Testing on Fluid Catalytic Cracking (FCC) Catalysts

Aurapun Angkasuwan

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Thesis Title	Testing on Fluid Catalytic Cracking (FCC) Catalysts
Author	Miss Aurapun Angkasuwan
Major Program	Chemical Engineering

Advisory committee	**Examining committee**
C. Tongurai ....(chairman)	C. Tongurai ....(chairman)
(Assistant Professor Dr. Chakrit Tongurai)	(Assistant Professor Dr. Chakrit Tongurai)
....(committee)	....(committee)
(Dr.Sutham Sukmanee)	(Dr.Sutham Sukmanee)
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(Professor Tu Shi-Ying)	(Professor Tu Shi-Ying)
	Charun Bunya ....(committee)
	(Dr. Charun Bunyakan)
	Sumpun Wongnawa ....(committee)
	(Assistant Professor Dr. Sumpun Wongnawa)

The Graduate School, Prince of Songkla University, has approved this thesis as partial fulfillment of the requirement for the Master of Engineering degree in Chemical Engineering.

....

(Associate Professor Dr. Kan Chantrapromma)

Dean, Graduate School

ชื่อวิทยานิพนธ์ การทดสอบตัวเร่งปฏิกิริยาการแตกตัวเชิงเร่งปฏิกิริยาในสภาพฟลูอิไดซ์
ผู้เขียน นางสาวอรพรรณ อังคสุวรรณ
สาขาวิชา วิศวกรรมเคมี
ปีการศึกษา 2541

บทคัดย่อ

ภาควิชาวิศวกรรมเคมีได้เริ่มงานวิจัยเพื่อเป็นพื้นฐานในการพัฒนาทางด้านปิโตรเลียมและปิโตรเคมีโดยเฉพาะในภาคใต้ของประเทศไทย วิทยานิพนธ์นี้เป็นการศึกษาเริ่มต้นโดยประกอบด้วย (1)การติดตั้งเครื่องและเทียบมาตรฐานอุปกรณ์ทดสอบจุลกัมมันตภาพ (MAT) และเครื่องเร่งบ่มแบบไฮโดรเทอร์มัล (hydrothermal aging) (2) การเตรียมแก๊สออยล์จากโรงกลั่นฝาง (3) การประเมินค่าตัวเร่งปฏิกิริยาสมดุลจากโรงกลั่นไทยและจีน (4) การประเมินค่าตัวเร่งปฏิกิริยาใหม่สด (5) การเปรียบเทียบเสถียรภาพระหว่างตัวเร่งปฏิกิริยา USY และ REY

ค่าจุลกัมมันตภาพโดยการทำซ้ำของตัวเร่งปฏิกิริยา CRC-1 ต่อแก๊สออยล์มาตรฐานจาก Research Institute of Petroleum Processing (RIPP), ปักกิ่ง มีค่าเท่ากับ 67±2.0 ที่ระดับความน่าเชื่อถือ 95 เปอร์เซนต์ ซึ่งอยู่ในระดับเดียวกับการวัดที่ RIPP ซึ่งมีค่าเท่ากับ 68 จุลกัมมันตภาพตัวเร่งปฏิกิริยาขึ้นอยู่กับชนิดของตัวเร่งปฏิกิริยาและวัสดุป้อน (feedstock) ตัวเร่งปฏิกิริยา Gong-Y (REY) มีความเสถียรภาพมากกว่า Lanet-35 (USY) ภายใต้สภาวะไฮโดรเทอร์มัล (hydrothermal) ในช่วง 4-16 ชั่วโมงซึ่งสามารถอธิบายได้ว่าการสูญเสียของอลูมิเนียมจากโครงกรอบ (framework) ของซีโอไลต์จะเกิดขึ้นภายใต้กระบวนการไฮโดรเทอร์มัลและเป็นเหตุให้ขนาดของหน่วยเซลล์และพื้นที่ผิวของตัวเร่งปฏิกิริยาลดลงซึ่งเป็นผลให้ค่าจุลกัมมันตภาพลดลง

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Abstract

Department of chemical engineering, Prince of Songkla University has established a project to start its research work to accommodate the future development of petroleum refining and petrochemical industries of Thailand, especially in southern part of Thailand.

This thesis is a preliminary study for starting the project, including (1) Installation and calibration of the two units - microactivity test (MAT) unit and hydrothermal treatment (aging) unit; (2)Preparation of Thai feedstock for MAT; (3) Evaluation of industrial FCC equilibrium catalysts from Thai and Chinese refineries;(4) Evaluation of fresh FCC catalysts; (5)Comparison of the stability between USY and REY catalysts.

After repeated testing, the 95% confidence limit (95%C.L.) of microactivity (MA) for REY catalyst CRC-1 (hydrotreated) was being identified as 67 ± 2.0 which meets the data measured by RIPP of 68. The repeatability of testing for these two units all meet the requirements.

REY is proved to be more stable than USY under high temperature hydrothermal conditions, as can be explained that dealumination would occur under hydrothermal treatments which is responsible for the decrease of unit cell size and loss in surface area subsequently microactivity (MA) decreased.

Acknowledgment

I wish to express deep gratitude to my advisor, Assistant Professor Dr. Chakrit Tongurai and co-advisors, Professor Tu Shi-Ying and Dr. Sutham Sukmanee for all their advice, encouragement and guidance throughout this work.

I am also grateful to Dr. Charun Bunyakan and Assistant Professor Dr. Sumpun Wongnawa for their comments and valuable suggestions. In particular I am especially grateful to Thai Oil Company and Star-Petroleum Refinery for catalysts and Fang Refinery for diesel oil in my experiment.

I also would like to thank Research Institute of Petroleum Processing SINOPEC (RIPP) for standard gas oil and their advice. In particular I would like to thank Associate Professor Dr. Suteera Prasertsan for his conscientious proof-reading and Scientific Equipment Center for analytical equipment services and also staff of Chemical Engineering Department for their helpful in my thesis.

Finally, I would like to express my deepest appreciation to my family for their love and attention throughout my life.

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Aurapun Angkasuwan

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Introduction

Introduction

Fluid catalytic cracking (FCC) is one of the major refining processes using in petroleum industry. In almost all refineries this process represents the primary conversion unit for producing gasoline directly from gas oil. While discussions about FCC tend to group all units into one, average type, there are in fact many differences among FCC units. These differences include configuration, operation, and feedstock. For each refiner, there are usually some limiting parameters in the unit that control the overall operation. These may be catalyst circulation, attrition, coke selectivity (either too much or too little), or gas selectivity (compressor- either wet (LPG) or dry gas limits).

Depending upon the needs of refiner he may be limited by any one of these at various times as he moves from a maximum octane operation to a maximum gasoline operation or switches from a light gas oil to a heavier gas oil feed. The selection of the proper catalyst provides flexibility to address these requirements in a manner otherwise unavailable.

In order to provide the refinery with as much flexibility as possible, catalyst vendors have developed a variety of FCC catalysts to meet specific demands. While all catalysts incorporate zeolites as the core, the type and amount vary-widely. At present there are probably 400 cracking catalysts variations (Sadeghbeigi, R., 1995)

Testing and choosing the best catalyst that suitable for their feedstock and unit is critical. Using the wrong FCC catalyst can cost a refiner millions of dollars per year in product value and also out of target demands.(Campagna, R.J. et.al., 1986). The best way for a refinery to test a cracking catalyst for use in his refinery is to run a sample of commercially deactivated catalyst in a laboratory unit that closely simulates a full-scale cat cracker, at the operating conditions encountered in the field. The only way to get an E-cat sample is to run a unit (commercially or large laboratory unit) for a sufficient length of time to achieve equilibrium activity. This procedure may take months, very expensive and the number of samples that can be evaluated is quite limited. To circumvent these problems, laboratory steam pretreatments are used to simulate commercial aging artificially. These treatments use high temperature and steam as substitutes for aging times. Despite the major differences in the nature of the "real" and artificially treatments (the former yielding a distribution of deactivated particles and the latter a uniformly deactivated sample), the products of these treatment can be quite similar. (Letzch, W.S., Ritter, R.E. and Vaughan, D.E.W., 1976). The major method of evaluation catalyst in laboratory are hydrothermal aging and MAT testing (including physical and chemical properties of catalysts). While ASTM procedures for both steaming and MAT testing have been established (ASTM D-4463 and D-3907, respectively), a general survey of the petroleum industry indicates that neither of these methods are specifically practiced. Instead, each laboratory has developed individualized steaming and MAT testing procedures that best their need such as fixed time and vary temperature in steaming, fixed temperature and vary time in steaming then test with MAT unit with one standard condition or fixed time and temperature but vary condition in MAT testing etc .(Moorehead, E.L, Margolis, M.J. and Mclean, J.B., 1989)

Department of Chemical Engineering, Prince of Songkla University was responsible for works to accommodate the future development of petroleum refinering and petrochemical industries of Thailand especially in southern of Thailand. The preliminary work was begun by evaluating the fresh and equilibrium catalysts collected from Chinese and Thai refineries and also using feedstocks from Chinese and Thai refineries. As mention above, the major method of evaluation catalyst are hydrothermal treatment and MAT testing, so the hydrothermal aging and MAT testing unit, which were invented from Research Institute of Petroleum Processing are set up.

In this work, the conditions of hydrothermal treatment and MAT testing were used according to standard of RIPP. Besides MA, the variations of USC and SA of catalysts under hydrothermal treatment are observed.

During operation in commercial cracking unit, the catalysts were deactivated by thermal and hydrothermal, so in this work also studied the effects of deactivation between thermal and hydrothermal treatments.

Literature Review

Evaluation of Fluid Catalytic Cracking Catalysts

Laboratory testing and evaluation of fresh FCC catalysts, when refinery change feedstock or specific demand, involves two steps- a deactivation step, usually use hydrothermal deactivation (hydrothermal aging) and a catalytic step (MAT testing). (Mclean, J.B. and Moorehead, E.L., 1991)

1. Hydrothermal Aging (ASTM D-4463-1988, 1996, Moorehead, E.L, Margolis, M.J. and Mclean, J. B., 1989)

Hydrothermal treatment of fresh FCC catalysts, prior to determination of catalytic cracking in microactivity test (MAT), is important because the catalytic activity of the catalyst in its fresh state is an inadequate measure of its true commercial performance. During operation in a commercial cracking unit, the catalyst is deactivated by thermal, hydrothermal and chemical degradation. Therefore, to maintain catalytic activity, fresh catalyst is added (semi) continuously to the cracking unit, to replace catalyst lost through the stack or by withdrawal, or both. Under steady state conditions, the catalyst inventory of the unit is called "equilibrium catalyst"; this catalyst has an activity level substantially below that of fresh catalyst. Therefore, artificially deactivating a fresh catalyst prior to determination of its cracking activity should provide more meaningful catalyst performance data.

Due to the large variations in properties among fresh FCC catalyst types as well as between commercial cracking unit designs and/ or operating condition no single set of steam deactivation conditions is adequate to artificially simulate the equilibrium catalyst for all proposes. In addition, there are many other factors that will influence the properties and performance of equilibrium catalyst. These include, but are not limited to deposition of heavy metals such as Ni, V, Cu; deposition of light metals such as Na; contamination from attrition refractory lining of vessel walls. Furthermore, commercially derived equilibrium catalyst represents a distribution of catalysts of different ages (from fresh to > 300 days). Despite these apparent problems, it is possible to obtain reasonably close agreement between the performance of steam deactivated and equilibrium catalysts. It is also recognized that it is possible to steam deactivate a catalyst so that its properties and performance poorly represent the equilibrium. It is therefore recommended that when assessing the performance of different catalyst types, a common steaming condition to be used.

The procedure for steaming treatment are non-shock steaming, catalyst is heated slowly during preheating, and shock steaming, predry sample at about 550 ^{o}C for one hour is introduced directly into a preheated steaming reactor.

The measurement of steamed catalysts properties such as zeolite unit cell size, surface area, MAT etc., can be used to target typical equilibrium properties for a particular catalyst. The choice of steaming conditions determines the physical and chemical characteristics of the catalyst. Therefore, under constant MAT condition, steaming condition are responsible for the observed activity, selectivity and stability. Laboratory steaming of fresh FCC catalysts is generally done in the presence of 100 percent steam in fixed bed or fluidized bed configuration. Catalysts are usually loaded at ambient temperature in the reactor under nitrogen flow (non-shock steaming), the temperature is increased to the desired target. Steam, obtained by vaporization of injected water, is then introduced and nitrogen flow is stopped. After a specific period of time, the water injection is stopped and the nitrogen is introduced again and the temperature is set back to an ambient or low level. The catalyst is unloaded.

In Table1-1 it can be observed that a wide range of steaming severities are used. In general, the minimum temperature is 1,300 ^{o}F, with a maximum of 1,600 ^{o}F. While steaming is used to artificially deactivate a fresh sample, such that it represents a typical "equilibrium" sample. The approaches used to achieve this are varied. A number of laboratories used a fixed time and vary temperature to achieve a range of deactivated samples that when evaluated in MAT unit will have a range of deactivated samples that when evaluated in a MAT unit will have a range of conversions so that they can make assessment of catalyst stability and selectivity.

An alternative approach for steaming uses a fixed temperature but the time is varied to generate a hydrothermal stability curve. Temperature in the range of 1,400 -1,500 ^{o}F are generally used with times ranging from 5-60 hrs. Prefered times however, tend to be 4 - 24 hrs. but some laboratory used between 4-17 hrs. (Moorehead, E.L., et.al,1989) . The times employed can be tied to either a target conversion or some physical property. The deactivated samples are then evaluated in a MAT unit under a standard set of condition.

A third approach involves one steaming severity in conjunction with varying MAT condition(usually cat/oil) to achieve equivalent conversion (McElhiney, G., 1988) .While this method provides for equivalent steaming of all catalysts it provides very little information on the relative stability of the catalysts to be evaluated.

