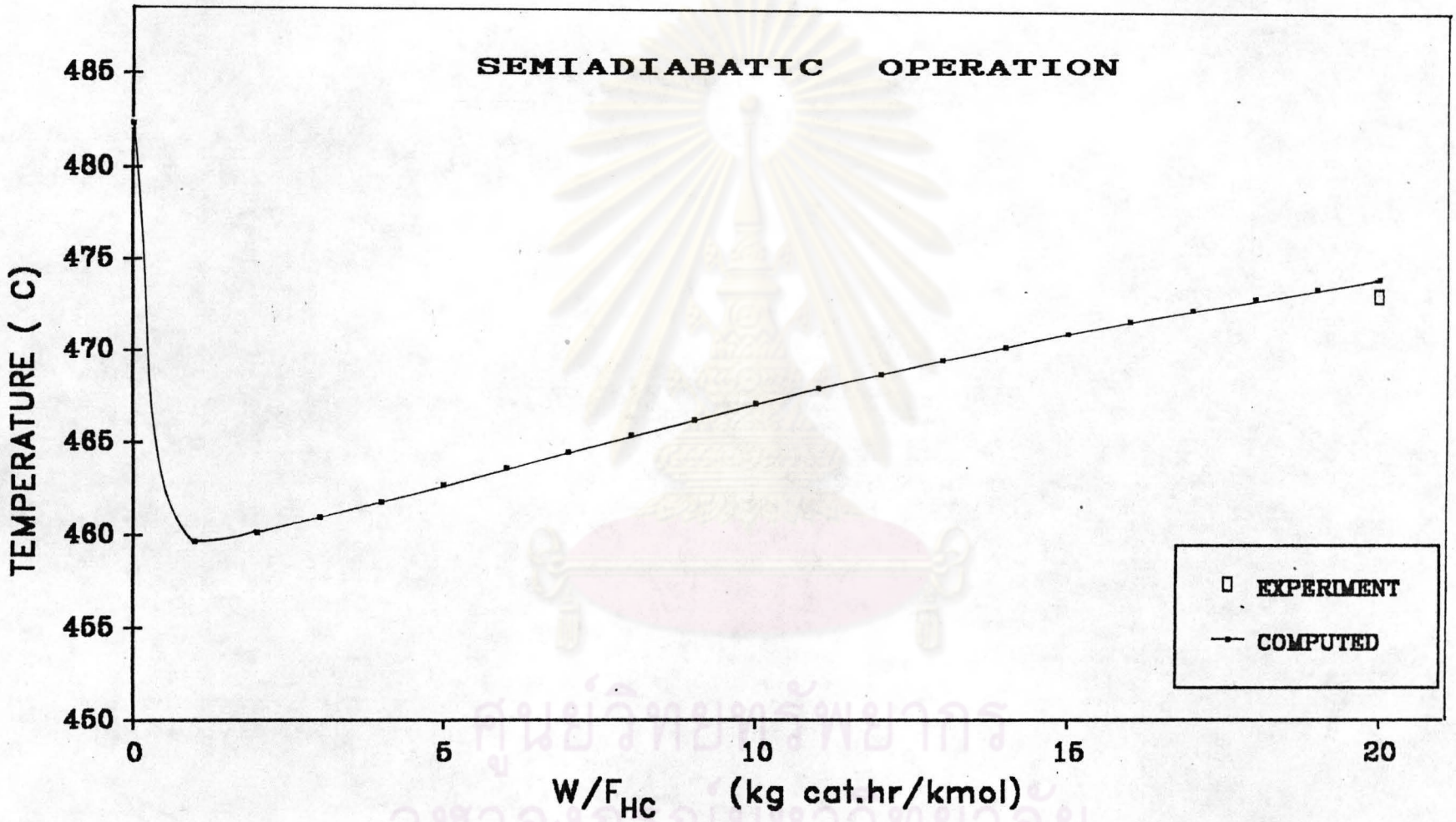

Figure 6-14 Comparison of temperature profile in one reactor between computed and experimental data (Meerbott, (1954)). Operating conditions are case 22 of Table 6-2. Catalyst: Platinum on alumina.

