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APPENDICES

Appendix A Temperature Profiles

Table A1 Pyrolysis conditions: Non-catalytic pyrolysis

Tire = 30.043 g, N₂ flow = 30 ml/min

Catalytic Temperature (T1): set value = 350 °C

Pyrolysis Temperature (T2): set value = 500 °C

Time (min)	T1	T2									
2	38	28	32	358	501	62	350	501	92	348	497
4	40	45	34	343	493	64	353	499	94	348	501
6	60	76	36	353	505	66	350	499	96	350	499
8	87	115	38	354	496	68	348	501	98	354	499
10	122	166	40	347	505	70	349	501	100	345	499
12	163	222	42	348	496	72	354	499	102	343	500
14	208	283	44	351	502	74	360	500	104	344	499
16	249	342	46	340	500	76	352	499	106	350	501
18	289	408	48	345	501	78	350	503	108	349	500
20	333	446	50	345	499	80	346	501	110	354	500
22	296	471	52	350	498	82	351	499	112	352	500
24	323	505	54	352	500	84	349	501	114	354	500
26	347	501	56	357	500	86	347	498	116	352	501
28	362	488	58	353	498	88	352	500	118	353	499
30	348	495	60	347	503	90	348	501	120	353	499

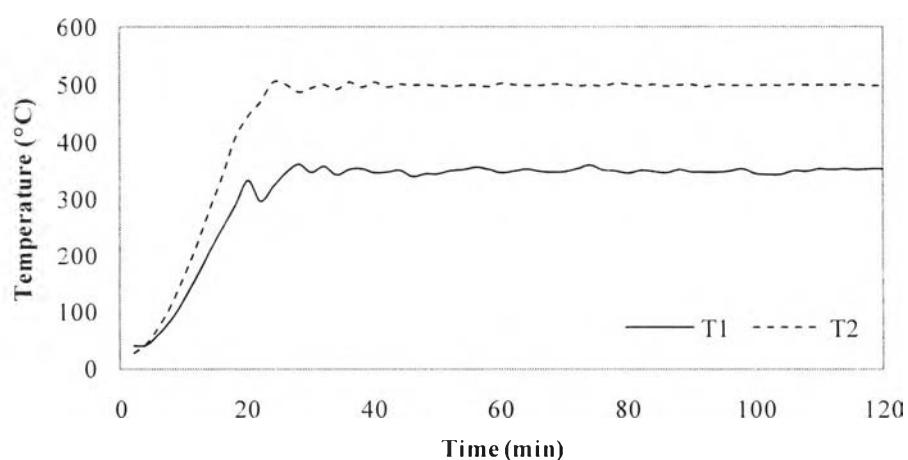


Figure A1 Temperature profiles of the non-catalytic pyrolysis.

Table A2 Pyrolysis conditions: Catalytic pyrolysis using Si-MCM-48Tire = 30.020 g, N₂ flow = 30 ml/min

Catalytic Temperature (T1): set value = 350 °C

Pyrolysis Temperature (T2): set value = 500 °C

Time (min)	T1	T2									
2	27	28	32	360	498	62	352	501	92	351	500
4	32	42	34	354	500	64	350	503	94	351	499
6	44	68	36	349	504	66	349	499	96	351	501
8	63	105	38	343	503	68	348	499	98	350	502
10	87	151	40	350	499	70	347	501	100	350	499
12	118	200	42	355	502	72	348	498	102	350	501
14	152	258	44	347	497	74	348	501	104	350	500
16	185	315	46	346	503	76	348	500	106	351	501
18	225	381	48	349	502	78	348	499	108	350	501
20	282	423	50	351	500	80	348	499	110	350	499
22	321	497	52	353	501	82	349	499	112	351	503
24	312	504	54	354	500	84	351	501	114	351	502
26	300	505	56	354	500	86	350	498	116	351	503
28	352	502	58	354	501	88	350	498	118	351	503
30	359	496	60	354	501	90	350	500	120	351	500