A fourth approach involves a variation from variable time/constant temperature by blending different portions of deactivated sample (Keyworth, D.A., et.al, 1988) .This method is not used to any extent at this time.

A fifth approach for using blends of 5% fresh and 95% steamed catalysts. (McLean, J.B., 1991) This method used in comparison of two catalysts which differ primarily in their fresh properties.

For all of these alternative the goal is to produce a sample that has chemical and physical properties that are indicative of commercially deactivated catalyst (Rawlence, D.J., 1988 quoting in Moorehead, E.L, Margolis, M.J. and Mclean, J. B., 1989)

Table 1-1 Summary of steaming conditions

	Precalcination	**Steaming Temperature, °F**	**Steaming Time, hrs.**
ASTM	None	1292-1562	5
RIPP	None	1472	4 & 17
Engelhard	None	1300-1600*	4
	1100/1 hr	1350-1454	17
	1100/1 hr	1350-1550*	4
		1360-1430 metals	
	1100/4 hrs	1375	4.75
	None	1382-1490	17
	1200/3 hrs	1400@15 psig	5&10
	None	1400&1500*	5
	1112/4 hrs	1400&1500	5
	1112/3 hrs	1418	15
	1300/ 1 hr.	1425*	4
	1000/ 1 hr	1430-1525	5-80/20% s/a
	None	1475*	5
	1000/ 1 hr	1475	6 &16
	None	1500	4

* Shock Addition Method

From: Moorehead, E.L., Margolis, M.J. and Mclean, J.B., 1989 :123; RIPP 92-90 standard for hydrothermal treatment quoting in Research Institute of Pretroleum Processing, SINOPEC., 1997(a):1

For example, if the goal of steaming is to target only the unit cell size, then it might be concluded that one steaming severity is needed. As suggested by McElhiney, This would be 1500°F steaming for 5 hrs. (Figure 1-1) (McElhiney, G., 1988). What this approach overlooks is that it does not account for the expected change in MAT activity, zeolite content or total surface area.

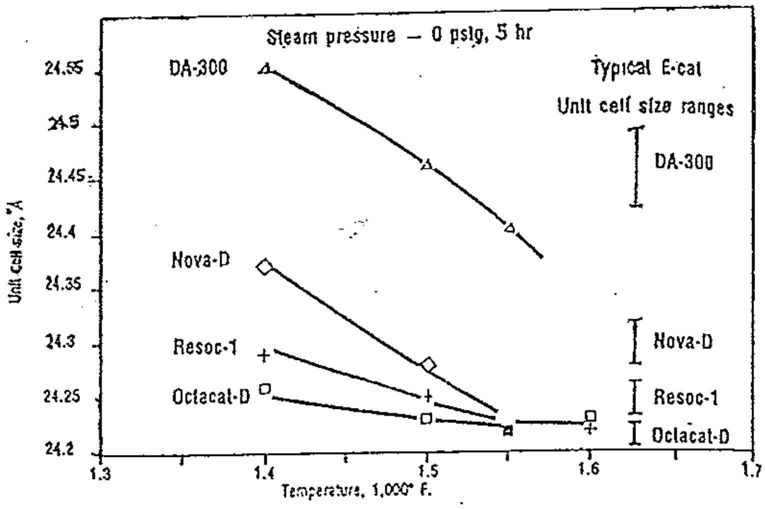


Figure. 1-1 Steaming temperature influence on unit cell size

From: McElhiney, G., 1988: 36

Figure 1-2 shows that an equilibrated unit cell size (UCS) for a zero rare earth USY catalyst can be obtained at relatively mild steaming condition; but as present in Figure 1-3, The MAT activity and surface areas will continue to change with steaming. As the differences between catalysts becomes greater, the need to be aware of these other parameters becomes more important. This is particularly true when comparisons between gasoline and octane catalysts are to be made. While this comparison may not be performed by a particular laboratory it appears that the currently employed steaming procedures were developed for gasoline catalysts and their applications to octane catalysts have to be investigated.

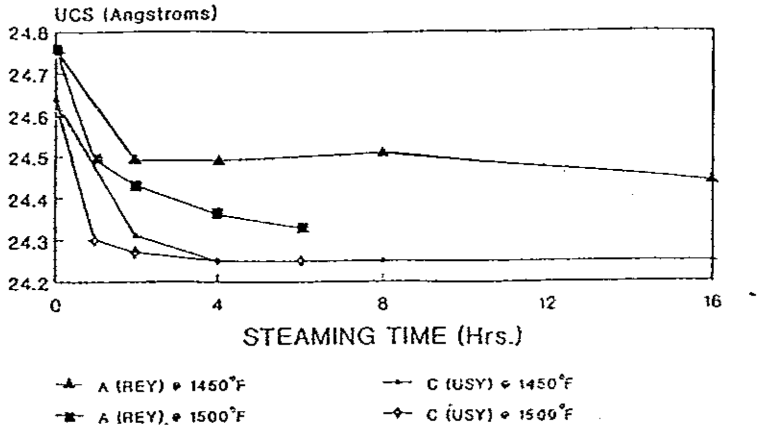


Figure 1-2 Unit cell size equilibration is dependent on steaming conditions.

From :Moorehead, E.L., Margolis, M.J. and McLean, J.B., 1989: 125

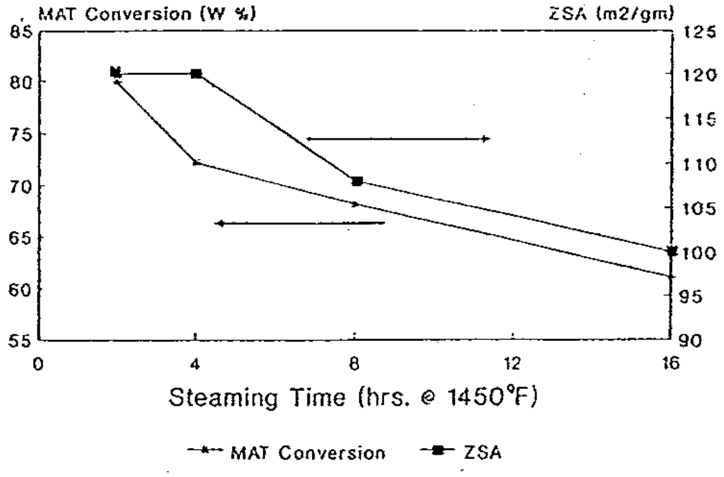


Figure 1-3 MAT Conversion and ZSA continue to decline for USY catalyst

From: Moorehead, E.L., Margolis, M.J. and McLean, J.B., 1989: 125

Figure 1-4 shows the effect of steaming severity on zeolitic surface area (ZSA) for catalyst REY and USY. What is seen is that the conditions needed to deactivate REY to typical equilibrium ZSA are different than for USY. If USY is deactivated using the preferred conditions for REY, then activity and surface areas are not in line with commercial experience. If the reverse is true, then REY is deactivated too severely.

The need to have more than one steaming procedures for extremely different catalysts has been proposed by Magee et. al.(Magee, J.S., Blazek, J.J., 1976) and is consistent with commercial observations in that a USY catalyst will generally have a lower equilibrium MAT activity than a REY catalyst. The difficulty, of course, is that it is not practical to have a unique steaming procedure for every catalyst. However, it is practical to target steaming severity such that the steamed properties for groups of catalysts are representative of what will be observed commercially.

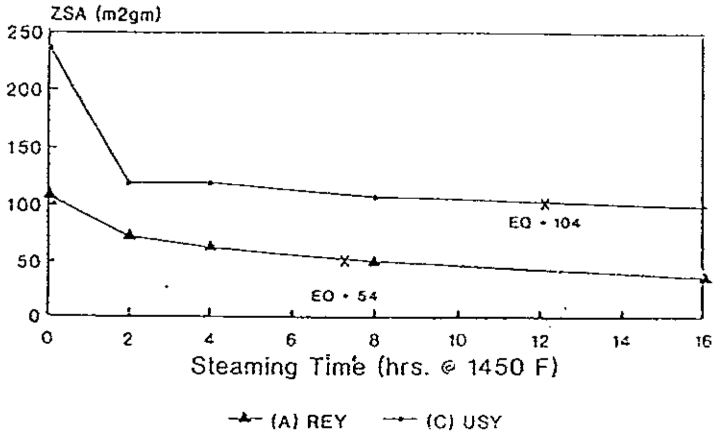


Figure 1-4 Steamed catalyst properties :Zeolite surface area reduction to EQ level is catalyst dependent.

From: Moorehead, E.L., Margolis, M.J. and McLean, J.B., 1989: 126

When compare between REY and USY catalyst at the same temperature and times of hydrothermal, deactivation REY catalyst has UCS and MAT higher than USY catalyst that presented in Table 1-2

Table 1-2 Steamed catalyst properties, all steamings 4 hrs.

Catalysts	REY	REY/USY	USY
Total surface area,m^2/gm:			
1,400°F (760°C)	109	156	217
1,450°F (788°C)	94	140	198
1,500°F (816°C)	67	103	162
Zeolite unit cell size, Å			
1,400°F(760°C)	24.55	24.34	24.33
1,450°F(788°C)	24.49	24.31	24.30
1,500°F(816°C)	24.36	24.31	24.25
Catalyst activity standard MAT	76.9	-	63.1

From : Mclean, J.B., Moorehead, E.L, 1991: 42

2 MAT Testing (ASTM-D3907-1978, 1980, 1987, 1992, ASTM-D5154-1991, RIPP 92-90 standard for microactivity test quoting in Research Institute of Petroleum Processing, 1997)

Microactivity test is to determine the activity and selectivity of equilibrium and/or lab-deactivated fluid catalytic cracking catalysts. The activity is evaluated on the basis of weight percent conversion of gas oil in a microactivity unit. The selectivity are evaluated on the weight percent yields to specifically defined products.

This testing provides data to assess the relative performance of fluid cracking catalyst. The MAT unit itself uses small amounts of catalyst (less than 10 g.), and small amounts of oil (less than 5 g.) in a heated, fixed bed configuration. The rate of oil injection or delivery time is controlled by the used of a syringe pump.

Product oil from MAT unit is analyzed chromatographically. Conversion (weight percent) is defined as

$$\text{Conversion(\%wt)} = \left(\frac{Coke + Gasoline + Light\ \text{gas}}{Feed\ \text{oil}}\right)x100$$

RIPP 92-90 standard for microactivity test

$$\text{Conversion (MA)} = 100 - \left[\left(\frac{100 - A}{C}\right)xB\right]$$

where

A = Gasoline yield, analyzed by GC, %wt

B = Liquid product from MAT, g

C = Feed oil, g

ASTM D3907-1978, 1980, 1987, 1992

$$\text{Conversion (MA)} = \frac{F - \frac{RxL}{100} - H}{F}x100$$

Where:

F = Grams of ASTM standard feed.

R = Weight percentage of material boiling above 216°C (416°F) in liquid product receiver.

L = Grams of liquid product in receiver

H = Grams of liquid holdup at reactor exit line and around reactor-receiver joint

ASTM D 5154-1991

$$\text{Conversion (MA)} = 100\% - (Y_l + Y_h)$$

$$Y_l = \frac{X_L\,(W_{L1} + W_{L2})}{W_F} x100\%$$

Where

Y_l = The raw yield of the LCO products, wt% of feed

X_L = The weight fraction of LCO products in the combined liquid product

W_{L1} = Weight of liquid product in receiver 1

W_{L2} = Weight of liquid product in receiver 2

$$Y_h = \frac{X_h(W_{L1} + W_{L2}) + W_q}{W_F} x100\%$$

Where

Y_h = The raw yield of the HCO products, wt% of feed

X_h = The weight fraction of HCO products in the combined liquid product

W_q = Grams of liguid hold up at reactor exit line

Like the case for steaming, there are a variety of procedures used for MAT evaluations, none of which follow the current ASTM protocol in all respects, a summary of procedures used within the industry is present in Table 1-3

Table1-3 Summary of MAT procedures

	MAT temperature °F	Cat/Oil Ratio	Delivery Time, sec.	WHSV, hr^{-1}
	850	2	300	6
RIPP	860	3.205	70	16
ASTM	900	3.0	75	16
	900	vary	75	vary
	900	2.79	94	13.7
Engelhard	910	5	48	15
	915	3.0	n/a	17
	925	1.875	75	25
	950	5-9	35	11 to 21
	950	2.5-5.5	45-75	13.5-15.5
	950	4.0	18	50
	950	4.5	40	20
	950-1022	4.5	<20	>40<100
	975	1.5-4.5	60	12.8-38.5
	985	3.3	75	14.5
	986	6.6	20	30

From: RIPP 92-90 standard quoting Research Institute of Pretroleum Processing, SINOPEC., 1997(b):1, Moorehead, E..L., Margolis, M.J. and Mclean, J.B., 1989:129

FCC Catalysts Deactivation Mechanisms.

There are two types of catalyst deactivation which occur in FCC systems-reversible and irreversible. Reversible deactivation occurs due to coke deposition each time the catalyst passes through the reactor and is reversed by coke burning in the unit's regenerator.

Irreversible deactivation of catalyst as it ages in the unit can be viewed as combination of four separate but interrelated, mechanisms:

- Zeolite dealumination
- Zeolite decomposition
- Matrix surface collapse
- Contaminant effects

Zeolite dealumination, as measured by unit cell size reduction, reduces the acid site density and, hence, the inherent activity per unit of zeolite. Zeolite decomposition, measured by crystallinity or micropore surface area loss, reduces activity. Both processes occur simultaneously under the hydrothermal atmosphere of an FCC regenerator. Matrix decomposition reduces activity by reducing catalytically active matrix sites, as well as by reducing porosity of the particle, which can restrict accessibility of the zeolite. Contaminants such as vanadium and sodium also contribute to deactivation in various ways. (Mclean, J.B., Moorehead, E.L., 1991)

Thermal and Hydrothermal Deactivation

Thermal deactivation of catalyst is a permanent deactivation that occurs at very high temperatures. Activity loss from thermal effects is caused by melting of a catalyst's active structures. It can be detected by loss of pore volume, surface area and the formation of certain alumina phase. The different between thermal and hydrothermal deactivation is thermal deactivation has not steam in the mechanism of deactivation.

