



CHAPTER IV

RESULTS AND DISCUSSION

4.1 Effect of feed compositions on *m*- and *p*-CNB crystallization

For this experiment, the effect of feed compositions on the *m*- and *p*-CNB crystallization was investigated. The feed compositions at 61.0, 62.9, and 65.0 wt% *m*-CNB were utilized. Figure 4.1 shows the binary phase diagram of *m*- and *p*-CNB. Seven grams of *m*- and *p*-CNB solid mixture were melted in the crystallizer to obtain a homogeneous solution. Then, the system was cooled by the cooling water from 30°C to a crystallization temperature. The precipitates were then collected, washed, and dissolved with hexane before quantitative analysis by GC. The CNB compositions of the feeds and precipitates are shown in Table 4.1.

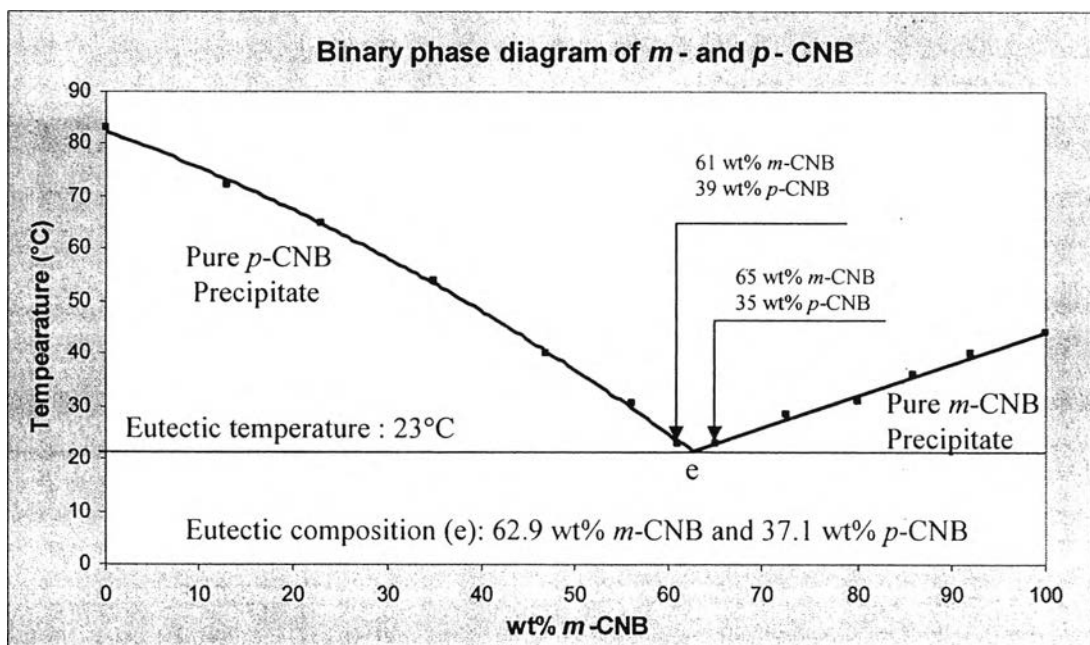


Figure 4.1 Binary phase diagram of *m*- and *p*-CNB (www.sulzerchemtech.com).

Table 4.1 Compositions of *m*- and *p*-CNB in the feeds and the precipitates, and crystallization temperature

Feed	Feed composition (wt%)		Precipitate composition (wt%)		Crystallization temperature (°C)
	<i>m</i> -CNB	<i>p</i> -CNB	<i>m</i> -CNB	<i>p</i> -CNB	
Below the eutectic composition	61.05	38.95	4.96	95.04	22.0
At the eutectic composition	62.89	37.11	62.80	37.20	23.5
Above the eutectic composition	64.97	35.03	92.73	7.27	23.0

Without any zeolite, the result shows that the crystallization of *m*- and *p*-CNB at the eutectic composition or 62.9 wt% *m*-CNB in the feed provides opaque precipitates with the CNB composition close to that of the feed at 23.5°C. Above the eutectic composition, the transparent precipitates appear with the composition being rich in *m*-CNB, 92.73 wt%, while the *p*-CNB enriched precipitates are observed for the composition below the eutectic composition. A possible reason why the precipitate purity is not close to 100% may be from the contamination in the feed. These results could be confirmed from the binary phase diagram as shown in Figure 4.1.

4.2 Effect of FAU zeolite on *m*- and *p*-CNB crystallization

4.2.1 Effect of FAU zeolites on the CNB feed solution compositions

The zeolites were calcined at 350°C for an hour before experiments. A zeolite was placed at the center of the crystallizer. The solution mixture and the zeolite were slightly stirred to minimize any concentration gradient in the solution. Then, the solution composition after adding the zeolite was analyzed. From the results in Tables 4.2, 4.3, and 4.4, the feed compositions before and after adding the zeolite are still similar. The similarity seems to be independent of the *m*-CNB composition in the feed and type of the zeolite. This implies that the presence of a zeolite hardly affects the *m*- and *p*-CNB compositions in the feed solution.

Table 4.2 *m*- and *p*-CNB compositions in the feed, 61.0 wt% of *m*-CNB, before and after adding the zeolites at 30°C

Zeolite	Feed composition before adding zeolite (wt%)		Feed composition after adding zeolite (wt%)		%difference*
	<i>m</i> -CNB	<i>p</i> -CNB	<i>m</i> -CNB	<i>p</i> -CNB	
NaX	60.99	39.01	61.02	38.98	0.03
CaX	61.00	39.00	61.03	38.97	0.03
BaX	61.05	38.95	60.99	39.01	0.06
NaY	61.04	38.96	60.95	39.05	0.09
CaY	60.97	39.03	60.98	39.02	0.01

*%difference is the difference between the *m*-CNB compositions in the feed with and without a zeolite.

Table 4.3 *m*- and *p*-CNB compositions in the feed, 62.9 wt% of *m*-CNB, before and after adding the zeolites at 30°C

Zeolite	Feed composition before adding zeolite (wt%)		Feed composition after adding zeolite (wt%)		%difference*
	<i>m</i> -CNB	<i>p</i> -CNB	<i>m</i> -CNB	<i>p</i> -CNB	
NaX	62.88	37.12	62.90	37.10	0.02
CaX	62.87	37.13	62.90	37.10	0.03
BaX	62.91	37.09	62.93	37.07	0.02
NaY	62.89	37.11	62.88	37.12	0.01
CaY	62.87	37.13	62.87	37.13	0.00

*%difference is the difference between the *m*-CNB compositions in the feed with and without a zeolite.