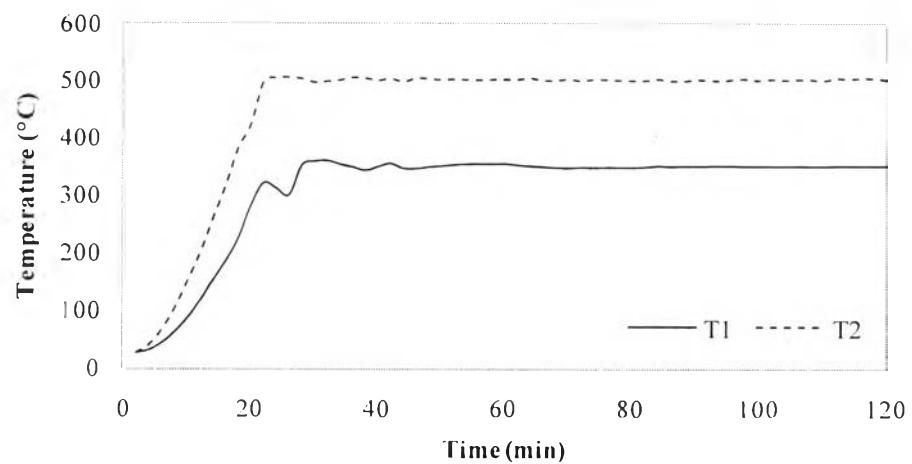
**Figure A2** Temperature profiles of catalytic pyrolysis using Si-MCM-48.

Table A3 Pyrolysis conditions: Catalytic pyrolysis using Al-MCM-48 (82)Tire = 30.009 g, N₂ flow = 30 ml/min

Catalytic Temperature (T1): set value = 350 °C

Pyrolysis Temperature (T2): set value = 500 °C

Time (min)	T1	T2									
2	26	29	32	371	497	62	352	500	92	350	500
4	31	43	34	354	499	64	351	502	94	350	499
6	44	68	36	342	504	66	349	499	96	350	500
8	62	105	38	343	502	68	348	499	98	350	501
10	87	151	40	349	499	70	347	501	100	350	499
12	117	200	42	354	501	72	348	499	102	350	501
14	151	258	44	346	496	74	348	501	104	350	500
16	185	314	46	346	503	76	349	501	106	350	501
18	225	380	48	348	502	78	348	500	108	350	501
20	282	422	50	350	500	80	348	499	110	350	499
22	322	497	52	352	501	82	348	499	112	350	503
24	281	503	54	353	500	84	350	502	114	350	502
26	317	504	56	354	499	86	349	499	116	350	503
28	352	502	58	354	500	88	350	498	118	350	503
30	359	495	60	354	500	90	350	501	120	350	500

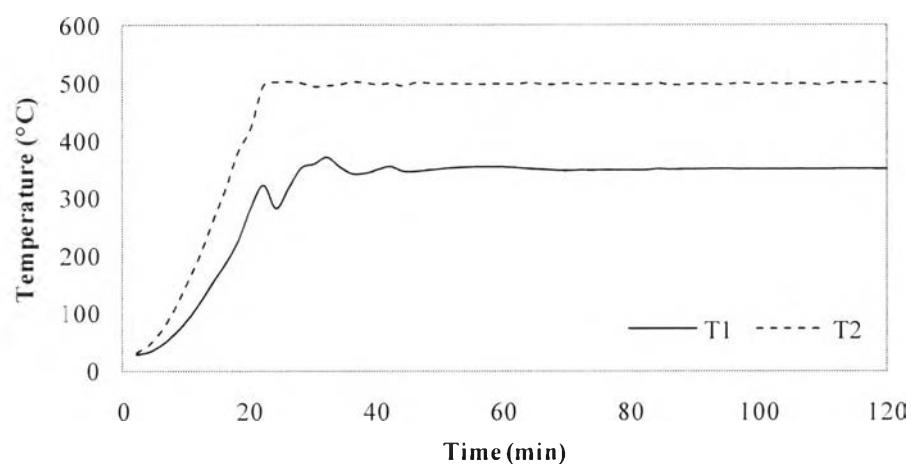
**Figure A3** Temperature profiles of catalytic pyrolysis using Al-MCM-48 (82).