Hydrothermal deactivation, also a permanent loss of catalyst activity, is the more prevalent mechanism for activity loss during the regeneration cycle. Hydrothermal deactivation results from zeolite dealumination and subsequent crystallinity (and surface area) loss, as well as pore size shifts and surface area loss in matrix.

Steam is always present in FCCU regenerators. It represents about 15 to 25 V% of gaseous mixtures in typical single-stage regenerators. Steam, time and temperature expels aluminum atoms from the zeolite structure,which cause a significant portion of them to collapse. Some zeolite actually "dealuminates" to a lower unit cell size without collapsing.The dealumination is similar to, though an uncontrolled version of, the manufacturing step involving steam calcination of Standard - Y zeolites to make USY.

Aging effects and catalyst deactivation can be minimized by using catalyst with "stable" components. Catalyst stability has many difinitions; percent surface area retention, percent MAT retention, and percent selectivity retention are some of more common. Catalyst stability is an inherent catalyst property based on type and manufacture of catalyst property. John and Mikovsky (1961) have shown that while amorphous catalysts deactivation thermally as well as hydrothermally, thermal deactivation is a significantly slower process. Letzch et al. (1976) have shown that, like amorphous catalysts, the zeolite component is more strongly deactivation hydrothermally than thermally. Dobrea et al. (1966) have shown that the porosity and surface area distributions of equilibrium catalysts are more similar to steam-aged than thermally aged catalysts (quoting in Chester, A.W. and Stover, W. A., 1977)

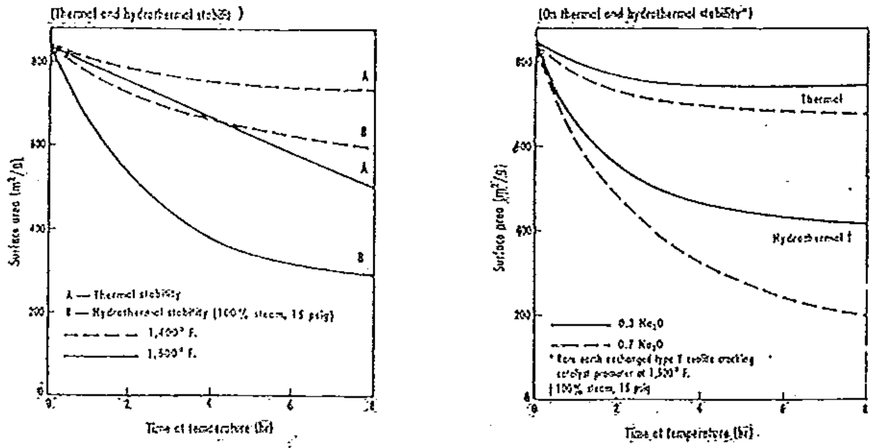


Figure1-5 Thermal and hydrothermal stability

From: Letzsch, W.S., Ritter,R.E. and Vaughan, D.E.W., 1976: 131

Objectives

1. To study the hydrothermal aging (deactivation) and microactivity test (MAT) on fluid catalytic cracking catalysts.
2. To compare the deactivation results between hydrothermal deactivation (100% steam) and thermal deactivation (0% steam)
3. To study the simulation and testing of the fluid catalytic cracking catalysts.

Possible Achievement

The possible achievement is to understand the laboratory testing procedures for both fresh and equilibrium catalysts. The knowledge from this wok can be recommended for practical procedure to Thai refineries and can be used as fundamental information for the development of the new catalysts in the future.

Content of Research

1. Study the pre-treatment (hydrothermal aging) and microactivity test of fluid catalytic cracking.
2. Study the deactivation processes.
   2.1 Hydrothermal deactivation
   2.2 Thermal deactivation
3. Perform testing and analysis on a certain amount of FCC catalysts.
   3.1 Hydrothermal - aged catalysts
      - Unknown sample A,B,C,D,E from Thai Oil Company Limited
      - Lanet-35(REHY USY Zeolite, Si-Al Kaolin matrix), Gong-Y(REY Zeolite, Si-Al matrix) from RIPP

3.2 Equilibrium catalysts

- H-EQ, I-EQ, CRC-EQ, MZ3-EQ from RIPP
- F-EQ from Thai Oil Company Limited
- G-EQ from Star Petroleum refining CO.,LTD.

3.3 Feed stocks

- RIPP standard gas oil
- Fang gas oil

Chapter 2

Fluid Catalytic Cracking

2.1 Fluid Catalytic Cracking Process (Meyers, R.A. 1986; Pramote Chaivate.,1990)

The fluid catalytic cracking (FCC) process is a process for the conversion of heavy, long-chain hydrocarbon molecules into lighter, shorter-chain molecules, usually high-octane gasoline. This process use high temperature and catalyst to instigates cracking reaction of hydrocarbon. FCC unit has 2 main sections, catalytic section (reactor - regenerator) and fractionator section.

2.1.1. Catalytic Section (Reactor and Regenerator)

In the operation of the FCC unit, fresh feed and (depending on product-distribution objectives) recycled cycle oils are introduced through a standpipe called "riser" and into the reactor (temperatue~500 °C) together with a controlled amount of regenerated catalyst.

The charge may be preheated, either by heat exchange or, for some applications, by means of a fired heater.

The hot regenerated catalyst vaporised the feed, and the resultant vapors carry the catalyst upward through the riser with a minimum of back mixing. At the top of the riser the desired cracking reactions have been completed and the catalyst is quickly separated from the hydrocarbon vapors to minimize secondary reactions. The catalyst-hydrocarbon mixture from the riser is discharged into the reactor vessel through a device that achieves a significant degree of catalyst-gas separation. Final separation of catalyst and product vapor is accomplished by cyclone separation.

The reactor effluent is directed to the FCC main fractionator for resolution into gaseous light olefin coproducts, FCC gasoline and cycle stocks. The spent catalyst drops from the reactor vessel into the stripping section, where a counter current flow of steam removes interstitial and some adsorbed hydrocarbon vapors. Stripped spent catalyst descends through a standpipe and into the regenerator (temperature ~ 600 °C).

During the cracking reaction, a carbonaceous by-product is deposited on the circulating catalyst. This material, termed "coke" is continuously burned off the catalyst in the regenerator. The main purpose of the regenerator is to reactivate the catalyst so that, when returned to the conversion section, it is in optimum condition to perform its cracking function. The regenerator serves to gasify the coke from the catalyst particles and, at the same time, to impart sensible heat to the circulating catalyst. The energy carried by the hot regenerated catalyst is used to satisfy the thermal requirements of the cracking section of the unit.

Depending on the specific application, the regenerator may be operated at conditions that achieve complete or partial internal combustion of CO to CO_2, or alternatively, CO may be converted to CO_2 in an external CO boiler. If internal conversion of CO to CO_2 is practiced, the sensible heat of the flue gas can be recovered in a waste- heat boiler. Flue gas is directed through cyclone separators to minimize catalyst entrainment prior to discharge from the regenerator.

In order to maintain the activity of the working-catalyst inventory at the desired level and to make up for any catalyst lost from the system with the flue gas, fresh catalyst is introduced into the circulating-catalyst system from a catalyst storage hopper. An additional storage hopper is provided to hold spent catalyst withdrawn from the circulating system as necessary to maintain the desired working activity and to hold all the catalyst inventory when the FCC unit is shut down for maintenance and repairs.

Reactor and regenerator in FCC unit work together in a closely relative continuous system because this unit is a system of balances - heat balance, pressure balance and coke balance.

Heat Balance

The overall energy balance can be written in the following simplified form:

Q_{RG} =	$[Q_P - Q_{FD}]$ +	$[Q_{FG} - Q_A]$ +	$[Q_{RX}]$ +	$[Q_{L1} + Q_{L2}]$
Heat of	Sensible - heat terms		Heat of	Heat
combustion	[Reactor]	[Regernerator]	reaction	Losses
4.87	[3.22 - 1.00]	[1.93 - 0.42]	[1.14]	[0]

The numbers below the heat-flow terms show the magnitude of each term relative to the heat brought in with the fresh feed. As written, the equation shows the basic concept of FCC heat balance. The energy released by the coke combustion in the regenerator, Q_{RG} is sufficient to supply the required heat load of the system, the heat of reaction and vaporization, the heat required to bring the feed to reaction temperature, and the heat required to sustain the regenerator at combustion temperature. Note that the heat brought in with the feed and the combustion air, Q_{FD} and Q_A , is relatively small compared with the heat from combustion and that heat losses, Q_{L1} and Q_{L2} , are negligible.

The circulating catalyst carries the energy from the regenerator via its own sensible heat, Q_{RC} . The circulating-catalyst rate then becomes a key operating variable in that it not only supplies heat but also affects conversion according to its concentration in the reactor relative to oil, expressible in terms of the well-known " cat- to- oil ratio"

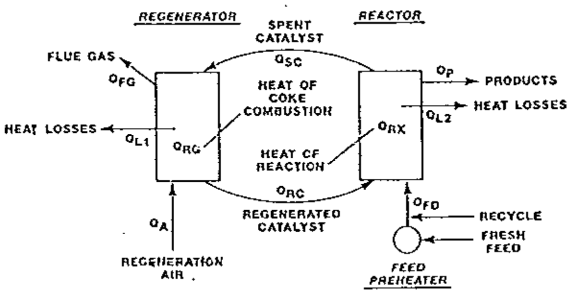


Figure 2-1 FCC heat balance

From: Meyers, R. A.,1986: 2-20

Coke Balance

Coke that deposit on the catalyst from cracking reaction in reactor is burned out in the regenerator. The quantity of coke on the spent catalyst should not too high (< 2% wt), alternative, the combustion is difficult and coke can accumulate on the catalyst

We can control the reaction in regenerator by controlling burning air rate and circulation rate of catalyst, if burning air rate is too low - coke will accumulate on catalyst and if too high - temperature of regenerator will be too high, then dangerous.

Pressure Balance

In FCC unit, pressure balance is the most important factor to receive a smooth work. The results from non-balance pressure are non-circulation of catalyst, heat in regenerator cann't transfer to reactor, vaporization of feed in riser stop. We can control pressure balance in the unit by adjusting flow rate of steam that carrier catalyst, height of dense bed, pressure in reactor and regenerator.

This process is complicated because the many interdependence of variables and can classify to independent variables - directly controlled usually with a control meter and dependent variables - change as a result of a change in an independent variable. Below are examples of the major independent and dependent variables.(Venato, P.B. and Habib, JR., E.T, 1979)

Independent Variables:

1.Reactor temperature: The temperature of the catalyst-oil reaction mixture in the reactor.

2.Fresh feed rate:The flow rate of non-catalytically cracked feed that are charged to the cat cracker. Some thermally cracked feeds such as coker gas oil are classified as fresh feed. Fresh feed is a term used to differentiate between outside feed to the cat cracker and recycle.

3. Recycle rate: The flow rate of cat cracked product that are returned to the reactor for further cracking. The products normally recycled are those heavier than light cycle oil although light cycle oil is sometimes recycled.

4. Feed preheat temperature: The temperature of the feed (including recycle) to the cat cracker.

5. Weight hourly space velocity (WHSV) : The weight / hour of total feed (fresh feed plus recycle) devided by the weight of catalyst in the reactor that contact the feed.

6. Catalyst activity: Catalyst activity is the ability of the catalyst to convert a feedstock to certain specified products at a set of fixed operating conditions are prescribed according to the activity test used. The most widely used activity test is the microactivity test.

Dependent Variables:

1. Catalyst-to-oil-ratio: The weight ratio of the catalyst circulation rate to the combined feed rate.

2. Regenerator temperature: The temperature of the catalyst during coke burn-off in the regenerator vessel.

3. Burning air rate: The air rate, usually given in SCFM (standard cubic feet per minute), required to support the combustion of the coke deposit on the catalyst in order to remove the coke and thereby regenerate the catalyst.

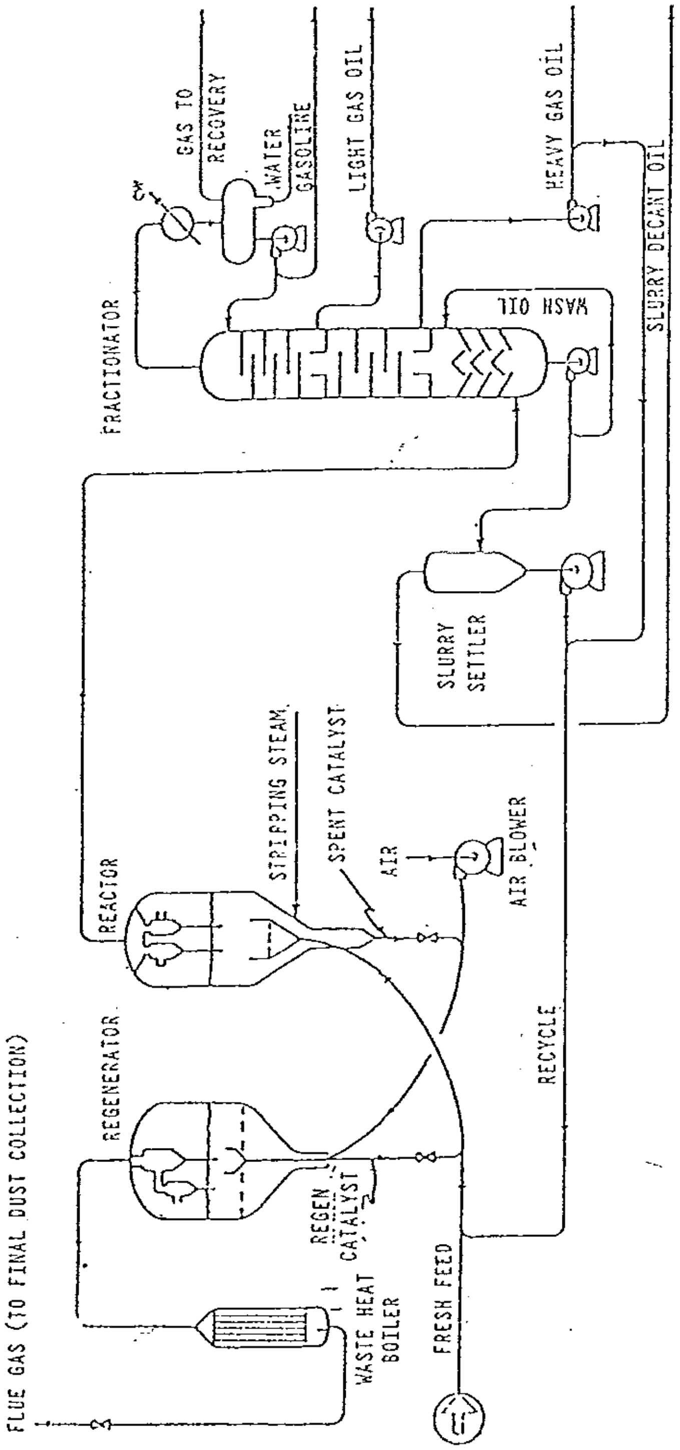
4. Conversion: Conversion is the percent of feed changed to gasoline (of a prescribed end point), lighter and coke in the catalytic cracking process. It is also defined as gas oil disappearance.