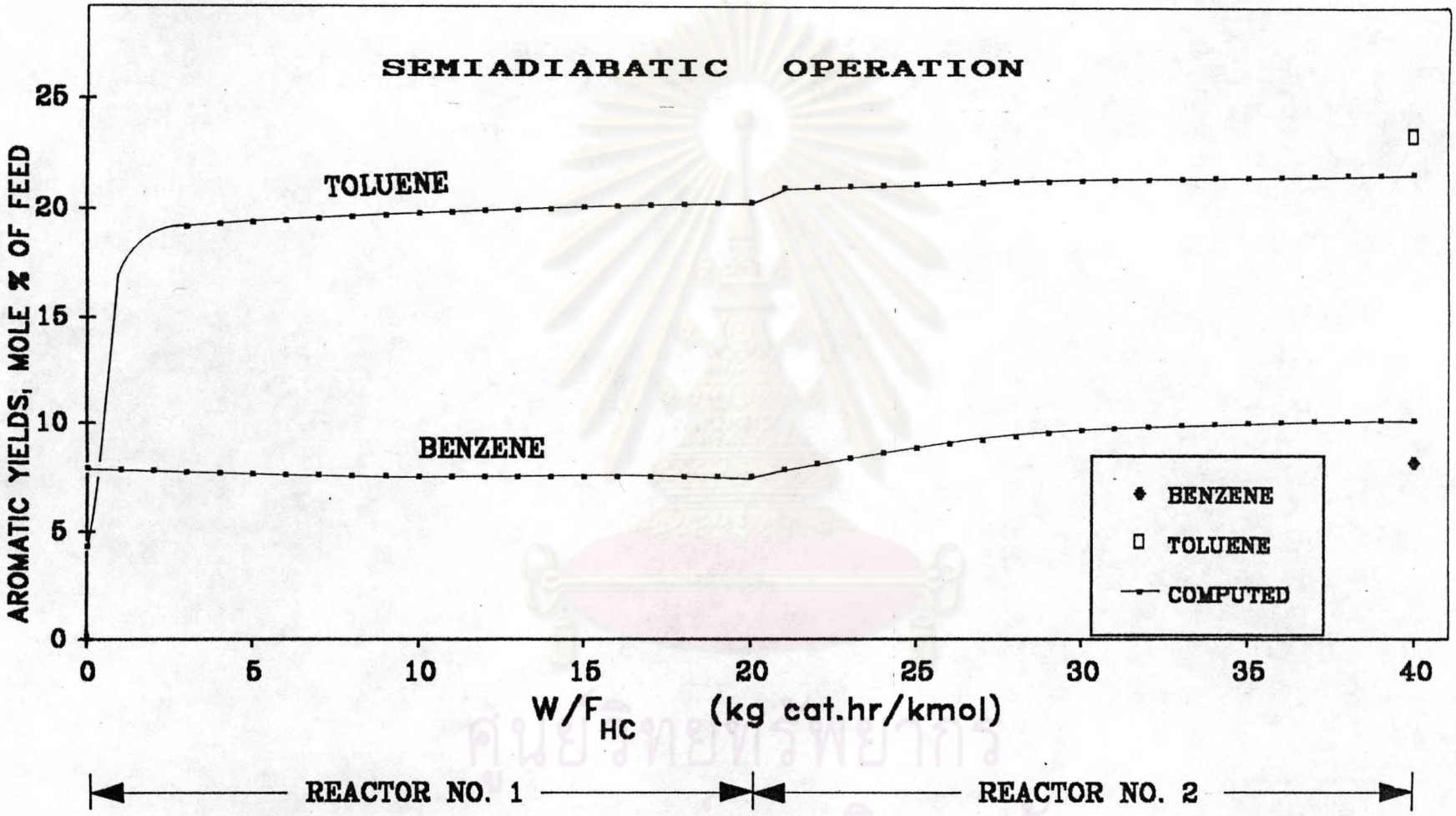

Figure 6-15 Comparison of aromatic yields between computed and experimental data (Meerbott, (1954)). Operating conditions are case 23 of Table 6-3. Catalyst: Platinum on alumina.