Table A4 Pyrolysis conditions: Catalytic pyrolysis using Al-MCM-48 (42)Tire = 30.009 g, N₂ flow = 30 ml/min

Catalytic Temperature (T1): set value = 350 °C

Pyrolysis Temperature (T2): set value = 500 °C

Time (min)	T1	T2									
2	25	24	32	367	494	62	342	502	92	351	501
4	31	35	34	357	501	64	346	502	94	351	500
6	44	57	36	344	504	66	352	500	96	351	500
8	62	93	38	347	504	68	356	500	98	349	501
10	86	134	40	354	498	70	355	500	100	349	500
12	118	186	42	358	500	72	354	500	102	351	500
14	148	241	44	349	497	74	352	499	104	350	501
16	185	295	46	347	501	76	350	500	106	349	501
18	224	353	48	354	501	78	351	500	108	349	499
20	262	414	50	357	500	80	350	500	110	349	500
22	326	459	52	356	498	82	348	501	112	351	500
24	275	497	54	347	500	84	349	499	114	352	499
26	314	505	56	353	500	86	349	501	116	349	500
28	354	500	58	360	499	88	350	500	118	349	501
30	378	497	60	357	499	90	351	500	120	348	500

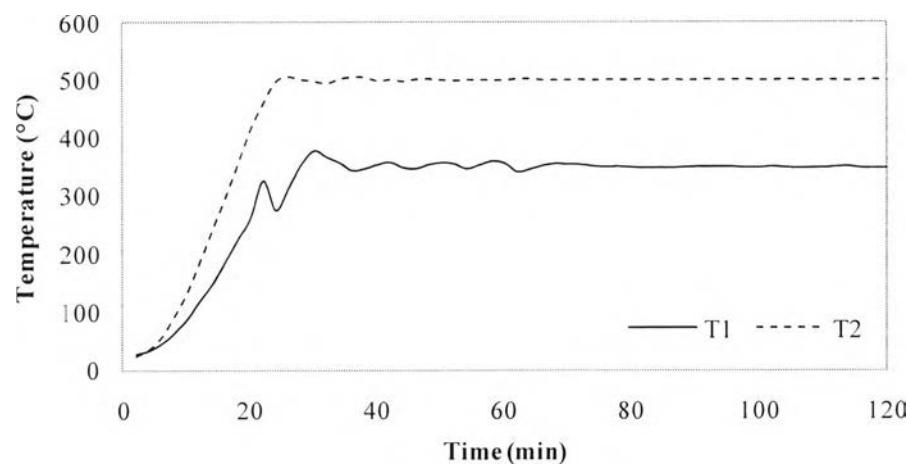
**Figure A4** Temperature profiles of catalytic pyrolysis using Al-MCM-48 (42).

Table A5 Pyrolysis conditions: Catalytic pyrolysis using Al-MCM-48 (25)Tire = 30.015 g, N₂ flow = 30 ml/min

Catalytic Temperature (T1): set value = 350 °C

Pyrolysis Temperature (T2): set value = 500 °C

Time (min)	T1	T2									
2	27	27	32	353	507	62	353	498	92	345	499
4	31	40	34	357	495	64	346	500	94	344	501
6	41	65	36	348	497	66	350	503	96	344	500
8	58	97	38	342	505	68	353	498	98	345	500
10	79	140	40	342	500	70	355	500	100	347	502
12	105	188	42	343	499	72	351	499	102	352	500
14	135	242	44	345	500	74	352	502	104	355	497
16	162	295	46	350	501	76	354	499	106	354	500
18	194	352	48	355	500	78	356	499	108	351	501
20	256	410	50	358	499	80	355	501	110	348	501
22	338	456	52	345	496	82	355	500	112	345	500
24	317	497	54	339	502	84	355	500	114	344	500
26	356	505	56	343	503	86	352	500	116	343	498
28	369	498	58	350	500	88	350	500	118	344	501
30	348	500	60	355	500	90	347	500	120	344	500