2.1.2 Fractionator Section

Reactor-product vapors are directed to the main fractionator, where gasoline and gaseous olefin-rich coproducts are taken overhead and routed to the gas-concentration unit. Light-cycle oil is recovered as a side cut, with the net yield of this material being stripped for removal of light ends and sent to storage. Net column bottoms are yielded as slurry or classified oil that can produce carbon black or decant oil after separated catalyst out. In some instances, heavy material can be recycled to the reactor riser.

Figure 2-2 Fluid catalytic cracking unit (FCCU)

From: Speight, J.G., 1991: 552



2.2 Fluid Catalytic Cracking Catalysts (FCC Catalysts)

(Sadeghbeigi, R., 1995, Upson, L.L., 1981(a),(b))

Fluid catalytic cracking catalyst is a fine porous powder composed of the oxides of silicon and aluminum. Other elements may also be present in very small amounts. Either Bronsted or Lewis acid sites are associated with the aluminum. The acid sites initiate and accelerate carbocation reaction that cause molecular size reduction of petroleum oil at FCCU reactor conditions. When aerated with gas, the powder attains a fluid-like property that allows it to behave like a liquid. This property permits the catalyst to be circulated between the reactor and regenerator - hence the name fluid catalytic cracking catalyst.

Fluid catalytic cracking were significantly improved when zeolite-cracking catalysts were introduced commercially around 1960. Zeolite catalysts were better than previously used catalysts. Their advantages include the following:

- Less sensitive to poisoning by metals
- More stable than previous catalysts
- Capable of withstanding higher temperatures
- Crystal structure permits a defined pattern that can be properly produced to emphasize the specific reactions desired
- Great cracking activity
- Very short contact time for cracking the feed oil

2.2.1 Catalyst Components

FCC catalysts are in the form of fine powder with an average particle size diameter in the range of 75 microns. A modern cat cracking catalyst had four major component system: zeolite, matrix, binder and filler.

2.2.1.1 Zeolite

The zeolite, or more properly, faujasite, is the key ingredient of the FCC catalyst. Its role in the catalyst is to provide product selectivity and much of the catalytic activity. The catalyst's performance dependent largely on the nature and quality of the zeolite. Understanding the zeolite structure, types, cracking mechanism, and properties is essential in choosing the " right" catalyst to produce the desired yields.

Zeolite Structure

Zeolite, sometimes called molecular sieve, has a well-defined lattice structure (framework of aluminosilicates). Its basic building blocks are silica and alumina tetrahedra. Each tetrahedron (Figure 2-3) consists of a silicon or aluminum atom at the center of the tetrahedron, with oxygen atoms at the corners. Then each tetrahedron linked to each other by sharing all of the oxygens.

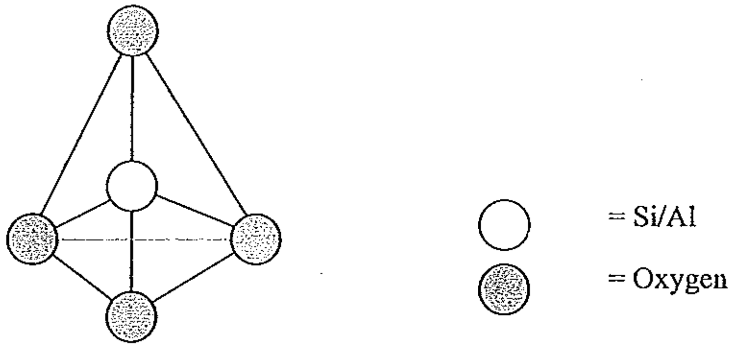


Figure 2-3 Silicon/aluminum-oxygen tetrahedron

From: Sadeghbeigi, R., 1995: 81

Zeolite lattices have an organized network of very small pores. The pore diameter of nearly all of today's FCC zeolite is approximately 8.0 angstroms(Å). These small openings, with an internal surface area of roughly 600 square meters per gram, do not readily admit hydrocarbon molecules with a molecular diameter greater than 8.0 Å to 10 Å

The elementary building block of the zeolite crystal is called a unit cell. The unit cell size (UCS) is the distance between the repeating cells in the zeolite structure. One unit cell in a typical fresh Y-zeolite lattice contains 192 framework atomic position: 55 atoms of aluminum and 137 atoms of silicon. This corresponds to a silica (SiO_2) to alumina (Al_2O_3) molal ratio (SAR) of 5. The UCS is an important parameter in characterizing the zeolite structure.

Structural formula of zeolite

$$M_{x/n}[(AlO_2)_x(SiO)_y] \cdot wH_2O$$

Where M is the cation of valence n,

w is the number of water molecules,

y/x usually has values of 1-5 (as formed in nature or synthesized. Highly polyvalent ions, e.g., rare earths, are readily introduced by cation exchange)

Empirical formula (in oxides)

$$M_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$$

$X \geq 2$ (AlO_4 tetrahedra are joined only to SiO_4 tetrahedra)

Zeolite Chemistry

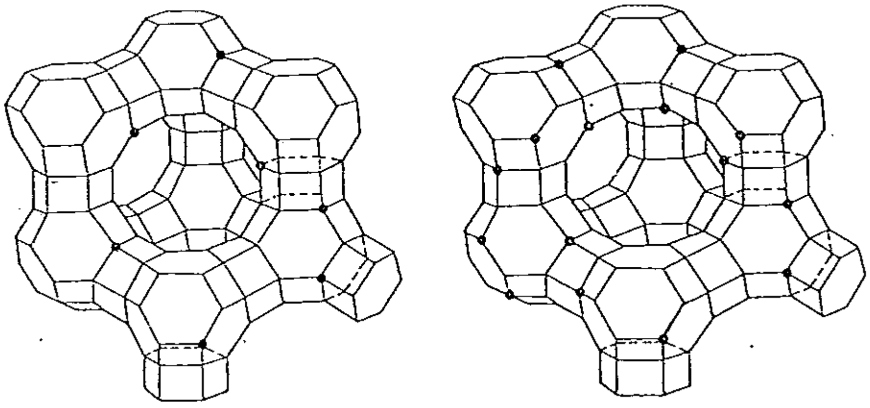
A typical zeolite consists of silicon and aluminum atoms that are tetrahedrally joined by four oxygen atoms. Silicon is in a +4 oxidation state, therefore, a tetrahedral containing silicon is neutral in charge. In contrast, aluminum is in a +3 oxidation state. This indicates that each tetrahedron containing aluminum has a net charge of -1 which must be balanced by a positive ion.

Solutions containing sodium hydroxide are commonly used in synthesizing the zeolite. The sodium serves as the positive ion to balance the negative charge of aluminum tetrahedron. This zeolite is called soda Y or NaY. The NaY zeolite is not hydrothermally stable because of the high sodium content. Ammonium ion is frequently used to displace sodium. Upon drying the zeolite, ammonia is vaporized. The resulting acid sites are both the Bronsted and Lewis types. The Bronsted acid sites can be further exchanged with rare earth material such as cerium and lanthanum to enhance their strengths. The zeolite activity comes from these acid sites.

Zeolite Types

Zeolites employed in the manufacture of the FCC catalyst are synthetic versions of naturally occurring zeolites called faujasites. There are about 40 known natural zeolites and over 150 zeolites which have been synthesized. Of this number, only a few have found commercial application. Table 2-1 shows properties of the major synthetic zeolites.

The zeolites with applications to FCC are type X, type Y, and ZSM-5.Both X and Y zeolites have essentially the same crystalline structure. The major difference is that the X zeolite has a lower silica/alumina ratio than the Y zeolite. The X zeolite also has a lower thermal and hydrothermal stability than Y zeolite. Some of the earlier FCC zeolite catalysts contained X zeolite, however, virtually all of today's catalysts contain Y zeolite or variations thereof (Figure 2-4).



USY Zeolite (~ 7 Al Atoms/u.c.)

Unit Cell Dimension = 24.25 Å (SiO_2/Al_2O_3=54)

Equilibrium REY (~ 23 Al Atoms/u.c.)

Unit Cell Dimension=24.39 Å (SiO_2/Al_2O_3 = 15)

Figure 2-4 Geometry of USY and REY zeolites

From: Grace, W.R.& Co., 1985 quoting in Sadeghbeigi, R.,1995 :83

Until the late 1970s, the NaY zeolite was mostly ion exchanged with rare earth and with NH_4^+ to form fully exchanged zeolite (REY) or partial exchanged zeolite.(REHY) Rare earth components such as lanthanum and cerium were used to replace sodium in the crystal. The rare-earth elements, being trivalent, simply form "bridges" between two to three acid sites in the zeolite framework. The bridging basically protects acid sites from being ejected from the framework and thus stabilizes the zeolite structure. Consequently, the rare earth exchanged adds to the zeolite activity and thermal and hydrothermal stability.

The reduction of lead in motor gasoline in 1986 created the need for the higher-FCC gasoline octane. Catalyst manufacturers responded by adjusting the zeolite formulations, an alternate that involved expelling a number of aluminum atoms from the zeolite framework. The removal of aluminum increased SAR, reduced UCS and in the process, lowered the sodium level of the zeolite. These changed increased the gasoline octane by raising its olefinicity. This aluminum-deficient zeolite was called ultrastable Y, or simply USY, because of its higher stability than the conventional Y.

Table2.1 Properties of major synthetic zeolites From : Sadeghbeigi, R., 1995: 82

Zeolite type	Pore size Dimensions (Å)	Silica-to-Alumina ratio	Processes
Zeolite A	4.1	2-5	Detergent manufacturing
Faujasite	7.4	3-6	Catalytic cracking and hydrocracking
ZSM-5	5.2x5.8	30-200	Xylene isomerization, benzene alkylation, catalytic cracking
Mordenite	6.7x7.0	10-12	Hydro-isomerization, dewaxing

Zeolite Properties

The properties of the zeolite play a significant role in the overall performance of the catalyst and familiarity with these properties increases our ability to predict catalyst response to continual changes in unit operation. From its inception in the catalyst plant, the zeolite must withstand and retain its catalytic properties under the hostile conditions of the FCC operation. The reactor/regenerator environment can cause significant changes in chemical and structural composition of the zeolite. In the regenerator, for instance, the zeolite must also retain its crystallinity against feedstock contaminants such as vanadium and sodium.