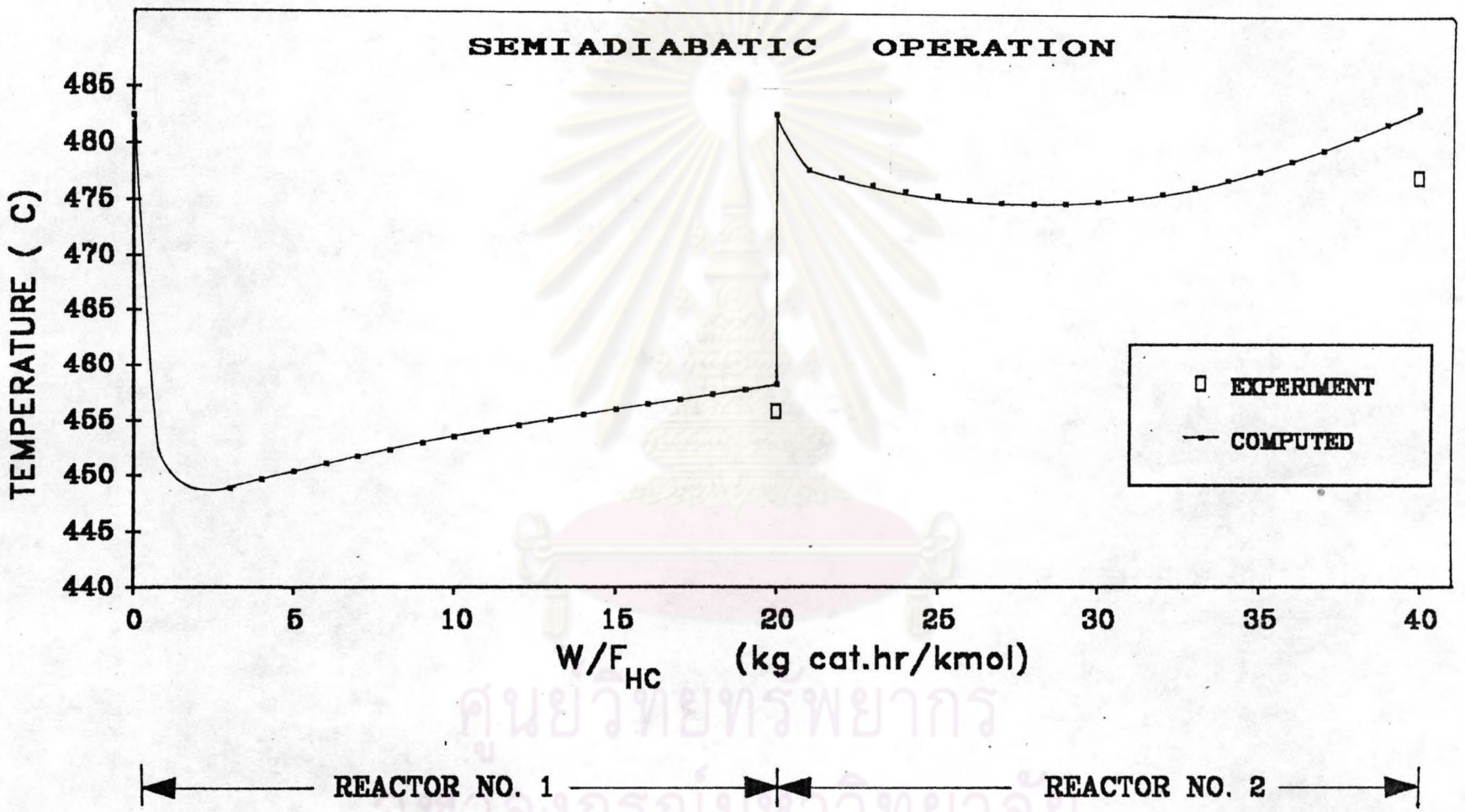

Figure 6-16 Comparison of temperature profiles in two reactors between computed and experimental data (Meerbott, (1954)). Operating conditions are case 23 of Table 6-3. Catalyst: Platinum on alumina.