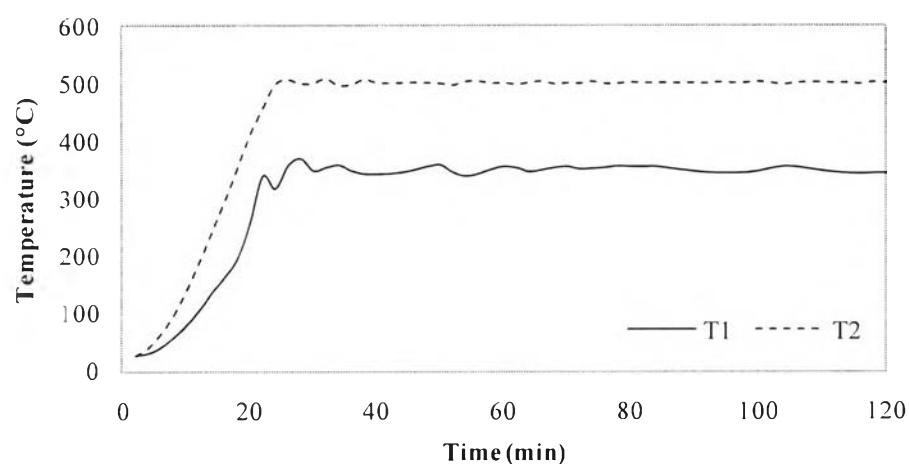
**Figure A5** Temperature profiles of catalytic pyrolysis using Al-MCM-48 (25).

Table A6 Pyrolysis conditions: Catalytic pyrolysis using Si-MCM-48/HZSM-5Tire = 30.016 g, N₂ flow = 30 ml/min

Catalytic Temperature (T1): set value = 350 °C

Pyrolysis Temperature (T2): set value = 500 °C

Time (min)	T1	T2									
2	26	27	32	357	501	62	352	500	92	350	500
4	28	33	34	348	500	64	352	499	94	350	500
6	42	9	36	353	498	66	352	499	96	351	500
8	51	70	38	354	500	68	350	500	98	351	500
10	63	90	40	356	499	70	349	500	100	352	500
12	89	120	42	351	499	72	350	500	102	351	500
14	119	182	44	346	500	74	350	501	104	349	499
16	145	247	46	345	502	76	343	500	106	350	500
18	190	288	48	345	501	78	347	500	108	349	500
20	261	345	50	346	499	80	367	500	110	350	500
22	287	419	52	348	500	82	346	500	112	351	500
24	317	430	54	349	500	84	346	499	114	350	500
26	333	479	56	350	499	86	347	501	116	350	500
28	347	496	58	350	500	88	349	500	118	350	500
30	352	498	60	351	501	90	349	500	120	350	500

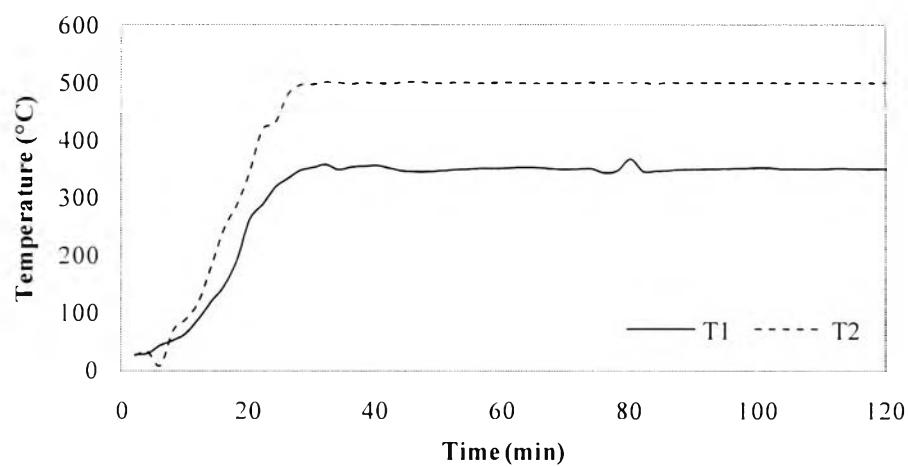
**Figure A6** Temperature profiles of catalytic pyrolysis using Si-MCM-48/HZSM-5.