Various analytical tests can be carried out to determine zeolite properties. These tests should supply information about strength, type, number, and distribution of acid sites. Additional tests can also provide information about surface area and pore size distribution. The three most common parameters governing zeolite behavior are as follows:

A. Unit cell size

B. Rare earth level

C. Sodium content

A. Unit Cell Size (UCS): The UCS is a measure of aluminum sites or the total potential acidity per unit cell. The negatively-charged aluminum atoms are sources of active sites in the zeolite. Silicon atoms do not possess any activity. The UCS is related to the number of aluminum atoms per cell (N_{Al}) (by Breck, D. W., 1974 quoting in Sadeghbeigi, R., 1995)

$$N_{Al} = 111x(UCS-24.215)$$

The number of silicon atoms (N_{Si}) is:

$$N_{Si} = 192 - N_{Al}$$

The SAR of the zeolite can be determined either from the above two equations or from a correlation such as the one shown in Figure 2-5

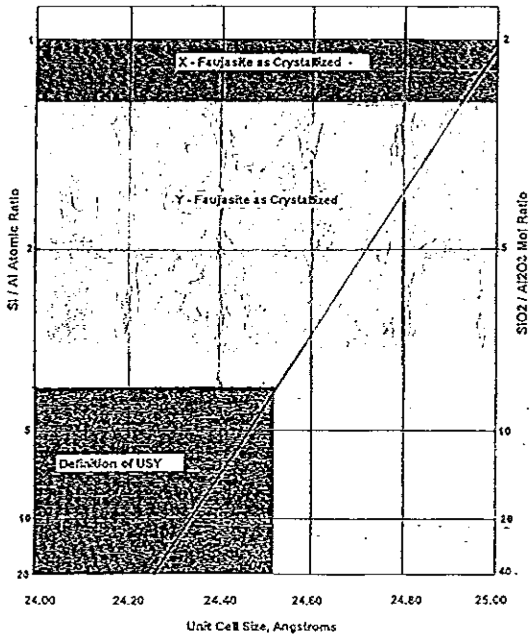
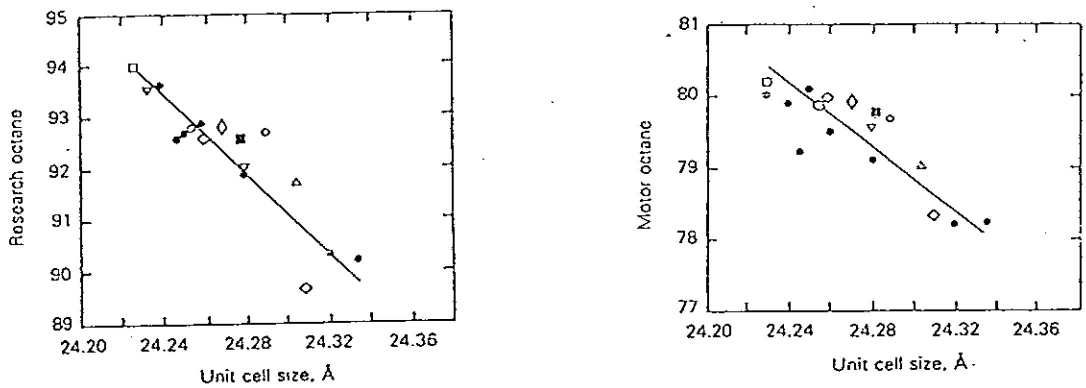


Figure 2-5 Silica-alumina ratio versus zeolite unit cell size

From: Sadeghbeigi, R.., 1995: 85

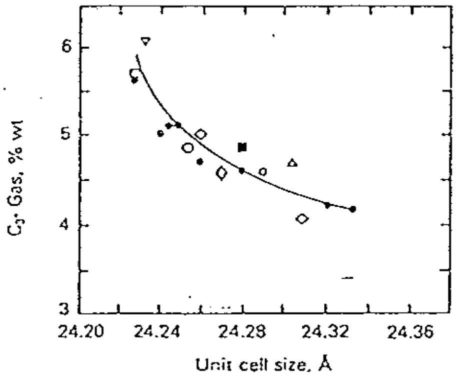
The UCS is also an indicator of zeolite acidity. Because the aluminum ion is larger than the silicon ion, as the UCS decreases, the acid sites become farther apart. The strength of the acid sites is determined by the extent of their isolation from the neighboring acid sites. The close proximity of these acid sites cause destabilization of the zeolite structure. Acid distribution of zeolite is a fundamental factor affecting zeolite activity and selectivity. Additionally, the UCS measurement can be used to indicate octane potential of the zeolite. A lower UCS presents fewer active sites per unit cell. The fewer acid sites are farther apart and therefore inhibit hydrogen transfer reactions, which in turn increases gasoline octane as well as the production of C_3 and lighter components. (Figure 2-6) The octane increase is due to a higher concentration of olefins in the gasoline.

Zeolite with lower UCS are initially less active than the conventional rare-earth-exchanged zeolite. (Figure2-7) However, the lower UCS zeolite tend to retain a greater fraction of their activity under severe thermal and hydrothermal treatments, hence the name ultrastable Y.



Dependence of research octane number on zeolite unit cell size

Dependence of motor octane number on zeolite unit cell size



Dependence of light gas yield on zeolite unit cell size

Figure 2-6 Effects of unit cell size on octane and C_3^- gas make

From: Pine, L. A., Maher, P.J. and Wacher, W.A., 1984: 471

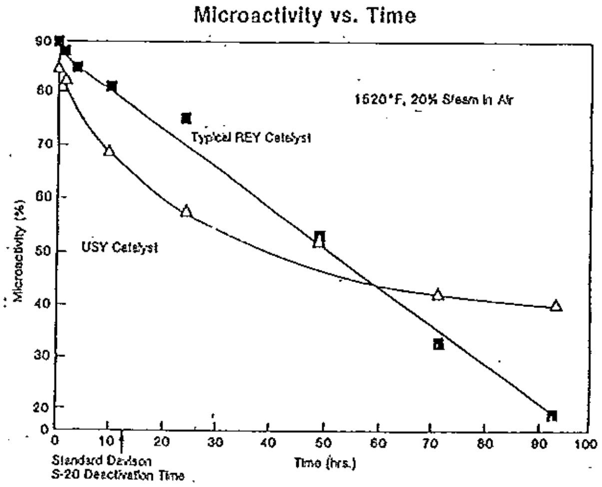


Figure2-7 Comparison of activity retention between rare earth exchanged zeolite versus USY zeolites.

From: Radeghbeigi, R., 1995: 87

A freshly-manufactured zeolite has a relatively high UCS in the range of 24.50 ^{o}A to 24.75 ^{o}A . The Thermal and hydrothermal environment of the regenerator extracts alumina from the zeolite structure and therefore reduces its UCS. The final UCS level depends on the rare earth and sodium level of the zeolite. The lower the sodium and rare earth content of the fresh zeolite, the lower UCS of the equilibrium catalyst (E-cat).

B. Rare Earth Level : Rare earth elements serve as a "bridge" to stabilize aluminum atoms in the zeolite structure. They prevent the aluminum atoms separating from the zeolite lattice when the catalyst is exposed to high-temperature steam in the regenerator.

A fully rare-earth-exchanged zeolite equilibrates at a high UCS where as a non rare earth zeolite equilibrates at a very low UCS in range of 24.25 (Upson,L.L.,1981) All intermediate levels of rare earth increases zeolite activity and gasoline selectivity with a loss in octane.

The octane loss is due to promotion of hydrogen transfer reactions. The insertion of rare earth maintains more and closer acid sites, which promotes hydrogen transfer reactions .In addition, rare earth improves thermal and hydrothermal stability of the zeolite. To improve the activity of a USY zeolite, the catalyst suppliers frequently add some rare earth to the zeolite.

The ratios of rare earth components in the zeolite are also important. Most significant is the ratio of La/ Ce for a given rare earth content, a higher La/ Ce Ratio will results in a significantly more stable zeolite.(Campagna, R.J. etal, 1986)

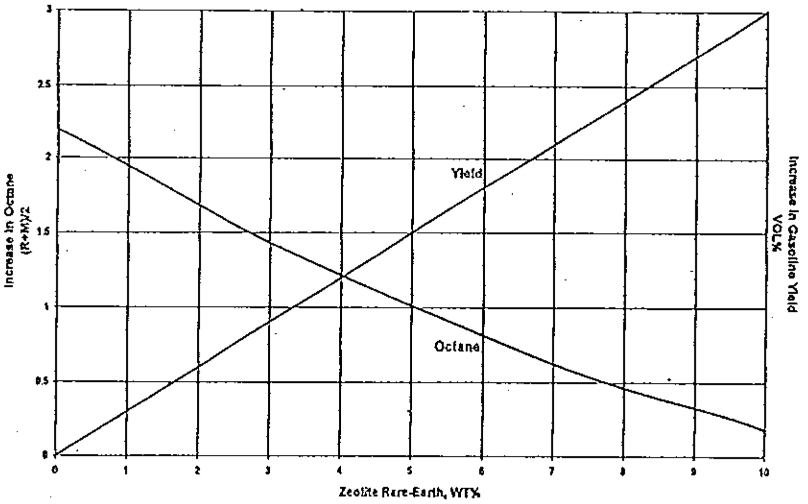


Figure 2-8 Effects of rare earth on gasoline octane and yield

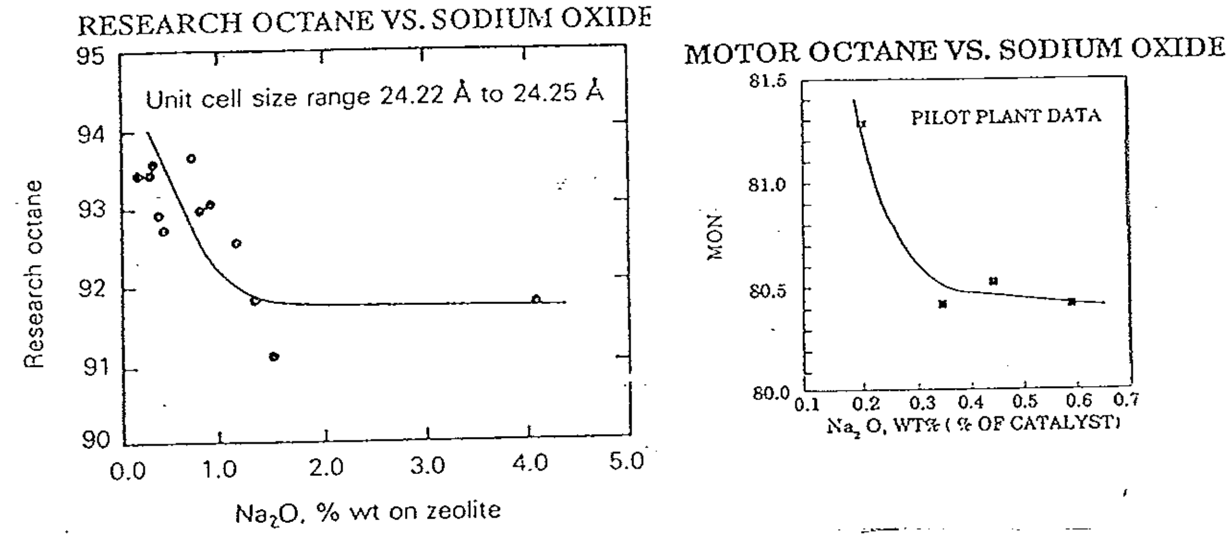
From: Sadeghbeigi, R., 1995:89

C. Sodium Content: The sodium on the catalyst originates either from zeolite during its manufacture or from the FCC feedstock. It is important for the fresh zeolite to contain very low amounts of sodium .

Sodium decreases the hydrothermal stability of the zeolite .It also reacts with the zeolite acid sites to reduce the catalyst activity. In the regenerator, sodium is mobile. Sodium ions tend to neutralize the strongest acids sites. In a dealuminated zeolite where the UCS is low (24.22 °A to 24.25 °A), the sodium can have an adverse affect on the gasoline octane (Figure2-9).The loss of octane is attributed to drop in number of strong acid sites.

FCC catalyst venders are now able to manufacture catalysts with a sodium content of less than 0.2 wt.%. Sodium is commonly reported as the weight percent sodium or soda (Na_2O) on the catalyst. The proper way to compare sodium is the weight fraction of sodium in the zeolite. This is because FCC catalyst have different zeolite concentrations.

UCS, rare earth, and sodium are just three of the parameters that are readily available to characterize the zeolite properties. They provide valuable information about catalyst behavior in the cat cracker. If required, additional tests can be conducted to examine other zeolite properties.



RESEARCH OCTANE VS. SODIUM OXIDE

MOTOR OCTANE VS. SODIUM OXIDE

Figure 2-9 Effects of a soda on motor and research octanes

From: Pine, L.A., Maher, P.J. and Wacher, W.A.,1984: 475

2.2.1.2 Matrix

The term matrix has different meanings to different people. For some, matrix refers to components of the catalyst other than the zeolite. For others, matrix is a component of the catalyst aside from the zeolite having catalytic activity. Yet for others, matrix refers to the catalyst binder . In this report, matrix means components of the catalyst other than zeolite and the term active matrix means the components of the catalyst other than zeolite having catalytic activity.

Alumina is the source for an active matrix. Most active matrices used in FCC catalysts are amorphous. However, some of the catalyst suppliers incorporate a form of alumina that also has a crystalline structure.

Active matrix contributes significantly to the overall performance of the FCC catalyst. The zeolite pores are not suitable for cracking of the large hydrocarbon molecules generally having an end point > 900 ^{o}F; they are too small to allow diffusion of the large molecules to the cracking sites. An effective matrix must have a porous structure to allow diffusion of hydrocarbons into and out of the catalyst.

An active matrix provides the primary cracking sites. The acid sites located in the catalyst matrix are not as selective as the zeolite sites but are able to crack larger molecules that are hindered from entering the small zeolite pores. The active matrix precracks heavy feed molecules for further cracking at the internal zeolite sites. The result is a synergistic interaction between matrix and zeolite in which the activity attained by their combined effects can be greater than the sum of their individual effects.

An active matrix can also serve as a trap to catch some of the vanadium and basic nitrogen. The high boiling point fraction of the FCC feed usually contains metals and basic nitrogen that poison the zeolite. One of the advantages of an active matrix is that it guards the zeolite from becoming deactivated prematurely by these impurities.

2.2.1.3 Filler and Binder

The filler is a clay incorporated into the catalyst to dilute its activity. Kaolin [$Al_2Si_2O_5(OH)_4$] is the most common clay used in the FCC catalyst. One FCC catalyst manufacturer uses kaolin clay as a skeleton to grow the zeolite in situ.

The binder serves as a glue to hold the zeolite, the matrix, and the filler together. Binder may or may not have catalytic activity. The important of the binder becomes more prominent with catalytics that contain high concentrations of zeolite.

The functions of the filler and the binder are to provide physical integrity (density, attrition resistance, particle size distribution, etc.), a heat transfer medium, and a fluidizing medium in which the more important and expensive zeolite component is incorporated.