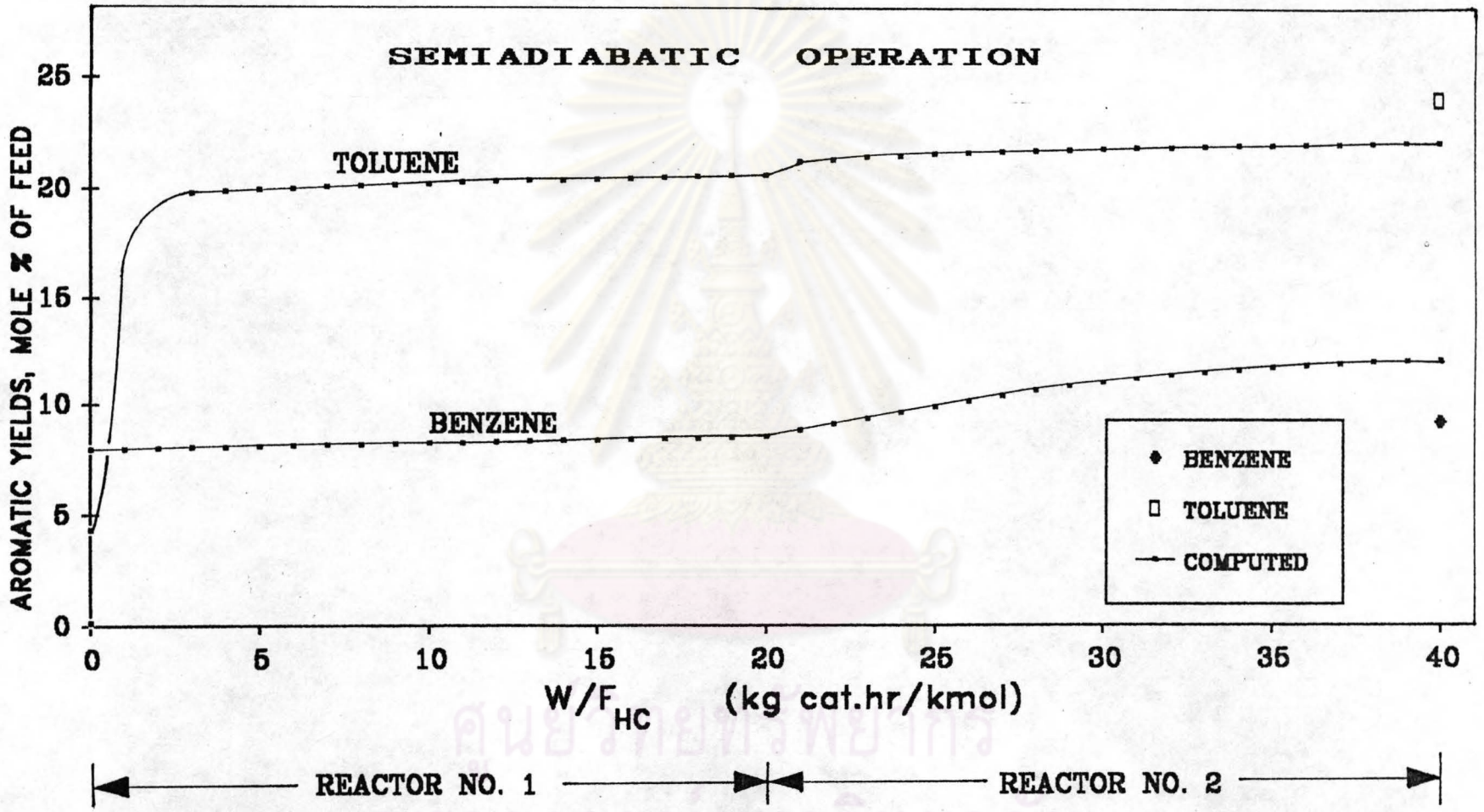

Figure 6-17 Comparison of aromatic yields between computed and experimental data (Meerbott, (1954)). Operating conditions are case 24 of Table 6-3.
Catalyst: Platinum on alumina.