Table A7 Pyrolysis conditions: Catalytic pyrolysis using Si-MCM-48/HBETATire = 30.004 g, N₂ flow = 30 ml/min

Catalytic Temperature (T1): set value = 350 °C

Pyrolysis Temperature (T2): set value = 500 °C

Time (min)	T1	T2									
2	26	27	32	357	501	62	352	500	92	350	500
4	28	33	34	348	500	64	352	499	94	350	500
6	42	9	36	353	498	66	352	499	96	351	500
8	51	70	38	354	500	68	350	500	98	351	500
10	63	90	40	356	499	70	349	500	100	352	500
12	89	120	42	351	499	72	350	500	102	351	500
14	119	182	44	346	500	74	350	501	104	349	499
16	145	247	46	345	502	76	343	500	106	350	500
18	190	288	48	345	501	78	347	500	108	349	500
20	261	345	50	346	499	80	367	500	110	350	500
22	287	419	52	348	500	82	346	500	112	351	500
24	317	430	54	349	500	84	346	499	114	350	500
26	333	479	56	350	499	86	347	501	116	350	500
28	347	496	58	350	500	88	349	500	118	350	500
30	352	498	60	351	501	90	349	500	120	350	500

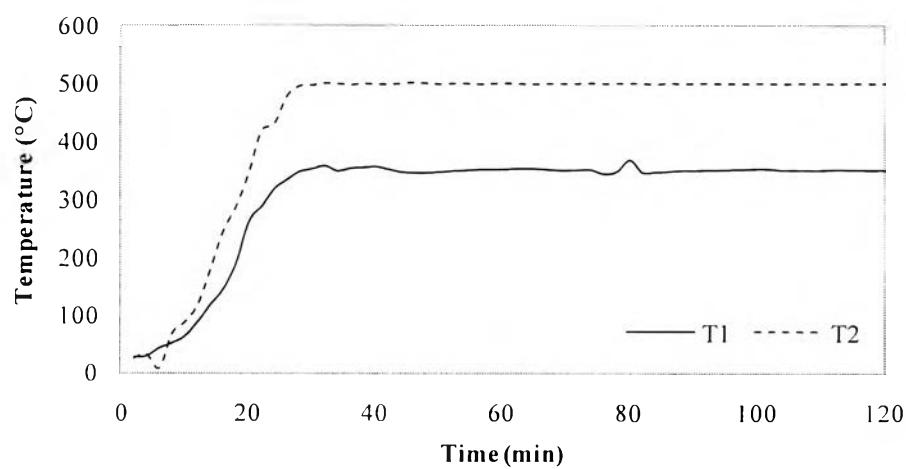
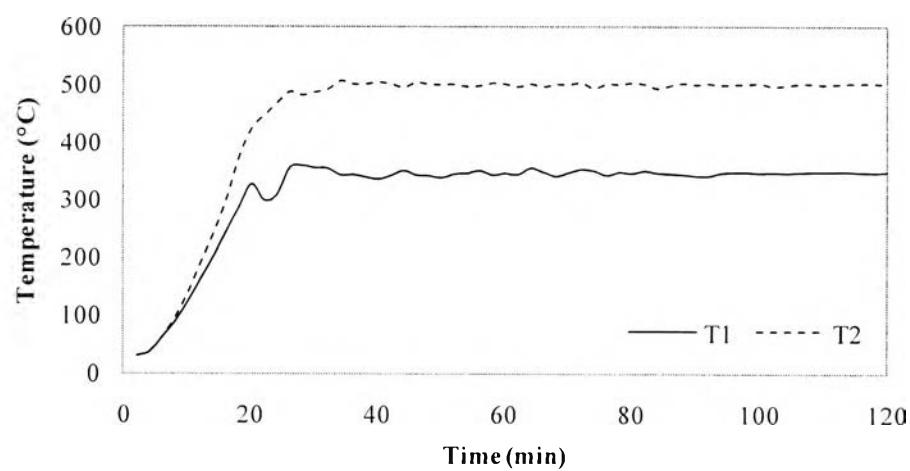
**Figure A7** Temperature profiles of catalytic pyrolysis using Si-MCM-48/HBETA.