2.2.2 Fresh Catalyst Properties

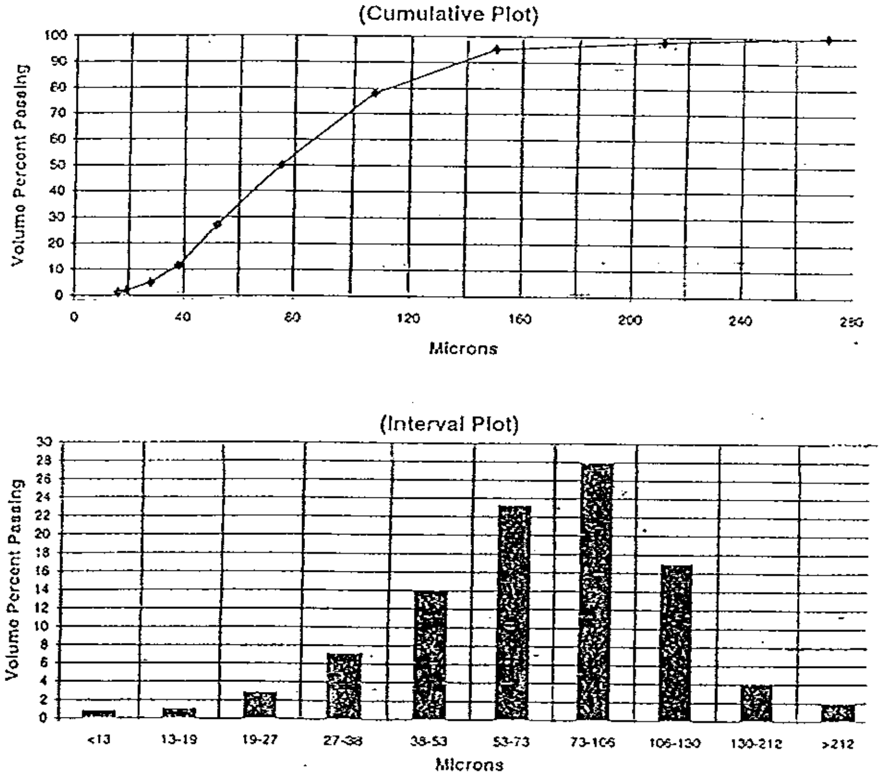
With each shipment of fresh catalyst, the catalyst suppliers typically mail refiner an inspection report that contains data on the catalyst's physical and chemical properties. This data is valuable and should be monitored closely to ensure that the catalyst received meets the agreed specifications. A number of refiners independently analyze random samples of the fresh catalyst to confrim the reported properties. In addition, quarterly review of the fresh catalyst properties with the catalyst vendor will ensure that the control targets are being achieved. The particle size distribution (PSD), the sodium (Na), the rare earth (RE), and the surface area (SA) are some of the parameters in the inspection sheet that require close attention.

Partical Size Distribution (PSD)

The PSD is an indicator of the fluidization properties of the catalyst. In general, fluidization improves as the fraction of the 0-40 micron particles is increased; however, a higher percentage of 0-40 micron particles will also result in greater catalyst losses.

The fluidization characteristics of an FCC catalyst depend largely on the mechanical configuration of the unit. The percentage of less than 40 microns in the circulating inventory is a function of cyclone efficiency. In units with good catalyst circulation, it may be economical to minimize the fraction of less than 40 micron particles. This is because after a few cycles, most of the 0-40 microns will escape the unit via the cyclones.

The catalyst manufacturers control PSD of the fresh catalyst mainly through the spray-drying cycle. In the spray dryer, the catalyst slurry must be atomized effectively to achieve proper distribution. As illustrated in Figure 2-10, The PSD does not have a normal distribution shape. The average particle size (APS) is not actually the average size of the catalyst particles but rather the median value.



Figture 2-10 Particle size distribution of a typical FCC catalyst.

From: Sadeghbeigi, R., 1995: 96

Surface Area (SA), M^2/g

The reported surface area is the combined surface area of zeolite and matrix. In zeolite manufacturing, the measurement of the zeolite surface area is one of the procedures used by catalyst suppliers to control quality. The surface area is commonly determined by the amount of nitrogen adsorbed by the catalyst.

The surface area correlates fairly well with the fresh catalyst activity. Upon request, catalyst suppliers can also report the zeolite surface area. This data is useful in that it is proportional to the zeolite content of the catalyst.

Sodium (Na), wt%

Sodium plays an intrinsic part in the manufacturing of FCC catalysts. Its detrimental effects are well known, and because it deactivates the zeolite and reduces the gasoline octane, every effort should be made to minimize the amount of sodium in the fresh catalyst. The catalyst inspection sheet expressed sodium or soda (Na_2O) as the weight percent on the catalyst. When comparing different grades of catalysts, it is more practical to express the sodium content on the zeolite.

Rare Earth (RE),wt%

Rare earth is a generic name for 14 metallic elements of the lanthanide series. These elements have similar chemical properties and are usually supplied as a mixture of oxides extracted from ores such as bastnaesite or monazite.

Rare earth improves the catalyst activity (Fig.2-11) and hydrothermal stability. Catalyst can have a wide range of rare earth levels depending on the refiner's objectives. Similar to sodium, the inspection sheet shows rare earth (RE) or rare earth oxide (RE_2O_3) as the weight percent on the catalyst. Again, when comparing different catalysts, the concentration of RE on the zeolite should be used.

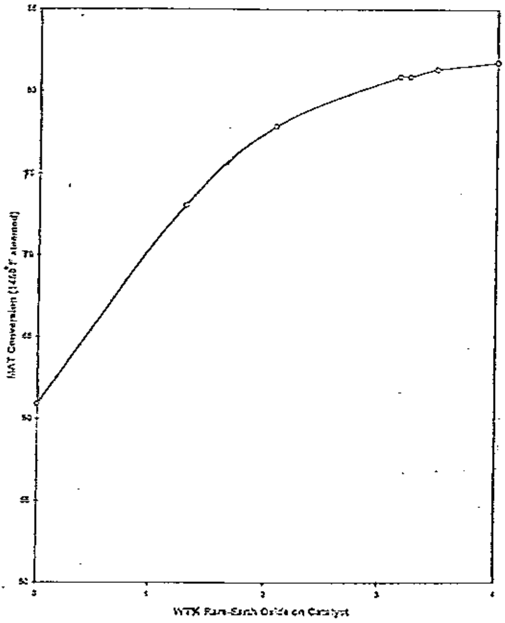


Figure 2-11 Effect of rare earth on catalyst activity.

From: Pine, L.A., Maher, P.J. and Wachter,W.A., 1984: 98

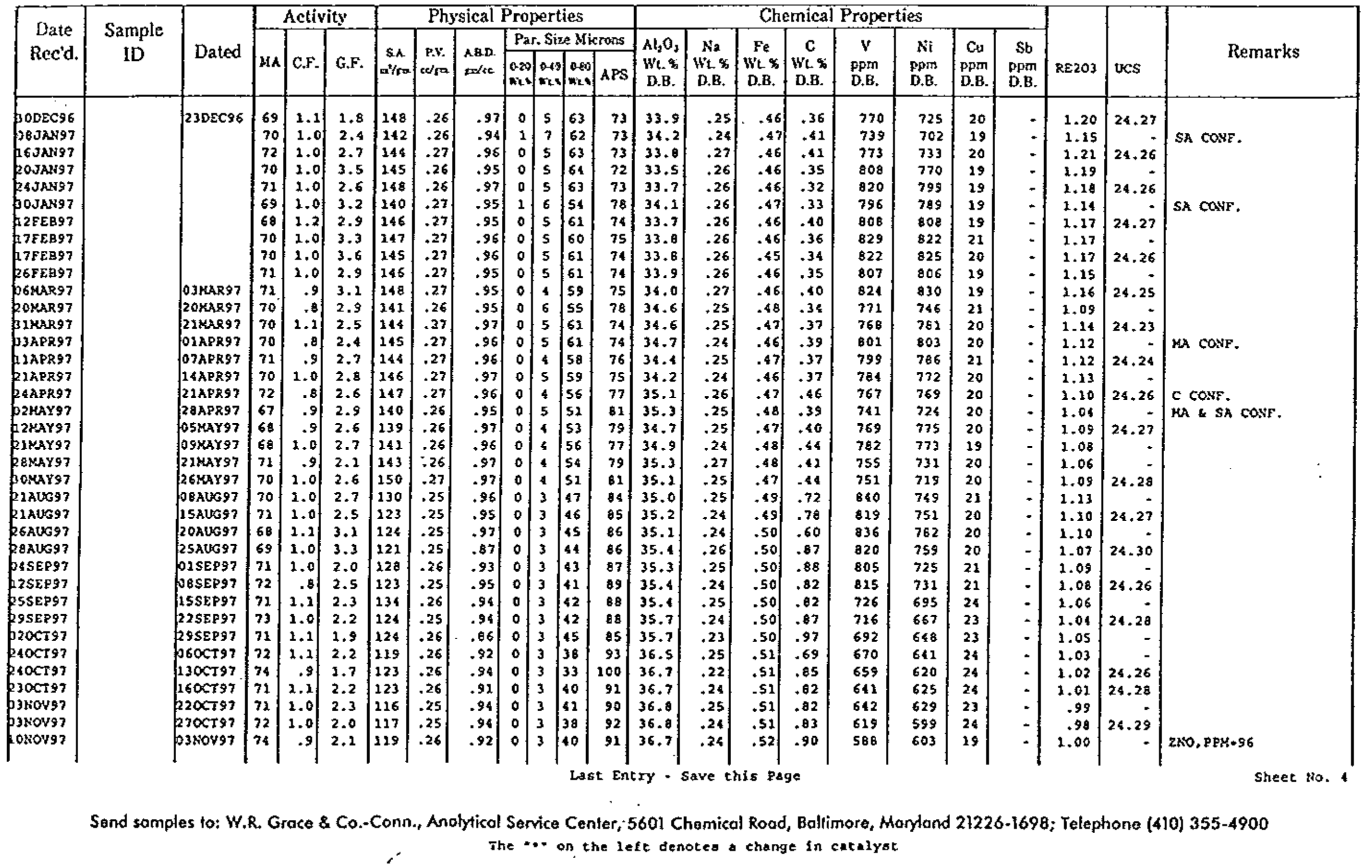
2.2.3 Equilibrium Catalyst Analysis

In cracking catalyst manufacturers routinely test equilibrium FCC catalyst samples from their customers. These tests generate a great deal of data which, when properly understood, can be very useful to the refinery FCCU operator.

The equilibrium catalyst report is one of the ways catalyst manufactures and refiners can work together to optimize the operations of cat crackers. Each item in the report can provide valuable information to help better understand the operations of the cat cracker. Better understanding then leads to better operations.

Catalyst reports are most useful as a trend indicator. When changes in catalyst properties are detected, the FCC management is alerted to look for the cause of the change and if necessary to modify the operation to return to more normal conditions.

In some case the refiner will be able to get two or more catalyst makers to test his equilibrium catalysts. In such a case, the refiner should not expect the absolute values from the two laboratories to agree - they probably would not. In many instances the values reported depend upon the testing techniques used and there is no standardization of techniques among the catalyst makers. What the refiner should look for is that the two reports show the same trend. Since all catalyst data have some variability associated with them (due both to sampling variability and to testing variability). If the results from both laboratories show the same trend, it is very likely that the reported change represents a real shift in catalyst properties.