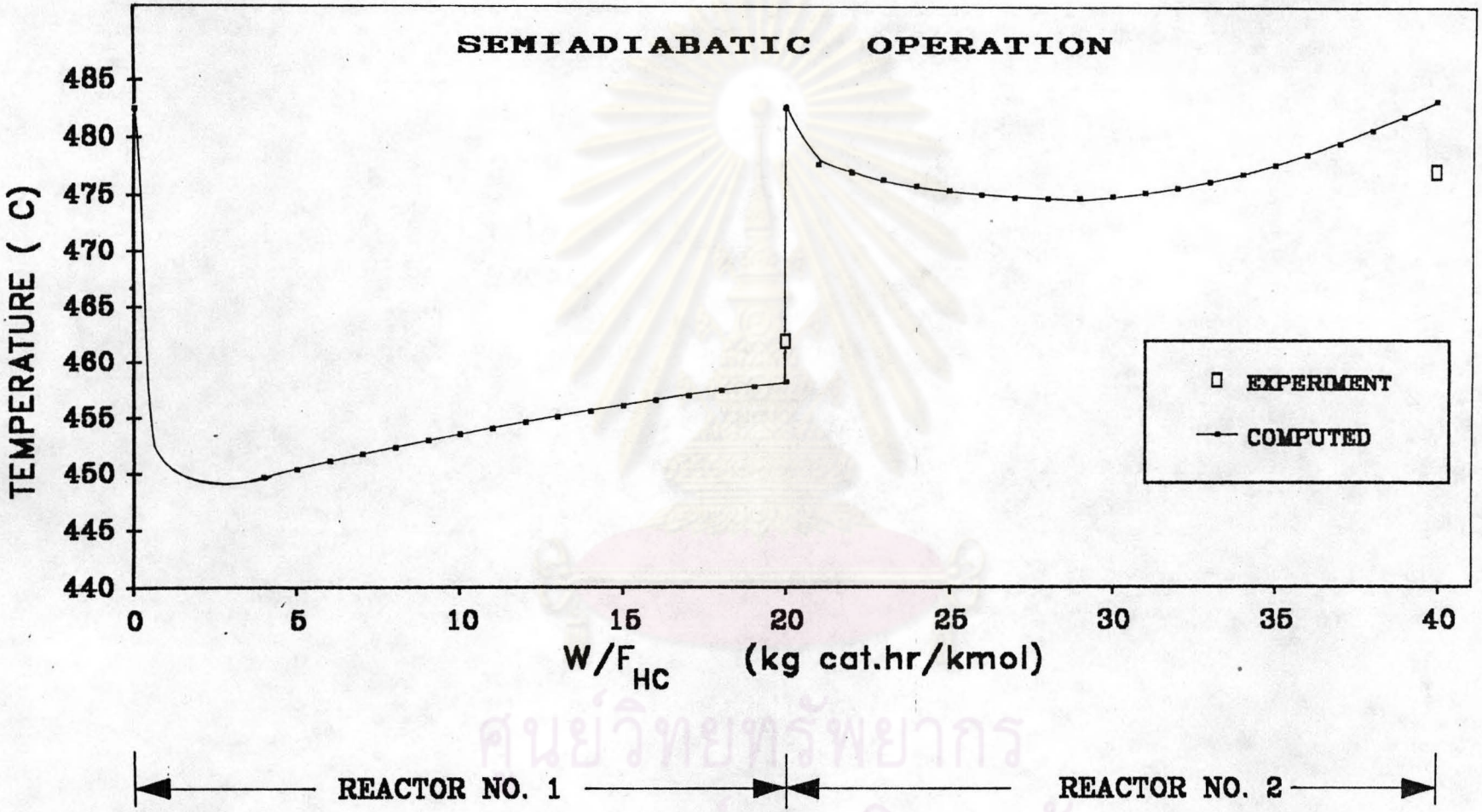

Figure 6-18 Comparison of temperature profiles in two reactors between computed and experimental data (Meerbott, (1954)). Operating conditions are case 24 of Table 6-3. Catalyst: Platinum on alumina.