Table A8 Pyrolysis conditions: Catalytic pyrolysis using Si-MCM-48/HYTire = 30.008 g, N₂ flow = 30 ml/min

Catalytic Temperature (T1): set value = 350 °C

Pyrolysis Temperature (T2): set value = 500 °C

Time (min)	T1	T2									
2	29	29	32	357	492	62	346	497	92	343	502
4	36	37	34	345	507	64	357	502	94	348	499
6	61	62	36	346	501	66	351	497	96	350	500
8	89	95	38	342	502	68	343	501	98	350	501
10	123	137	40	338	505	70	349	501	100	348	502
12	162	189	42	344	502	72	355	503	102	349	497
14	201	240	44	353	496	74	352	494	104	348	498
16	245	298	46	345	504	76	345	501	106	349	501
18	287	373	48	344	501	78	350	501	108	350	501
20	329	424	50	341	500	80	348	503	110	350	500
22	301	447	52	347	501	82	352	501	112	350	501
24	310	468	54	348	497	84	348	494	114	350	502
26	358	488	56	353	499	86	347	499	116	349	502
28	362	482	58	345	503	88	346	503	118	349	502
30	358	487	60	348	502	90	344	500	120	350	500

**Figure A8** Temperature profiles of catalytic pyrolysis using Si-MCM-48/HY.

Appendix B Product Distribution

Table B1 Effect of mesoporous MCM-48 on product distribution (wt%)

	Non-Cat.	Si-MCM-48	Al-MCM-48 (82)	Al-MCM-48 (42)	Al-MCM-48 (25)
Gas	8.9	10.6	6.9	8.3	7.3
Liquid	46.2	38.9	43.3	43.3	43.8
Solid	44.9	43.7	43.2	43.1	42.9
Coke	-	6.8	6.6	5.4	6.0

Table B2 Effect of double beds of silica MCM-48 and zeolites on product distribution (wt%)

	Si-MCM-48/HZSM-5	Si-MCM-48/HBETA	Si-MCM-48/HY
Gas	11.2	5.7	5.6
Liquid	39.1	44.0	44.5
Solid	43.2	43.4	42.9
Coke	6.5	6.9	6.9

Table B3 Effect of mesoporous MCM-48 on product compositions (wt%)

	Non-Cat.	Si-MCM-48	Al-MCM-48 (82)	Al-MCM-48 (42)	Al-MCM-48 (25)
<i>Gas Products</i>					
Methane	2.0	2.3	1.5	1.6	1.4
Ethylene	0.8	1.0	0.7	0.7	0.6
Ethane	1.5	2.1	1.3	1.4	1.2
Propylene	0.9	1.1	0.8	0.9	0.7
Propane	0.8	1.2	0.7	0.8	0.7
Mixed-C ₄	1.9	2.2	1.6	1.9	1.6
Mixed-C ₅	1.0	0.8	0.8	01.0	0.7
<u>Total</u>	<u>8.9</u>	<u>10.6</u>	<u>7.3</u>	<u>8.3</u>	<u>6.9</u>
<i>Petroleum Products</i>					
Full range naphtha	13.4	19.7	20.4	16.1	18.8
Kerosene	11.3	10.5	12.9	12.8	12.0
Light gas oil	8.5	5.4	6.0	8.3	7.3
Heavy gas oil	7.0	2.5	2.8	4.5	4.4
Long residue	6.0	0.8	1.1	1.6	1.2
<u>Total</u>	<u>46.2</u>	<u>38.9</u>	<u>43.3</u>	<u>43.3</u>	<u>43.8</u>

Table B4 Effect of double beds of silica MCM-48 and zeolites on product compositions (wt%)