Table 4.4 *m*- and *p*-CNB compositions in the feed, 65.0 wt% of *m*-CNB, before and after adding the zeolites at 30°C

Zeolite	Feed composition before adding zeolite (wt%)		Feed composition after adding zeolite (wt%)		%difference*
	<i>m</i> -CNB	<i>p</i> -CNB	<i>m</i> -CNB	<i>p</i> -CNB	
NaX	64.99	35.01	64.97	35.03	0.02
CaX	64.96	35.04	64.98	35.02	0.02
BaX	65.02	34.98	65.01	34.99	0.01
NaY	65.06	34.94	65.02	34.98	0.04
CaY	64.98	35.02	64.96	35.04	0.02

*%difference is the difference between the *m*-CNB compositions in the feed with and without a zeolite.

4.2.2 Effect of FAU zeolites on the CNB precipitate compositions

After adding a zeolite in the feed, the system was cooled from 30°C until precipitates were observed. Then, the precipitates were collected, washed and

dissolved with hexane. The CNB composition was analyzed by GC (Run#1). In addition, the mother liquor was also analyzed for its composition. In order to ensure that the system was reproducible and was not affected by the adsorption, the mixture was heated backwards to the homogeneous phase and then cooled until precipitates were formed again. Another CNB composition analysis (Run#2) was then carried out. Normally, the precipitates were formed throughout the crystallizer; the positions where precipitates were collected are specified as shown in Figure 4.2. The positions 1 to 4 are located near the zeolite or area (a) and the positions 5 to 8 are located far from the zeolite or area (b). From the experiment, the CNB compositions in the precipitates for both Run#1 and Run#2 at every position are illustrated in Tables 4.5-4.10.

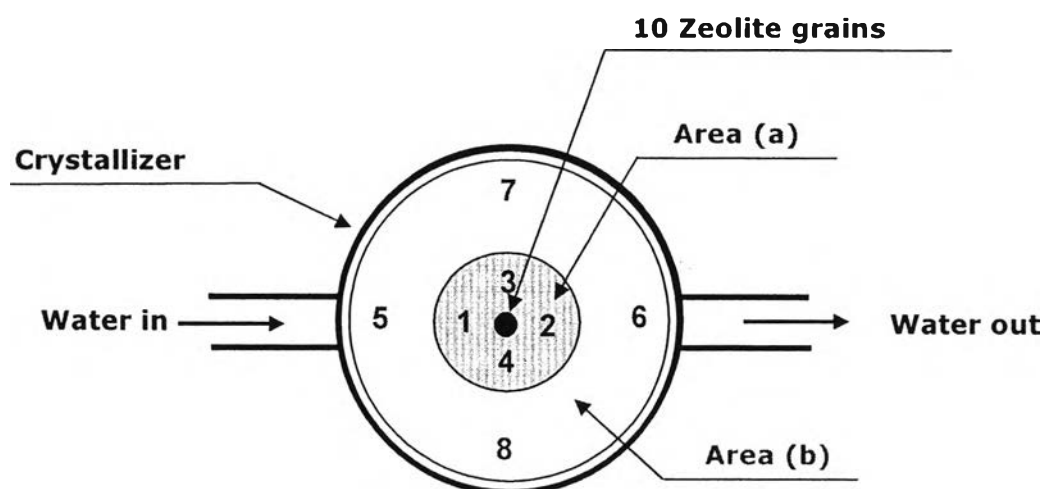


Figure 4.2 Locations where precipitates were collected for *m*- and *p*-CNB composition analysis.

Table 4.5 Compositions of *m*- and *p*-CNB in the precipitates located near and far from zeolites (Run#1) with 61.0 wt% *m*-CNB in the feed

Zeolite	Precipitate near zeolite			Precipitate far from zeolite		
	Composition (wt%)		%	Composition (wt%)		%
	<i>m</i> -CNB	<i>p</i> -CNB	difference*	<i>m</i> -CNB	<i>p</i> -CNB	difference*
NaX	7.73 (1)	92.27 (1)	53.27	10.29 (5)	89.71 (5)	50.71
	8.32 (2)	91.68 (2)	52.68	11.19 (6)	88.81 (6)	49.81
	8.62 (3)	91.38 (3)	52.38	11.67 (7)	88.33 (7)	49.33
	6.38 (4)	93.62 (4)	54.62	12.69 (8)	87.31 (8)	48.31
CaX	5.02 (1)	94.98 (1)	55.98	11.11 (5)	88.89 (5)	49.89
	6.58 (2)	93.42 (2)	54.42	10.58 (6)	89.42 (6)	50.42
	8.21 (3)	91.79 (3)	52.79	12.45 (7)	87.55 (7)	48.55
	5.35 (4)	94.65 (4)	55.65	12.02 (8)	87.98 (8)	48.98
BaX	5.82 (1)	94.18 (1)	55.18	10.56 (5)	89.44 (5)	50.44
	6.24 (2)	93.76 (2)	54.76	11.79 (6)	88.21 (6)	45.21
	6.69 (3)	93.31 (3)	54.31	11.06 (7)	88.94 (7)	49.94
	5.07 (4)	94.93 (4)	55.93	11.70 (8)	88.30 (8)	49.30
NaY	10.39 (1)	89.61 (1)	50.61	23.25 (5)	76.75 (5)	37.75
	9.11 (2)	90.89 (2)	51.89	20.02 (6)	79.98 (6)	40.98
	17.55 (3)	82.45 (3)	43.45	23.25 (7)	76.75 (7)	37.75
	17.93 (4)	82.07 (4)	43.07	22.05 (8)	77.95 (8)	38.95
CaY	6.76 (1)	93.24 (1)	54.24	13.97 (5)	86.03 (5)	47.03
	7.78 (2)	92.22 (2)	53.22	15.71 (6)	84.29 (6)	45.29
	11.22 (3)	88.78 (3)	49.78	17.93 (7)	82.07 (7)	43.07
	7.67 (4)	92.33 (4)	53.33	17.70 (8)	82.30 (8)	43.30

*%difference is the difference between the *m*-CNB compositions in the feed and the precipitates with a zeolite.

**The number in the parenthesis refers to the position where precipitates were collected as shown in Figure 4.2.

Table 4.6 Compositions of *m*- and *p*-CNB in the precipitates located near and far from zeolites (Run#2) with 61.0 wt% *m*-CNB in the feed