Figure 6-19 Comparison of the step size in the simulation of case 11

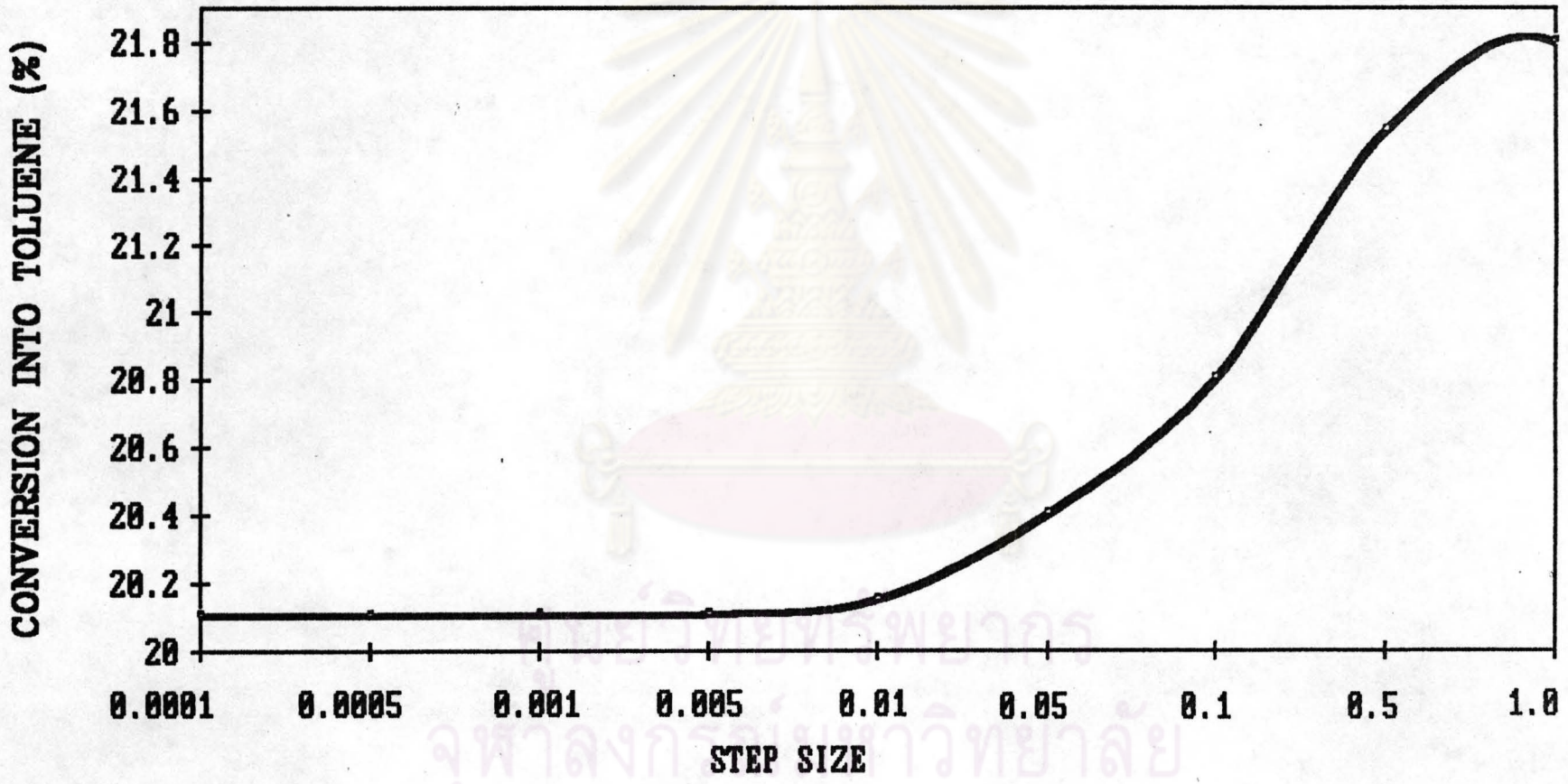

Table 6-4 The error of the simulation

Product output	Experimental Data (mol)	Simulated Results (mol)	%Error base on True Experiment
Case 1			
Product output at W/F = 143			
2-methylpentane	15.0	11.2	-25.3
3-methylpentane	11.0	8.1	-26.0
2,2-dimethylbutane	4.8	2.7	-43.6
2,3-dimethylbutane	4.0	2.5	-37.2
methylcyclopentane	2.1	0.9	-56.0
methylcyclopentane	110.0	117.2	6.5
Case 2			
Product output at W/F = 157			
2-methylpentane	27.0	29.9	10.7
3-methylpentane	14.0	9.7	-30.7
2,2-dimethylbutane	22.0	18.2	-17.3
methylcyclopentane	0.0	0.0	0.0
cracked product	35.0	34.5	-1.4
Case 3			
Product output at W/F = 45			
n-hexane	21.3	30.7	44.1
2-methylpentane	19.5	17.4	-10.9
3-methylpentane	16.2	17.6	8.6
2,2-dimethylbutane	12.1	18.8	55.3
2,3-dimethylbutane	6.6	6.6	0.0
MCP+benzene+C5-	23.6	17.362	-26.4
Case 4			
Product output at W/F = 35			
n-hexane	14.1	19.0	35.1
2-methylpentane	23.9	26.8	12.3
3-methylpentane	29.4	34.8	18.5
2,2-dimethylbutane	6.5	7.1	9.1
2,3-dimethylbutane	3.8	3.3	-12.4
MCP+benzene+C5-	21.0	17.557	-16.4
Case 5			
at MCP conversion of 33%			
benzene	19.1	24.5	28.3
n-hexane	7.4	7.0	-5.4
2-methylpentane	1.5	1.0	-33.3
3-methylpentane	1.3	1.0	-23.1

Table 6-4 (continued)

Product output	Experimental Data (mol)	Simulated Results (mol)	%Error base on True Experiment