	Si-MCM- 48/HZSM-5	Si-MCM- 48/HBETA	Si-MCM- 48/HY
<u>Gas Products</u>			
Methane	1.8	0.9	1.0
Ethylene	0.7	0.3	0.4
Ethane	1.5	0.7	0.9
Propylene	0.9	0.4	0.5
Propane	2.4	0.8	0.7
Mixed-C ₄	2.8	1.8	1.4
Mixed-C ₅	1.2	0.8	0.7
Total	<u>11.2</u>	<u>5.7</u>	<u>5.6</u>
<u>Petroleum Products</u>			
Full range naphtha	20.8	20.9	19.5
Kerosene	11.1	13.3	12.4
Light gas oil	5.2	6.7	7.8
Heavy gas oil	2.0	2.9	4.0
Long residue	0.0	0.3	0.8
Total	<u>39.1</u>	<u>44.0</u>	<u>44.5</u>

Appendix C Maltene Compositions

Table C1 Maltene compositions in mesoporous MCM-48 cases

	Non-Cat	Si-MCM-48	Al-MCM-48 (82)	Al-MCM-48 (42)	Al-MCM-48 (25)
P	2.94	3.52	4.01	4.02	4.16
Ole	9.39	10.08	8.04	8.75	6.95
Nap	15.53	13.52	10.21	10.24	7.49
Mono	47.74	54.26	56.22	53.18	56.31
Di	7.55	4.31	5.11	6.03	8.66
Poly	9.09	6.68	8.24	9.67	10.28
Polar	7.77	7.63	8.16	8.11	6.17

Table C2 Maltene compositions in double beds of silica MCM-48 and zeolite cases

	Si-MCM-48/HZSM-5	Si-MCM-48/HBETA	Si-MCM-48/HY
P	2.80	2.99	4.75
Ole	11.42	7.28	6.19
Nap	15.92	11.63	11.56
Mono	54.36	53.49	48.31
Di	5.61	8.31	8.07
Poly	4.95	9.31	13.17
Polar	4.93	6.99	7.95

P = Paraffins

Mono = Mono-aromatics

Polar = Polar-aromatics

Ole = Olefins

Di = Di-aromatics

Nap = Naphthenes

Poly = Poly-aromatics

Appendix D Sulfur-containing Compound Species in Oils

Table D1 Sulfur-containing compound species in oils in mesoporous MCM-48 cases

	Non-Cat	Si-MCM-48	Al-MCM-48 (82)	Al-MCM-48 (42)	Al-MCM-48 (25)
Thiophenes	0.74	0.96	0.69	0.62	0.62
Benzothiophenes	0.98	0.60	0.98	1.10	0.79
Dibenzothiophenes	0.05	0.02	0.02	0.03	0.03
Benzothiazoles	1.31	1.62	1.22	1.09	0.96
Isothiocyanates	0.59	0.34	0.56	0.56	0.36
Others	0.10	0.25	0.25	0.22	0.08

Table D2 Sulfur-containing compound species in oils in double beds of silica MCM-48 and zeolite cases.

	Si-MCM-48/HZSM-5	Si-MCM-48/HBETA	Si-MCM-48/HY
Thiophenes	0.7	0.8	0.5
Benzothiophenes	0.6	1.2	1.0
Dibenzothiophenes	0.0	0.1	0.1
Benzothiazoles	0.5	0.7	0.9
Isothiocyanates	0.0	0.3	0.4
Others	0.3	0.2	0.3

Appendix E Sulfur Analysis by Using S-Analyzer

Table E1 Effect of mesoporous MCM-48 on overall sulfur distribution (wt%)

	Non-Catalyst	Si-MCM-48	Al-MCM-48 (82)	Al-MCM-48 (42)	Al-MCM-48 (25)
Oil	29	16	26.14	24.05	21.89
Spent Catalyst	-	10	7.14	5.16	6.40
Gas	18	19	15.18	17.11	20.28
Char	53	55	51.53	53.68	51.44

Table E2 Effect of double beds of silica MCM-48 and zeolites on overall sulfur distribution (wt%)

	Si-MCM-48/HZSM-5	Si-MCM-48/HBETA	Si-MCM-48/HY
Oil	16.26	21.01	21.44
Spent Catalyst	20.16	14.06	12.84
Gas	11.19	13.71	14.79
Char	52.39	51.22	50.92

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