Zeolite	Precipitate near zeolite			Precipitate far from zeolite		
	Composition (wt%)		%	Composition (wt%)		%
	<i>m</i> -CNB	<i>p</i> -CNB	difference*	<i>m</i> -CNB	<i>p</i> -CNB	difference*
NaX	9.47 (1)	90.53 (1)	51.53	14.26 (5)	85.74 (5)	46.74
	10.27 (2)	89.73 (2)	50.73	15.87 (6)	84.13 (6)	45.13
	10.48 (3)	89.52 (3)	50.52	17.27 (7)	82.73 (7)	43.73
	10.50 (4)	89.41 (4)	50.50	18.89 (8)	81.11 (8)	42.11
CaX	6.32 (1)	93.68 (1)	54.68	12.85 (5)	87.15 (5)	48.15
	7.52 (2)	92.48 (2)	53.48	14.46 (6)	85.54 (6)	46.54
	9.77 (3)	90.23 (3)	51.23	15.15 (7)	84.85 (7)	45.85
	7.89 (4)	92.11 (4)	53.11	14.09 (8)	85.91 (8)	46.91
BaX	6.39 (1)	93.61 (1)	54.61	11.29 (5)	88.71 (5)	49.71
	5.72 (2)	94.28 (2)	55.28	11.34 (6)	88.66 (6)	49.66
	7.26 (3)	92.74 (3)	53.74	13.01 (7)	86.99 (7)	47.99
	6.69 (4)	93.31 (4)	54.31	12.09 (8)	87.91 (8)	48.91
NaY	8.61 (1)	91.39 (1)	52.39	19.82 (5)	80.18 (5)	41.18
	12.38 (2)	87.62 (2)	48.62	21.97 (6)	78.03 (6)	39.03
	15.95 (3)	84.05 (3)	45.05	21.31 (7)	78.69 (7)	39.69
	14.35 (4)	85.65 (4)	46.65	20.87 (8)	79.13 (8)	40.13
CaY	8.81 (1)	91.19 (1)	52.19	13.23 (5)	86.77 (5)	47.77
	6.52 (2)	93.48 (2)	54.48	15.72 (6)	84.28 (6)	45.28
	9.58 (3)	90.42 (3)	51.42	17.28 (7)	82.72 (7)	43.73
	9.22 (4)	90.78 (4)	51.78	16.67 (8)	83.33 (8)	44.33

*%difference is the difference between the *m*-CNB compositions in the feed and the precipitates with a zeolite.

**The number in the parenthesis refers to the position where precipitates were collected as shown in Figure 4.2.

Table 4.7 Compositions of *m*- and *p*-CNB in the precipitates located near and far from zeolites (Run#1) with 62.9 wt% *m*-CNB in the feed

Zeolite	Precipitate near zeolite			Precipitate far from zeolite		
	Composition (wt%)		%	Composition (wt%)		%
	<i>m</i> -CNB	<i>p</i> -CNB	difference*	<i>m</i> -CNB	<i>p</i> -CNB	difference*
NaX	7.13 (1)	92.87 (1)	55.77	10.51 (5)	89.49 (5)	52.39
	8.25 (2)	91.75 (2)	54.65	12.90 (6)	87.10 (6)	50.00
	8.41 (3)	91.59 (3)	54.49	17.61 (7)	82.39 (7)	45.29
	8.37 (4)	91.63 (4)	54.53	16.25 (8)	83.75 (8)	46.65
CaX	6.75 (1)	93.25 (1)	56.15	10.83 (5)	88.17 (5)	52.07
	7.22 (2)	92.78 (2)	55.68	11.41 (6)	88.59 (6)	51.49
	9.33 (3)	90.67 (3)	53.57	15.93 (7)	84.07 (7)	46.97
	8.64 (4)	91.36 (4)	54.26	14.47 (8)	85.53 (8)	48.43
BaX	7.17 (1)	92.83 (1)	55.73	10.24 (5)	89.76 (5)	52.66
	6.22 (2)	93.78 (2)	56.68	12.03 (6)	87.97 (6)	50.87
	9.16 (3)	90.84 (3)	53.74	18.43 (7)	81.57 (7)	44.47
	8.12 (4)	91.88 (4)	54.78	15.04 (8)	84.96 (8)	47.86
NaY	6.49 (1)	93.51 (1)	56.41	10.91 (5)	89.09 (5)	51.99
	7.07 (2)	92.93 (2)	55.83	11.23 (6)	88.77 (6)	51.67
	9.16 (3)	90.84 (3)	53.74	16.06 (7)	83.94 (7)	46.84
	8.39 (4)	91.61 (4)	54.51	14.57 (8)	85.43 (8)	48.33
CaY	5.91 (1)	94.09 (1)	56.99	12.81 (5)	87.19 (5)	50.09
	6.16 (2)	93.84 (2)	56.74	12.65 (6)	87.35 (6)	50.25
	8.66 (3)	91.34 (3)	54.24	15.87 (7)	84.13 (7)	47.03
	8.04 (4)	91.96 (4)	54.86	14.84 (8)	85.16 (8)	48.06

*%difference is the difference between the *m*-CNB compositions in the feed and the precipitates with a zeolite.

**The number in the parenthesis refers to the position where precipitates were collected as shown in Figure 4.2.

Table 4.8 Compositions of *m*- and *p*-CNB in the precipitates located near and far from zeolites (Run#2) with 62.9 wt% *m*-CNB in the feed

Zeolite	Precipitate near zeolite			Precipitate far from zeolite		
	Composition (wt%)		%	Composition (wt%)		%
	<i>m</i> -CNB	<i>p</i> -CNB	difference*	<i>m</i> -CNB	<i>p</i> -CNB	difference*
NaX	6.92 (1)	93.08 (1)	55.98	12.46 (5)	87.54 (5)	50.44
	8.34 (2)	91.66 (2)	54.56	11.89 (6)	88.11 (6)	51.01
	9.21 (3)	90.79 (3)	53.69	18.78 (7)	81.22 (7)	44.12
	8.66 (4)	91.34 (4)	54.24	14.29 (8)	85.71 (8)	48.61
CaX	5.55 (1)	94.45 (1)	57.35	11.91 (5)	88.09 (5)	50.99
	7.51 (2)	92.49 (2)	55.39	11.41 (6)	88.59 (6)	51.49
	8.23 (3)	91.77 (3)	54.67	14.49 (7)	85.51 (7)	48.41
	9.06 (4)	90.94 (4)	53.84	12.22 (8)	87.78 (8)	50.68
BaX	6.94 (1)	93.06 (1)	55.96	11.29 (5)	88.71 (5)	51.61
	8.37 (2)	91.63 (2)	54.53	12.95 (6)	87.05 (6)	49.95
	9.03 (3)	90.97 (3)	53.87	18.74 (7)	81.26 (7)	44.16
	8.79 (4)	91.21 (4)	54.11	16.12 (8)	83.88 (8)	46.78
NaY	6.86 (1)	93.14 (1)	56.04	10.58 (5)	89.42 (5)	52.32
	7.30 (2)	92.70 (2)	55.60	11.82 (6)	88.18 (6)	51.08
	9.86 (3)	90.14 (3)	53.03	19.44 (7)	80.56 (7)	43.46
	9.57 (4)	90.43 (4)	53.33	13.23 (8)	86.77 (8)	49.67
CaY	5.88 (1)	94.12 (1)	57.02	12.39 (5)	87.61 (5)	50.51
	7.11 (2)	92.89 (2)	55.79	14.00 (6)	86.00 (6)	48.90
	8.14 (3)	91.86 (3)	54.76	15.77 (7)	84.24 (7)	47.13
	6.48 (4)	93.52 (4)	56.42	15.75 (8)	84.25 (8)	47.15

*%difference is the difference between the *m*-CNB compositions in the feed and the precipitates with a zeolite.