Case 6			
Product output at W/F = 210			
SBP7	42.0	28.9	-31.3
MBP7	14.0	16.8	20.4
toluene	3.5	0.1	-98.0
5N7	1.0	0.9	-7.6
cracked product	32.0	25.8	-19.3
Product output			
cracked product of case 7	49.3	33.3	-32.5
cracked product of case 8	61.2	56.3	-8.0
cracked product of case 9	55.0	50.6	-7.9
Product output is toluene			
case 10 at W/F = 3.5	5.6	6.4	13.5
case 11 at W/F = 2.8	19.0	20.6	8.6
case 12 at W/F = 3.0	2.6	3.1	19.8
case 13 at W/F = 3.6	8.9	34.6	287.0
case 14 at W/F = 1.2	6.2	11.2	82.1
case 15 at W/F = 1.2	8.4	7.9	-5.6
case 16 at W/F = 20.0	56.0	61.9	10.5
case 17 at W/F = 20.0	52.9	63.7	20.4
case 18 at W/F = 20.0	45.3	48.4	6.8
case 19 at W/F = 33.0	83.0	86.2	3.9
case 20 at W/F = 33.0	92.0	97.2	5.6
case 21 at W/F = 33.0	48.0	46.3	-3.5
Case 22			
Product output at W/F = 20			
benzene	5.0	2.5	50.0
toluene	18.5	23.0	24.1
temperature, (C)	472.8	473.7	0.2

Table 6-4 (continued)

Product output	Experimental Data (mol)	Simulated Results (mol)	%Error base on True Experiment
Case 23			
Product output at W/F = 40			
benzene	8.1	9.9	22.2
toluene	23.1	21.4	7.4
temperature, (C)			
Reactor No.1	455.5	457.9	0.5
temperature, (C)			
Reactor No.2	476.6	482.6	1.3
Case 24			
Product output at W/F = 40			
benzene	9.1	11.8	29.9
toluene	23.7	21.8	8.0
temperature, (C)			
Reactor No.1	461.6	459.9	0.4
temperature, (C)			
Reactor No.2	476.6	482.6	1.3