Date Rec'd.	Sample ID	Dated	Activity			Physical Properties							Chemical Properties								RE203	UCS	Remarks
			MA	C.F.	G.F.	S.A. m²/gm	P.V. cc/gm	A.B.D. gm/cc	Par. Size Microns 0-20 Wt.%	0-40 Wt.%	0-80 Wt.%	APS	Al_2O_3 Wt.% D.B.	Na Wt.% D.B.	Fe Wt.% D.B.	C Wt.% D.B.	V ppm D.B.	Ni ppm D.B.	Cu ppm D.B.	Sb ppm D.B.			
30DEC96		23DEC96	69	1.1	1.8	148	.26	.97	0	5	63	73	33.9	.25	.46	.36	770	725	20	-	1.20	24.27	
08JAN97			70	1.0	2.4	142	.26	.94	1	7	62	73	34.2	.24	.47	.41	739	702	19	-	1.15	-	SA CONF.
16JAN97			72	1.0	2.7	144	.27	.96	0	5	63	73	33.8	.27	.46	.41	773	733	20	-	1.21	24.26	
20JAN97			70	1.0	3.5	145	.26	.95	0	5	64	72	33.5	.26	.46	.35	808	770	19	-	1.19	-	
24JAN97			71	1.0	2.6	148	.26	.97	0	5	63	73	33.7	.26	.46	.32	820	799	19	-	1.18	24.26	
30JAN97			69	1.0	3.2	140	.27	.95	1	6	54	78	34.1	.26	.47	.33	796	789	19	-	1.14	-	SA CONF.
12FEB97			68	1.2	2.9	146	.27	.95	0	5	61	74	33.7	.26	.46	.40	808	808	19	-	1.17	24.27	
17FEB97			70	1.0	3.3	147	.27	.96	0	5	60	75	33.8	.26	.46	.36	829	822	21	-	1.17	-	
17FEB97			70	1.0	3.6	145	.27	.96	0	5	61	74	33.8	.26	.45	.34	822	825	20	-	1.17	24.26	
26FEB97			71	1.0	2.9	146	.27	.95	0	5	61	74	33.9	.26	.46	.35	807	806	19	-	1.15	-	
06MAR97		03MAR97	71	.9	3.1	148	.27	.95	0	4	59	75	34.0	.27	.46	.40	824	830	19	-	1.16	24.25	
20MAR97		20MAR97	70	.8	2.9	141	.26	.95	0	6	55	78	34.6	.25	.48	.34	771	746	21	-	1.09	-	
31MAR97		21MAR97	70	1.1	2.5	144	.37	.97	0	5	61	74	34.6	.25	.47	.37	768	761	20	-	1.14	24.23	
03APR97		01APR97	70	.8	2.4	145	.27	.96	0	5	61	74	34.7	.24	.46	.39	801	803	20	-	1.12	-	MA CONF.
11APR97		07APR97	71	.9	2.7	144	.27	.96	0	4	58	76	34.4	.25	.47	.37	799	786	21	-	1.12	24.24	
21APR97		14APR97	70	1.0	2.8	146	.27	.97	0	5	59	75	34.2	.24	.46	.37	784	772	20	-	1.13	-	
24APR97		21APR97	72	.8	2.6	147	.27	.96	0	4	56	77	35.1	.26	.47	.46	767	769	20	-	1.10	24.26	C CONF.
02MAY97		28APR97	67	.9	2.9	140	.26	.95	0	5	51	81	35.3	.25	.48	.39	741	724	20	-	1.04	-	MA & SA CONF.
12MAY97		05MAY97	68	.9	2.6	139	.26	.97	0	4	53	79	34.7	.25	.47	.40	769	775	20	-	1.09	24.27	
21MAY97		09MAY97	68	1.0	2.7	141	.26	.96	0	4	56	77	34.9	.24	.48	.44	782	773	19	-	1.08	-	
28MAY97		21MAY97	71	.9	2.1	143	.26	.97	0	4	54	79	35.3	.27	.48	.41	755	731	20	-	1.06	-	
30MAY97		26MAY97	70	1.0	2.6	150	.27	.97	0	4	51	81	35.1	.25	.47	.44	751	719	20	-	1.09	24.28	
21AUG97		08AUG97	70	1.0	2.7	130	.25	.96	0	3	47	84	35.0	.25	.49	.72	840	749	21	-	1.13	-	
21AUG97		15AUG97	71	1.0	2.5	123	.25	.95	0	3	46	85	35.2	.24	.49	.78	819	751	20	-	1.10	24.27	
26AUG97		20AUG97	68	1.1	3.1	124	.25	.97	0	3	45	86	35.1	.24	.50	.60	836	762	20	-	1.10	-	
28AUG97		25AUG97	69	1.0	3.3	121	.25	.87	0	3	44	86	35.4	.26	.50	.87	820	759	20	-	1.07	24.30	
04SEP97		01SEP97	71	1.0	2.0	128	.26	.93	0	3	43	87	35.3	.25	.50	.88	805	725	21	-	1.09	-	
12SEP97		08SEP97	72	.8	2.5	123	.25	.95	0	3	41	89	35.4	.24	.50	.82	815	731	21	-	1.08	24.26	
25SEP97		15SEP97	71	1.1	2.3	134	.26	.94	0	3	42	88	35.4	.25	.50	.82	726	695	24	-	1.06	-	
29SEP97		22SEP97	73	1.0	2.2	124	.25	.94	0	3	42	88	35.7	.24	.50	.87	716	667	23	-	1.04	24.28	
02OCT97		29SEP97	71	1.1	1.9	124	.26	.86	0	3	45	85	35.7	.23	.50	.97	692	648	23	-	1.05	-	
24OCT97		06OCT97	72	1.1	2.2	119	.26	.92	0	3	38	93	36.5	.25	.51	.69	670	641	24	-	1.03	-	
24OCT97		13OCT97	74	.9	1.7	123	.26	.94	0	3	33	100	36.7	.22	.51	.85	659	620	24	-	1.02	24.26	
23OCT97		16OCT97	71	1.1	2.2	123	.26	.91	0	3	40	91	36.7	.24	.51	.82	641	625	24	-	1.01	24.28	
03NOV97		22OCT97	71	1.0	2.3	116	.25	.94	0	3	41	90	36.8	.25	.51	.82	642	629	23	-	.99	-	
03NOV97		27OCT97	72	1.0	2.0	117	.25	.94	0	3	38	92	36.8	.24	.51	.83	619	599	24	-	.98	24.29	
10NOV97		03NOV97	74	.9	2.1	119	.26	.92	0	3	40	91	36.7	.24	.52	.90	588	603	19	-	1.00	-	ZNO,PPM=96

Last Entry - Save this Page

Sheet No. 4

Send samples to: W.R. Grace & Co.-Conn., Analytical Service Center, 5601 Chemical Road, Baltimore, Maryland 21226-1698; Telephone (410) 355-4900

The "*" on the left denotes a change in catalyst

Table 2-2 Typical equilibrium catalyst (E-cat) analysis

From : Thai Oil Refinery report ,1997

A typical report is shown in Table 2-2. The results concern 1.catalytic properties(MAT results) 2.physical properties and 3.chemical analysis.

2.2.3.1 Catalytic Properties

Catalytic properties are determined by a micro-activity test (MAT). A sample of the decoked equilibrium catalyst is placed in a laboratory reactor, a typical FCC feed is passed over the catalyst at cracking conditions and the results analyzed.

Table 2-3 Example of microactivity test (MAT) conditions.

From: Upson., L. L. 1981(b):254

Catalyst quantity, g		4.0
Feed quantity, g		1.3
Cat/oil ratio		3.0
Reaction time, sec		75
Space velocity(WHSV),hr^{-1}		15
Reactor temperature, °C		482(900°F)
Feed(ASTM standard feed)	**°C**	**°F**
Boiling point		
Initial	198	388
5 vol%	262	504
50vol%	412	773
95%	552	1025
Final	572	1061
Sulfur, wt%	0.64	
Rams carbon, wt%	0.21	
UOP"K"	12.0	

Activity.

The value reported as activity is the conversion achieved in the MAT laboratory test. Since this conversion is obtained on a decoked sample at standard test conditions, any change in activity is due to catalyst changes.

In commercial operations it is sometimes difficult to determine the reason for a change in unit conversion. It can be due to change in processing conditions, change in feed quality, or change in catalyst characteristics. The MAT activity data allows the refiner to separate the catalyst effect from the process and feed effect when he evaluates unit performance.

In Katalistiks Laboratory (Upson, L.L., 1981) they run each sample in duplicate and sometime in triplicate. The 95% confidence level of their MAT activity value is still ± 1.5 numbers. Thus it always takes at least two consecutive samples to establish confidence that the activity changes represent a real trend.

A change in catalyst activity should produce a corresponding change in the conversion of the commercial unit, providing such thing as reactor temperature and feed quality remain constant. Normally unit conversion will not change as much as the MAT activtiy value changes. As general rule, the expected change in unit conversion will be about 80-90% of change in MAT activity. Yet many factors can influence the MAT activity value.

- Catalyst makeup rate :For a typical unit with an average catalyst makeup rate of 1% per day, doubling the catalyst makeup rate would be expected to increase the MAT activity value 4-6 numbers.

- Metal contamination: Feed metal contamination reduces catalyst activity. A typical example of the effect of metals is shown in table 2-4. A total metals level of less than 1000 ppm has very little effect upon equilibrium catalyst activity. Activity then begins to drop off rapidly as the metals level exceeds 2000 ppm.

Table 2-4 Equilibrium catalyst, metal and activity

From: Upson, L.L, 1981(a) :2-3

Ni+V total ppm	**Activity, MAT**
400	70
2500	68
7000	60

- Catalyst poisoning: By other contaminations, particularly sodium, can cause significant loss in activity. Sodium acts as a fluxing agent for alumina, reducing the melting point of the catalyst structure. Normal regenerator temperatures are then sufficiently high to melt the contaminated part of the catalyst, destroying both sieve and matrix.

Hydrothermal deactivation: Regenerator can reduce catalyst activity by the combined action of steam and high temperature. This process is known as hydrothermal deactivation

Catalyst Selectivity

Catalytic selectivity normally shown in the form of a Coke Factor (CF) ,a Gas Factor(GF), and a H_2/CH_4. The CF and GF represent the coke- and gas -forming tendencies of an E-cat compared to a standard steam-aged catalyst sample at the same conversion. The CF and GF are influenced by the type of fresh catalyst and the level of metals deposited on the E-cat. Both the coke and gas factors can be indicative of the dehydrogenation activity of the metals on the catalyst. The addition of amorphous alumina to the catalyst will tend to increase the nonselective cracking which forms coke and gas.

2.2.3.2 Physical Properties

Partical Size Distribution (PSD)

Particle size data provide information about (1) the circulating characteristics of the catalyst. (2) the cyclone performance and (3) the attrition characteristics of the system.

Good catalyst circulation is achieved in an FCCU when the circulating catalyst has a broad partical size distribution. There should be a significant amount of catalyst having a particle size <40μ and a significant amount >100 μ. If these fractions become small, circulating problems will occur. Each unit has its own characteristics. Some units run well with 3-5% in the < 40μ while other units required 10-15% of this fraction.

Surface Area (SA), m^2/g

For an identical fresh catalyst, the surface area of an E-cat is an indirect measurement of its activity. The SA is the sum of zeolite and matrix surface areas.

Hydrothermal condition in the cat cracker destroy the zeolite cage structure and thus reduce its surface area. They also dealuminate the zeolite framework. Hydrothermal treatment has less effect on the matrix surface area, but the matrix surface area is affected by the collapse of small pores to become larger pores.

Apparent Bulk Density (ABD), g/cc

Bulk density can be used to troubleshoot catalyst flow problems. A too-high ABD can restrict fluidization, and a too-low ABD can result in excessive catalyst loss. Normally, the ABD of the equilibrium catalyst is higher than the fresh catalyst ABD due to thermal and hydrothermal changes in pore structure that occur in the unit.

Pore Volume (PV), cc/g

Pore volume is an indication of the quantity of voids in the catalyst particles and can be a clue in detecting the type of catalyst deactivation that take place in a commercial unit. Hydrothermal deactivation has very little effect on pore volume, whereas thermal deactivation decreases pore volume.

Pore Diameter (Å)

The average pore diameter (APD) of a catalyst can be calculated from the E-cat analysis sheet by using the following equation:

$$\text{APD(Å)} = \frac{PV x 4 x 10{,}000}{SA}$$

2.2.3.3 Chemical Properties

The key elements that characterize chemical composition of the catalyst are alumina, sodium, metals and carbon on the regenerated catalyst.

Alumina (Al_2O_3)

The alumina content of the E-cat is the total weight percent of alumina (active and inactive) in the bulk catalyst. The alumina content of the E-cat is directly related to the alumina content of the fresh catalyst. When changing catalyst grades, the alumina level of the E-cat is often used to determine the percent of new catalyst in the unit.

Sodium (Na)

The sodium in the E-cat is the sum of sodium added with the feed and sodium on fresh catalyst. A number of catalyst suppliers report sodium as soda (Na_2O). Sodium deactivates the catalyst acid sites and cause collapse of the zeolite crystal structure. Sodium in the cracker feed (<20%) normally is deposited on the catalyst. Sodium levels in the feed of 1-2 ppm are normal and present no problems to catalyst.

Metals

The deposition of contaminant metals on the catalyst cause a loose of catalyst activity and selectivity. Nickel, copper, vanadium, and iron are all catalysts themselves, they are particularly effective in catalyzing hydrogenation and dehydrogenation reactions and they have some cracking activity. Such reactions are also catalyzed in the cat cracker by these metals, resulting in an increase in hydrogen, olefins, coke and light hydrocarbons with a decrease in gasoline yield.

Nickel, copper and vanadium come from high molecular weight organo-metallic compounds in the cracker feed.

Only a portions of the iron came in with the feed as an organo-iron compound. This iron, when deposited upon the equilibrium catalyst, is catalytically active. The major portion of the iron on the catalyst have originated from metal scale from the equipment and from the catalyst itself. This iron is not catalytically active.

Metals content of the equilibrium catalyst can be determined fairly accurately by conducting a metals balance around the unit.

$$\text{Metals}_{in} - \text{Metals}_{out} \quad = \text{Metals Accumulated}$$

This is a first order differential equation. Its solution is:

$$M_e \quad = A + [M_0 - A] \exp [(C_a x t) / I]$$

Where:

M_e = E-cat metals content, ppm

A = $(W \times M_f)/C_a$

W = Feed rate, lb/day

M_f = Feed Metals ,ppm

C_a = Catalyst Addition Rate, lb/day

M_o = Initial Metals on the E-cat, ppm

t = Time, day

I = Catalyst Inventory, lb

At steady state, the concentration of any metal on catalyst is:

$$M_e = A = \frac{W x M_f}{C_a}$$

$$M_e = \frac{\frac{141.5}{131.5^o API_{feed}} x350.4xM_f}{B}$$

B = Catalyst Addition Rate, pounds of catalyst per barrel of feed

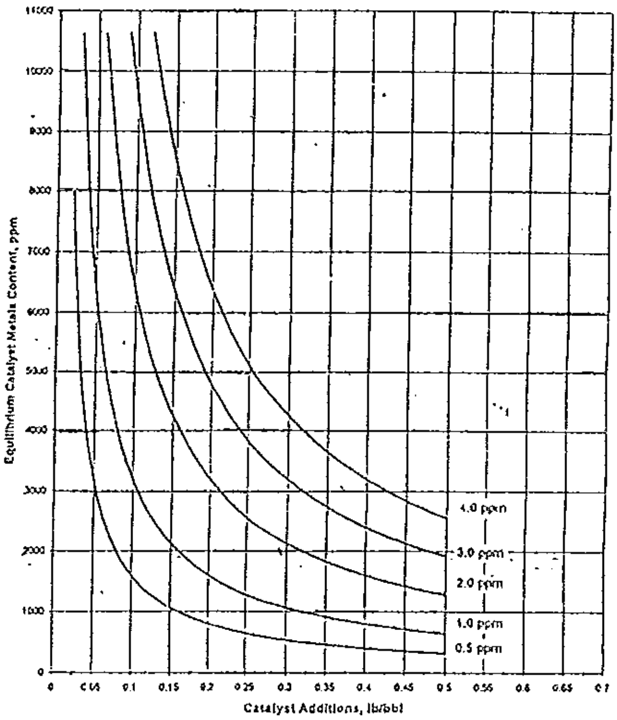


Figure 2-12 Catalyst metals content versus catalyst addition rate.

From: Sadeghbeigi, R., 1995: 107

Carbon(C)

The deposition of carbon on the E-cat during cracking will temporarily block some of the catalytic sites. Then will lower the catalyst activity. It has been report that increase 0.1 wt% of carbon on regenerated catalyst (CRC) will results 3% decrease in unit conversion (Jaras, S.,1980 quoting in Upson, L.L., 1981(b)).CRC is an indicator of regenerator performance. If the CRC shows signs of increasing, this could reveal malfunction of the regenerator's air/spent catalyst distributors. When a CO combustion promoter is used, the CRC value is generally in the range 0.05-0.15 wt%. When no promoter is used, the CRC is normally in the range 0.25-0.40 wt%.