**The number in the parenthesis refers to the position where precipitates were collected as shown in Figure 4.2.

Table 4.9 Compositions of *m*- and *p*-CNB in the precipitates located near and far from zeolites (Run#1) with 65.0 wt% *m*-CNB in the feed

Zeolite	Precipitate near zeolite			Precipitate far from zeolite		
	Composition (wt%)		% difference*	Composition (wt%)		% difference*
	<i>m</i> -CNB	<i>p</i> -CNB		<i>m</i> -CNB	<i>p</i> -CNB	
NaX	7.96 (1)	92.04 (1)	57.04	12.27 (5)	87.73 (5)	52.73
	7.25 (2)	92.75 (2)	57.75	11.71 (6)	88.29 (6)	53.29
	8.39 (3)	91.61 (3)	56.61	18.61 (7)	81.39 (7)	46.39
	9.66 (4)	90.34 (4)	55.34	16.82 (8)	83.18 (8)	48.18
CaX	7.53 (1)	92.47 (1)	57.47	11.88 (5)	88.12 (5)	53.12
	7.31 (2)	92.69 (2)	57.69	12.34 (6)	87.66 (6)	52.66
	9.86 (3)	90.14 (3)	55.14	18.98 (7)	81.02 (7)	46.02
	8.17 (4)	91.82 (4)	56.83	14.72 (8)	85.28 (8)	50.28
BaX	7.50 (1)	92.50 (1)	57.50	12.65 (5)	87.35 (5)	52.35
	7.12 (2)	92.88 (2)	57.88	13.99 (6)	86.01 (6)	51.01
	10.27 (3)	89.73 (3)	54.73	14.74 (7)	85.26 (7)	50.26
	9.27 (4)	90.73 (4)	55.73	14.69 (8)	85.31 (8)	50.31
NaY	6.09 (1)	93.91 (1)	58.91	10.65 (5)	89.35 (5)	54.35
	6.35 (2)	93.65 (2)	58.65	11.89 (6)	88.11 (6)	53.11
	9.61 (3)	90.39 (3)	55.39	12.21 (7)	87.79 (7)	52.79
	8.40 (4)	91.60 (4)	56.60	13.56 (8)	86.44 (8)	51.44
CaY	7.29 (1)	92.71 (1)	57.71	10.10 (5)	89.90 (5)	54.90
	8.64 (2)	91.36 (2)	56.36	13.35 (6)	86.65 (6)	51.65
	9.45 (3)	90.55 (3)	55.55	16.27 (7)	83.73 (7)	48.73
	8.13 (4)	91.87 (4)	56.87	17.44 (8)	82.56 (8)	47.56

*%difference is the difference between the *m*-CNB compositions in the feed and the precipitates with a zeolite.

**The number in the parenthesis refers to the position where precipitates were collected as shown in Figure 4.2.

Table 4.10 Compositions of *m*- and *p*-CNB in the precipitates located near and far from zeolites (Run#2) with 65.0 wt% *m*-CNB in the feed

Zeolite	Precipitate near zeolite			Precipitate far from zeolite		
	Composition (wt%)		%	Composition (wt%)		%
	<i>m</i> -CNB	<i>p</i> -CNB	difference*	<i>m</i> -CNB	<i>p</i> -CNB	difference*
NaX	7.43 (1)	92.57 (1)	57.57	13.21 (5)	86.79 (5)	51.79
	7.35 (2)	92.65 (2)	57.65	14.92 (6)	85.08 (6)	50.08
	9.89 (3)	90.11 (3)	55.11	16.45 (7)	83.55 (7)	48.55
	8.25 (4)	91.75 (4)	56.75	15.74 (8)	84.26 (8)	49.26
CaX	7.53 (1)	92.47 (1)	57.47	11.88 (5)	88.12 (5)	53.12
	7.31 (2)	92.69 (2)	57.69	12.34 (6)	87.66 (6)	52.66
	9.86 (3)	90.14 (3)	55.14	18.98 (7)	81.02 (7)	46.02
	8.17 (4)	91.82 (4)	56.83	14.72 (8)	85.28 (8)	50.28
BaX	7.54 (1)	92.46 (1)	57.46	15.64 (5)	84.36 (5)	49.36
	8.82 (2)	91.18 (2)	56.18	15.94 (6)	84.06 (6)	49.06
	9.21 (3)	90.79 (3)	55.79	16.99 (7)	83.01 (7)	48.01
	10.87 (4)	89.13 (4)	54.13	17.78 (8)	82.22 (8)	47.22
NaY	5.69 (1)	94.31 (1)	59.31	11.12 (5)	88.88 (5)	53.88
	6.58 (2)	93.42 (2)	58.42	11.77 (6)	88.23 (6)	53.23
	9.51 (3)	90.49 (3)	55.49	12.33 (7)	86.22 (7)	52.67
	8.96 (4)	91.04 (4)	56.04	13.78 (8)	87.67 (8)	51.22
CaY	7.52 (1)	92.48 (1)	57.48	11.00 (5)	89.00 (5)	54.00
	7.05 (2)	92.95 (2)	57.95	11.40 (6)	88.60 (6)	53.60
	8.11 (3)	91.89 (3)	56.89	15.29 (7)	84.71 (7)	49.71
	8.91 (4)	91.09 (4)	56.09	13.66 (8)	86.34 (8)	51.34

*%difference is the difference between the *m*-CNB compositions in the feed and the precipitates with a zeolite.

**The number in the parenthesis refers to the position where precipitates were collected as shown in Figure 4.2.

The presence of the zeolites in the feed at the eutectic composition results in the transparent precipitate formation instead of opaque precipitates and their compositions are rich in *p*-CNB. Below the eutectic composition, the CNB composition in the precipitates remains rich in *p*-CNB although its composition slightly decreases, whereas the composition of the precipitates obtained from the feed above the eutectic composition is shifted from being rich in *m*-CNB to rich in *p*-CNB. Considering the two areas where the precipitates were collected, area (a) and area (b), the results show that the precipitates located near the zeolites (area (a)) have a higher amount of *p*-CNB than those located far from the zeolites (area (b)). Moreover, the precipitates from Run#2 of every feed provide the composition of CNBs close to those from Run#1. The result can confirm that this system could be reproduced.

The CNB compositions in the precipitates from Run#1 were calculated in terms of *m*- to *p*-CNB ratio as illustrated in Figures 4.3-4.5 to give a clearer picture in the tendency of the precipitate compositions. The *m*-/*p*-CNB ratio of the precipitates far from the zeolites is higher than that near the zeolites, which means that around the zeolites the precipitates have higher amount of *p*-CNB than those far from the zeolites. From Figure 4.3, when *m*-CNB in the feed composition is below that at the eutectic point, the result shows that the X zeolites give slightly lower *m*-/*p*-CNB ratio of the precipitates than the Y zeolites in both areas. Considering the precipitates near the zeolites, the presence of the alkaline-earth cation-exchanged zeolites decreases the *m*-/*p*-CNB ratio of the precipitates compared with the alkaline cation-exchanged zeolites except CaY which provides the higher *m*-/*p*-CNB ratio of the precipitates than NaX. For the precipitates collected far from the zeolites, the *m*-/*p*-CNB ratios of the precipitates are similar whether alkaline or alkaline-earth cation-exchanged X zeolite is present. However, the ratio increases when CaY and NaY are used. In the feed at the eutectic composition, the *m*-/*p*-CNB ratio of the precipitates seems to be independent of the type of a zeolite as shown in Figure 4.4. This remark is true for the precipitates near the zeolite, while far from the zeolite the ratio is slightly decreased under CaX and NaY. Above the eutectic composition, the tendency of the precipitate compositions with the zeolites as shown in Figure 4.5 is different from that below the eutectic composition. Using BaX, NaX,

and CaY results in the similarity of the m/p -CNB ratio of the precipitates near the zeolites. However, the ratios are slightly higher than those obtained from CaX and NaY. This result indicates the decrease in the amount of p -CNB in the precipitates under BaX, NaX and CaY. Far from the zeolites, both X and Y zeolites give almost the same m/p -CNB ratio of the precipitates except NaY.

Comparison between the m/p -CNB ratios of the precipitates obtained from all feeds shows that, at the feed below the eutectic composition, most of the ratios change with the change in the cation or type of the zeolite, while the change in the cation or type of the zeolite in the feed at and above the eutectic composition has very little influence on the CNB ratio. In other words, the cation and type of the zeolite have an influence on the p -CNB composition in the precipitates in the feed below the eutectic composition more than those in the feed at and above the point. Moreover, the range of the m/p -CNB ratio of the precipitates in the feed below the eutectic composition ($\approx 0.05-0.30$) is boarder than that of the other two ($\approx 0.08-0.20$). The presence of BaX in the feed below the eutectic composition leads to the lowest m/p -CNB ratio or the highest p -CNB composition in the precipitates. Similarly, NaY gives the highest p -CNB composition in the precipitates when the feed composition is at and above the eutectic composition.

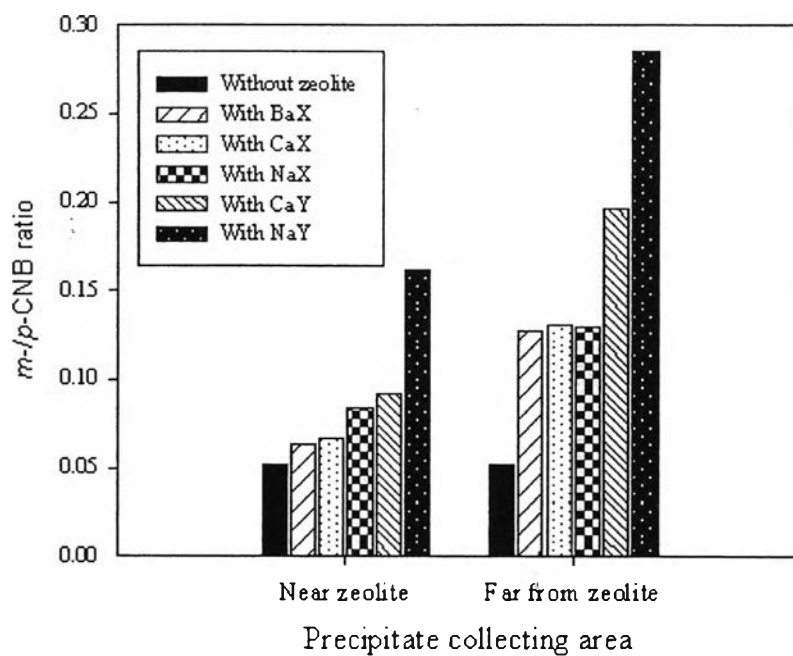


Figure 4.3 Comparison of m/p -CNB ratio of the precipitates from 61.0 wt% m -CNB in the feed without and with zeolites (BaX, CaX, NaX, CaY, and NaY).

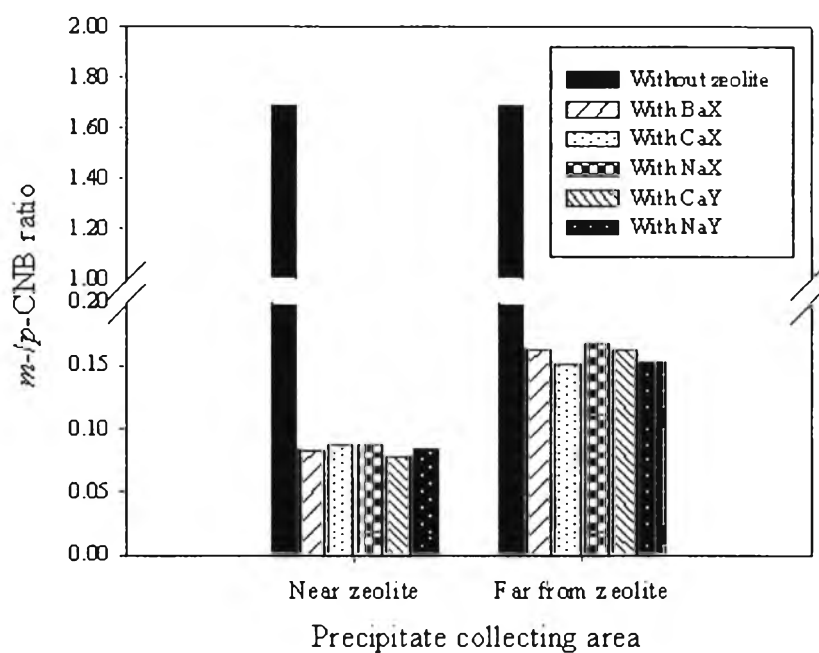


Figure 4.4 Comparison of m/p -CNB ratio of the precipitates from 62.9 wt% m -CNB in the feed without and with zeolites (BaX, CaX, NaX, CaY, and NaY).

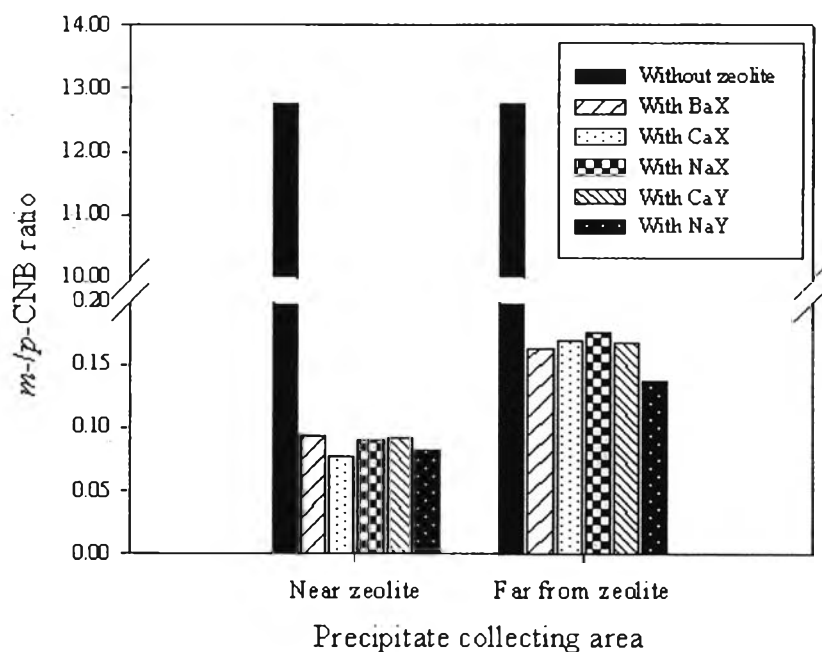


Figure 4.5 Comparison of m/p -CNB ratio of the precipitates from 65.0 wt% m -CNB in the feed without and with zeolites (BaX, CaX, NaX, CaY, and NaY).

From the results, the presence of the zeolite affects the CNB compositions in the precipitates, especially those obtained from the feed above the eutectic point. It may be because of the formation of the temperature variation of the mixture inside the crystallizer when the temperature was being decreased. According to this hypothesis, the addition of a zeolite may cause the change in the solution temperature; therefore, the temperatures of the solution with and without zeolite were measured by a thermocouple in five positions as shown in Figure 4.6. The results were then compared and shown in Figure 4.7.

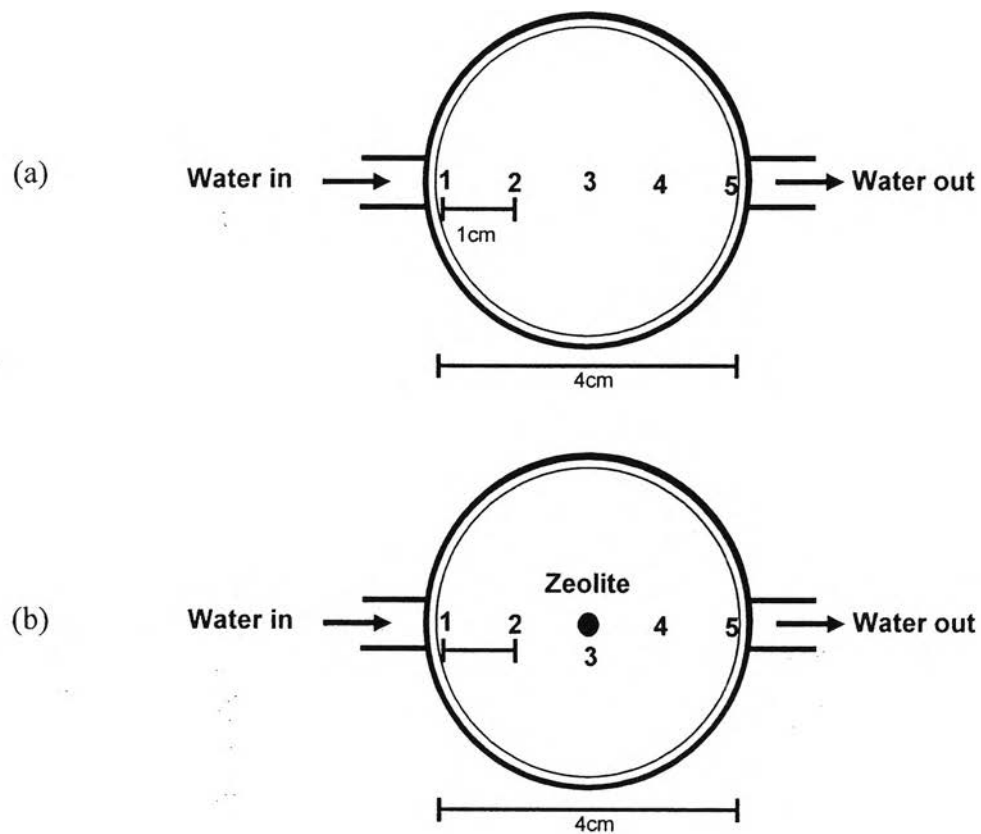
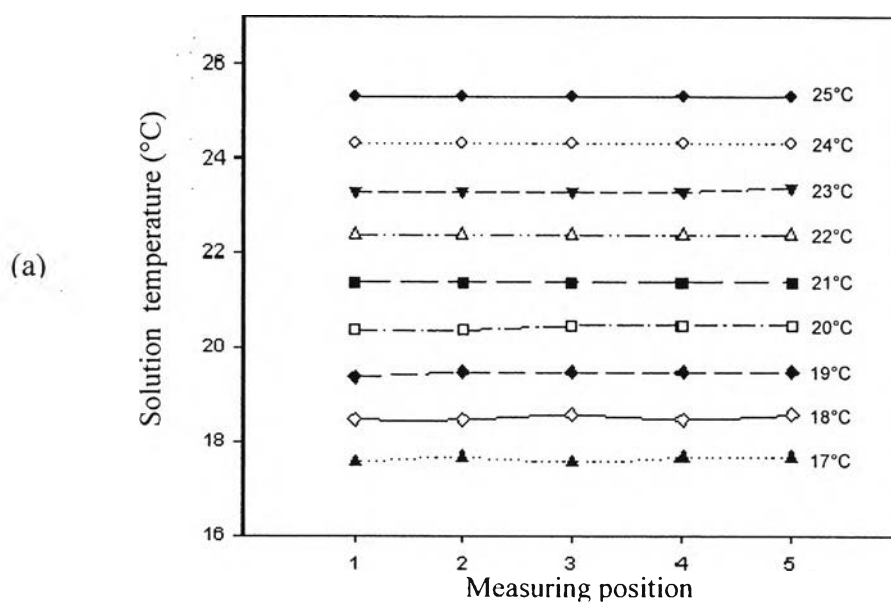


Figure 4.6 Positions in the crystallizer, where the temperature of the solution was measured (a) without zeolite and (b) with zeolite.



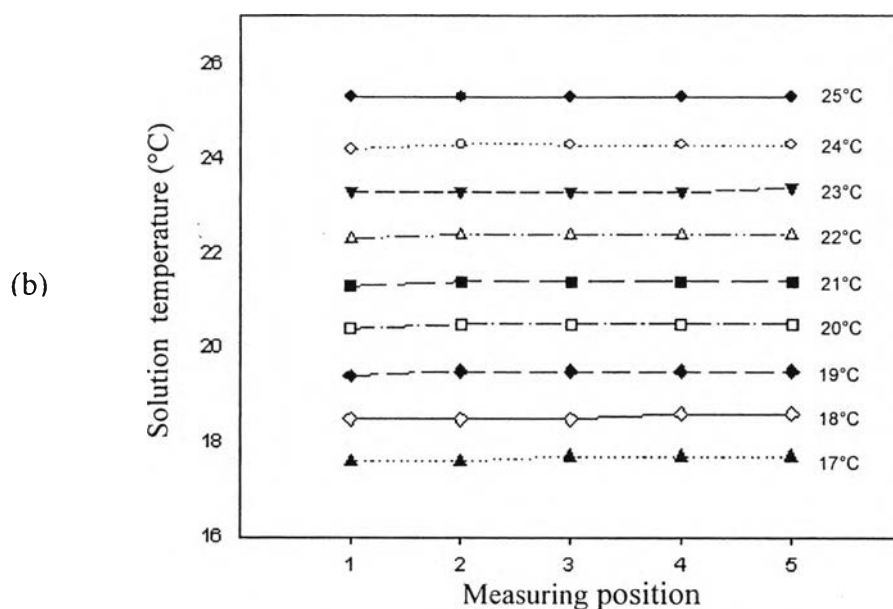


Figure 4.7 Temperature of the solution containing 65.0 wt% *m*-CNB in the feed (a) without zeolite and (b) with CaX.

Figure 4.7 shows the temperature of the solution containing 65.0 wt% *m*-CNB in the feed without and with CaX. The temperature was decreased from 25 to 17°C. The result reveals that the solution temperature is independent of the position even with the presence of the zeolite.

The FAU zeolites preferentially adsorb *m*-CNB more than *p*-CNB due to the higher basicity of *m*-CNB (Lerdsakulthong, 2007; Yensukjit, 2008). Thus, an adsorption selectivity of the zeolite might be a possible cause of the shift of *m*-CNB composition to be rich in *p*-CNB in the precipitates. To prove whether the zeolite selectivity plays any roles in the precipitate composition, a silicalite, which selectively adsorbs *p*-CNB more than *m*-CNB because of its shape selectivity effect (Guo *et al.*, 2009), was used in further study. The precipitate composition was compared with that with NaY because NaY gives the highest *m*/*p*-CNB selectivity among the studied FAU zeolites in the adsorption (Lerdsakulthong, 2007). Furthermore, in the crystallization, NaY also provides the maximum and the minimum *p*-CNB composition in the precipitates when the feed composition is below and above the eutectic composition, respectively.

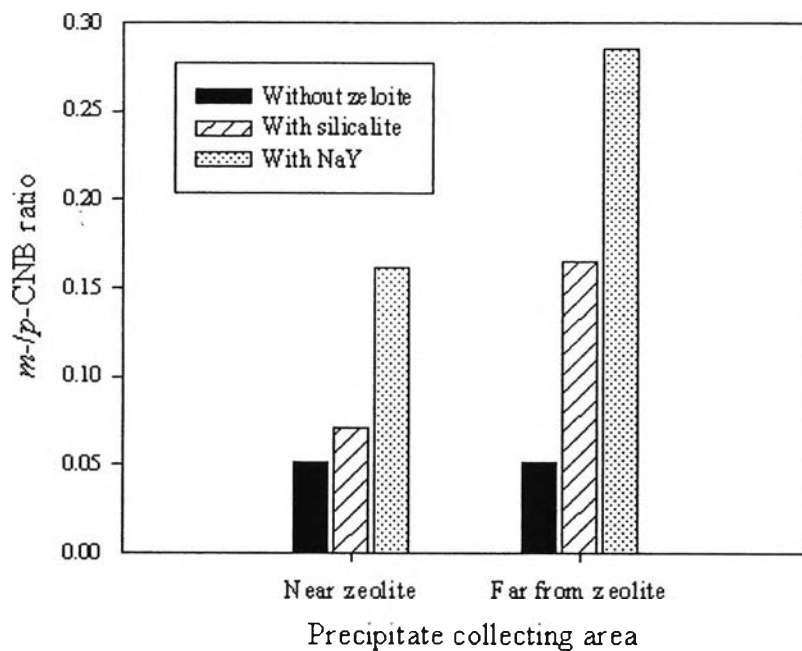


Figure 4.8 Comparison of m/p -CNB ratio of the precipitates from 61.0 wt% m -CNB in the feed with Silicalite, NaY and without zeolite.

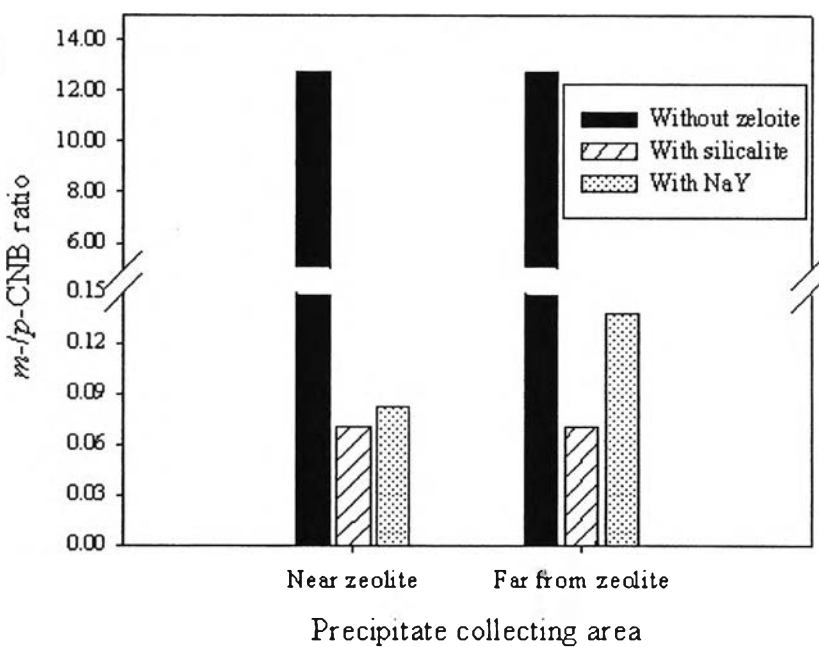


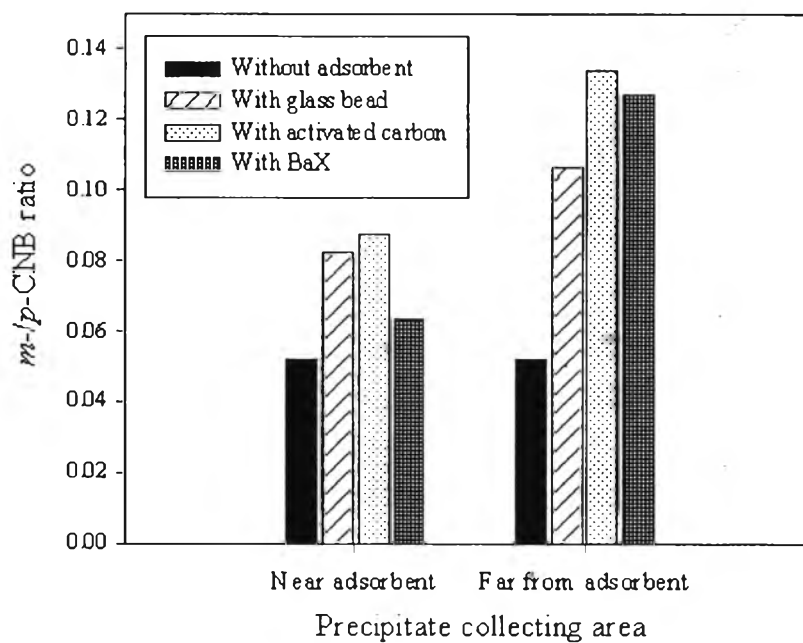
Figure 4.9 Comparison of m/p -CNB ratio of the precipitates from 65.0 wt% m -CNB in the feed with Silicalite, NaY and without zeolite.

It was postulated that the composition of the precipitates with the silicalite might be rich in *m*-CNB if the selectivity of a zeolite has the effect on the shift in the CNB precipitate composition. From Figures 4.8 and 4.9, the precipitate composition with the silicalite from both feeds is still rich in *p*-CNB as the same as with NaY. Moreover, the presence of the silicalite provides the *m*-/*p*-CNB ratio of the precipitates lower than that with NaY. In the feed below the eutectic composition, the precipitates near the silicalite have a lower *m*-/*p*-CNB ratio than those far from the silicalite as in the case of NaY, while the ratio becomes similar for both areas when the feed composition is above the eutectic composition. These results indicate that the shift in CNB precipitate composition is independent of the zeolite selectivity.

In addition, an activated carbon, a non-selective and high surface area sorbent, was used in this crystallization to investigate whether the difference in adsorbent structure and surface area, as listed in Table 4.11, has any influence on the CNB precipitate composition. Glass bead, an inert and non-porous material, was also included in the study. It is expected that *p*-CNB may be selectively adsorbed by the activated carbon more than *m*-CNB as *m*-CNB has a lower polarity (its dipole moment is 3.73 compared to 2.83 of *p*-CNB (Lerdsakulthong, 2007)). To minimize the effect of the adsorption selectivity, BaX, which has the lowest *m*-/*p*-CNB selectivity or the greatest *p*-CNB adsorption capacities among the studied FAU zeolites (Lerdsakulthong, 2007; Yensukjit, 2008), was chosen to compare the result with the activated carbon and glass bead.

Table 4.11 General properties of glass bead, activated carbon, and BaX

Material	Structure	Property	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Type of surface
Glass bead	Glass	inert	N/A	N/A	Non-porous
Activated carbon	A modified graphite-like structure	Hydrophobicity	540	0.62	Non-Uniform Porous
BaX	A crystalline aluminosilicate	Hydrophilicity	422	0.20	Uniform Porous

**Figure 4.10** Comparison of $m-/p$ -CNB ratio of the precipitates from 61.0 wt% m -CNB in the feed with glass bead, activated carbon, BaX and without zeolite.

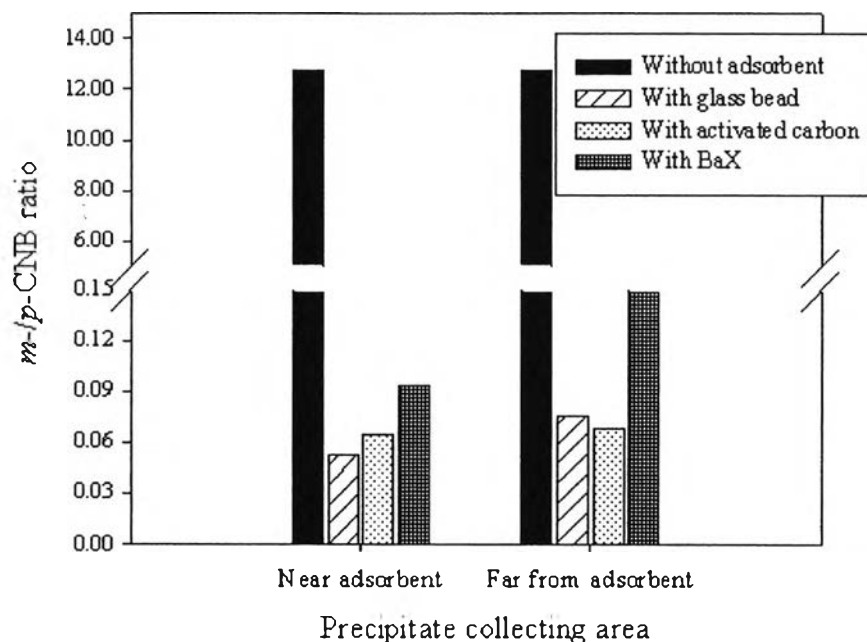


Figure 4.11 Comparison of m/p -CNB ratio of the precipitates from 65.0 wt% m -CNB in the feed with glass bead, activated carbon, BaX and without zeolite.

The m/p -CNB ratio of the precipitates around the adsorbent in the feed below the eutectic composition decreases when the adsorbent is changed from the activated carbon to glass bead; and BaX provides the lowest ratio albeit higher than that without an adsorbent. Far from the adsorbent, the activated carbon still provides the highest m/p -CNB ratio of the precipitates but the lowest one is offered by the glass bead as illustrated in Figure 4.10. From Figure 4.11, the m/p -CNB ratio of the precipitates with the activated carbon for both areas is similar with the feed above the eutectic composition. Near the adsorbent, the m/p -CNB ratio of the precipitates increases from the glass bead, activated carbon, and BaX, respectively. The ratio with the activated carbon slightly changes with the collection areas, while the ratios with the glass bead and BaX slightly increase. The lowest m/p -CNB ratio of the precipitates far from the adsorbent is obtained with the presence of the activated carbon and the highest ratio is from BaX. From the results, considering the ratio of the precipitates from both feeds, it shows that the m/p -CNB ratio of the precipitates in the feeds is changed with the change in the adsorbent. In other words,

the difference in adsorbent structure and surface area has an influence on the ratio of the precipitates in the feeds both below and above the eutectic composition. However, the tendency of CNB precipitate composition still remains rich in *p*-CNB. It implies that the difference in type of adsorbent and adsorbent structure affects the change in the CNB precipitate composition, while the reason why the precipitates composition in the feed above the eutectic composition is shifted from being *m*-CNB to *p*-CNB has to be further investigated.