2.3 FCC Feed Characterization (Sadeghbeigi, R., 1995)

Refiners are faced with processing many different types of crude oil. As market conditions and crude quality fluctuate, so do cat cracking feedstock properties. Feed characterization is the process of determining physical and chemical properties of the feed. Two feeds with similar boiling point ranges may exhibit dramatic differences in cracking performances and product yields. Because of these variable conditions, often the only constant in FCC operations is the continual change in the feedstock quality.

FCC feed characterization is one of the most important requirements of cat cracking. Understanding feed properties and knowing their impact on unit performance are essential in anything that has to do with FCC operations, including troubleshooting, catalyst selection, unit optimization, and subsequent process evaluation. Feed characterization is a means of relating feed quality to product yields and qualities. Knowing the effects of a feedstock on unit yields, a refiner can purchase the feedstock that would maximize profitability.

2.3.1 Hydrocarbon Classification

The hydrocarbon types in the FCC feed are broadly classified as paraffins, olefins, naphthenes, and aromatics (PONA).

2.3.1.1 Paraffins

Paraffins are straight or branched chain hydrocarbons having the chemical formula C_nH_{2n+2}. The name of each member end with *-ane*;

In general, FCC feeds are predominantly paraffinic. The paraffin content is typically between 50 wt% and 65 wt% of the total feed. Paraffinic stock are easy to crack.

2.3.1.2 Olefins

Olefins are unsaturated compounds with a formula of C_nH_{2n}. Compared to paraffins, olefins are unstable and can react with themselves or with other compounds such as oxygen and bromine solution.

Olefins are not the preferred feedstocks to an FCC unit. They usually crack to form undesirable products, such as slurry and coke. Typical olefin content of FCC feed is less than 5 wt. %

2.3.1.3 Naphthenes

Naphthenes (C_nH_{2n}) have the same formula as olefins, but their characters are significantly different. Unlike olefins that are straight-chain compounds, naphthenes are paraffins that have been " bent" into a ring or a cyclic shape. Naphthenes, like paraffins, are saturated compounds.

Naphthenes are desirable FCC feedstocks because they produce high-octane gasoline. The gasoline derived from the cracking of naphthenes has more aromatics and is heavier than the gasoline produced from the cracking of paraffins.

2.3.1.4 Aromatics

Aromatics (C_nH_{2n-6}) are similar to naphthenes, but they contain a stabilized unsaturated ring core. Aromatics are compounds that contain at least one benzene ring. The benzene ring is very stable and does not crack to smaller components. Aromatics are not preferable as FCC feedstocks because most of the molecules will not crack. The cracking of aromatics mainly involves breaking off the side chains, and this can result in excess fuel gas yield.

2.3.2 Feedstock Physical Properties

To properly characterize an FCC feedstock, one must determine both its chemical and physical properties. Because sophisticated analytical techniques, are not practical in determining the chemical composition of an FCC feedstock, physical properties are often used to provide qualitative measurement to carry out these physical property tests on a routine basis.

2.3.2.1 °API Gravity

The °API gravity measures the lightness or heaviness of a hydrocarbon liquid. The liquid specific gravity (SG) is another common term used in the conversion of volume to weight.

$$\mathrm{SG}\,(60\,^{O}\mathrm{F}) = \frac{141.5}{131.5 + {}^{O}API_{gravity}}$$

$$^{O}\mathrm{API}_{\mathrm{gravity}} = \frac{141.5}{SG\,(\mathrm{at}\,60\,^{O}\mathrm{F})} - 131.5$$

These equations show that the higher the °API gravity, the lighter the liquid sample. In petroleum refining, the measurement of °API gravity is widely practiced for virtually any feed or product stream.

2.3.2.2 Distillation

Boiling point distillation data provide information about the quality and composition of a feed. The feed to the cat cracker in a typical refinery is a blend of gas oils from such refiners purchase outside FCC feedstock to keep the FCC feed rate maximized. Other refiners process varying amounts of residue in their cat crackers. In recent years, the trend has been toward cutting heavier in distillation and adding residue in the from of either atmospheric or vacuum bottoms.

The fractional distillation test conducted in the laboratory involves measuring the temperature of the distilled vapor at the initial boiling point (IBP), as volume percent fractions 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 95 are collected and at end point (EP).

Distillation data provide information about the fractions of feed that boil at less than 650 °F (343 °C) and also the fractions that boil over 900 °F (482 °C). The inclusion of a light virgin feed, the fraction that boils under 650 °F, often results in a greater LCO yield and thus a lower unit conversion than the corresponding heavier fraction. Sources of these fractions are atmospheric gas oil, vacuum light gas oil, and coker light gas oil. The reasons for observing a lower conversion of light virgin feed are as follows:

1. Lower molecular weight means less cracking
2. Light processed stocks are very aromatic
3. Light aromatics have fewer crackable side chains

2.3.2.3 Aniline Point

Aniline is an aromatic amine ($C_6H_5NH_2$) and, when used as a solvent, is selective in aromatic molecules. Aniline is used to determine aromaticity of FCC feedstocks. Aromatics are more soluble in aniline than paraffins and naphthenes. Aniline point (AP) is the minimum temperature for a complete miscibility of equal volumes of aniline and the sample.

The aniline point increases with paraffinicity and decreases with aromaticity. It also increases with molecular weight.

2.3.2.4 Refractive Index

Similar to aniline point, refractive index (RI) also shows how paraffin or aromatic a sample is. The higher the RI, the less crackable the sample.

Both refractive index and aniline point tests are employed to qualitatively measure aromaticity of a stock.

2.3.2.5 Bromine Number and Bromine Index

Both bromine number (ASTM D-1159) and bromine index (ASTM D-2710) are qualitative methods to measure the reactive sites of a sample. Bromine reacts not only with olefin bonds but also with other molecules in the sample that have basic nitrogen and some aromatic sulfur derivatives. Nevertheless, olefins are the most common reactive sites and the bromine number is used to indicate olefinicity of the feed.

2.3.2.6 Viscosity

Measuring viscosity provides information about chemical composition of a substance. As the viscosity of a sample increases, there is an increase in hydrogen content and a decrease in the fraction of aromatics.

Viscosity of an oil is a measurement of its resistance to flow. Although the unit of absolute viscosity is *poise*, its measurement is difficult. Instead, kinematic viscosity is determined by measuring the pressure drop at a given flow through a capillary tube of specific diameter and length. The unit of kinematic viscosity is the *stoke*. However, in general practice, *centistoke* is used. Poise is related to stoke by the equation:

$$\text{Centistock} = \frac{Centipoise}{Density}$$

2.3.2.7 Conradson, Ramsbottom, and Heptane Insoluble

Carbon residue is defined as the carbonaceous resid formed after thermal destruction of a sample. Cat crackers are generally limited in coke burn-off capacity, therefore, the inclusion of residue produces more coke and forces a reduction in FCC throughput. The carbon residue of conventional gas oil feeds are generally less than 0.5%, whereas in feeds containing residue the number could be as high as 15 wt%.

Three popular tests are presently used to measure carbon residue or concarbon of FCC feedstock: Conradson, Ramsbottom, and Heptane Insoluble. Each test has some advantages and disadvantages, but none of them provide a rigorous definition of carbon residue or asphaltenes.

2.3.3 Impurities

In recent years, refiners have been processing heavier crudes because the conversion of these heavy crudes to valuable products provides the refiners with financial benefits. The cat cracker, as the main conversion unit, is designed to handle a variety of feedstocks. Today's FCC feedstock are generally heavier and contain higher levels of nitrogen, sulfur, and metals. These impurities have negative effects on unit performance. Understanding the nature and effects of these contaminants is essential in feed and catalyst selection as well as trouble-shooting of the unit.

2.3.3.1 Nitrogen

Nitrogen in the FCC feed refers to organic nitrogen compounds. The nitrogen content of FCC feed is often reported as basic and total nitrogen.

The word "basic" denotes having the capability of reacting with acids. FCC catalysts have acid sites that these basic nitrogen compounds will neutralize. The result is a temporary loss of catalyst activity and a subsequent drop in unit conversion. In the regenerator, the nitrogen is converted predominantly to nitrogen oxide (NO). The NO leaves the unit with the flue gas. The burning of nitrogen in the regenerator restores the activity of the catalyst.

Directionally, lowering temperature of the feed to the riser will help to reduce the negative effects of nitrogen.

Besides catalyst poisoning, nitrogen in the FCC feed is detrimental to the unit operation in several other areas. First, in the riser some of the nitrogen is converted to ammonia and cyanide (H-CN). Cyanide accelerates the corrosion rate of the FCC gas plant equipment by removing the protective sulfide scale and exposing bare metals to further corrosion. Second, some of the nitrogen compounds will end up in FCC light cycle oxidized and will affect color stability.

Generally speaking heavier crudes contain more nitrogen than the lighter crudes. In addition nitrogen tends to concentrate in the residue portion of the crude.

2.3.3.2 Sulfur

FCC feedstocks contain sulfur in the form of organic-sulfur compounds such as mercaptan, sulfide, and thiophenes.

Although desulfurization is not a main goal of cat cracking operations, approximately 50% of sulfur in the feed are converted to H_2S.

2.3.3.3 Metals

Metals, such as nickel, vanadium, and sodium are present in crude oil. These metals are concentrated in the heavy boiling range of atmospheric or vacuum residue, unless they are carried over with the gas oil by entrainment.

These metals are catalysts themselves and therefore promote some undesirable reactions, such as dehydrogenation and condensation. The results are increased hydrogen and coke yields and lower gasoline yields. Feed that contain more nickel than vanadium tend to be more paraffinic.

Nickel

The nickel promotes dehydrogenation reactions, which remove hydrocarbon molecules. These reactions result in a higher hydrogen and coke, yields. The higher coke content will result in a higher regenerator temperature that lowers the catalyst-to-oil ratio and causes loss of conversion at constant preheat temperature.

Vanadium

Like nickel, vanadium also promotes dehydrogenation reactions. But vanadium contributions to hydrogen yield are anywhere from 25 to 50 percent of those of nickel, and problems due to vanadium are more severe. Unlike nickel, vanadium does not stay on the surface of the catalyst. Instead, vanadium migrates to the inner (zeolite) part of the catalyst and destroys the zeolite frame structure, causing loss of catalyst surface area and activity.

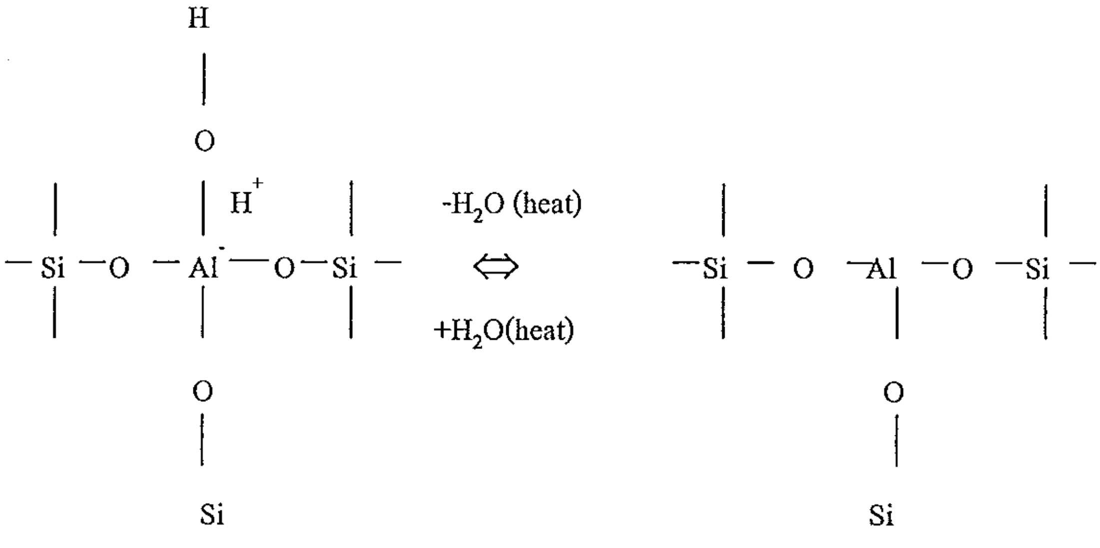
Alkaline Earth Metals

Alkaline earth metals in general and sodium in particular are detrimental to the FCC catalyst. Sodium in the riser permanently deactivates the catalyst by neutralizing its acid sites. In the regenerator, it causes the zeolite to collapse, particularly in the presence of vanadium.

2.4 Catalytic Cracking of Hydrocarbons (Meyers., R.A., 1986 and Satterfield, C. N., 1991)

2.4.1 Acidity of Cracking Catalysts

Catalytic activity occur from acidity of zeolite lattice and forming carbocations of hydrocarbon. Source of acidity are silica-alumina on zeolite lattice,the net negative charge of zeolite must be stabilized by a nearby positive ion such as proton, positive ion produced by the dissociation of water, forming a hydroxyl group on the aluminium atom. The resulting structure, in which the aluminium and the silicon are both tetrahedrally coordinated, is a Bronsted acid. If this structure is heated, water of constitution is driven off and Bronsted acid sites are converted to Lewis acid sites



B-acid

L-acid

B-acid $\xrightarrow{\text{heat,}-H_2O}$ L-acid

L-acid $\xrightarrow{\text{heat,}+H_2O}$ B-acid

Bronsted acid A substance that can donate a hydrogen ion (H^+) to a base.

Lewis acid A substance that can accept a pair of electrons.

2.4.2 Carbocations

Carbocations are positively charged organic species, bring the intermediates formed in variety of chemical reaction.

Hydrocarbons → physically adsorbed on the surface of catalysts →capture of surface protons or electron holes (chemisorption) → carbocations → conversion reactions.

Physical Adsorption or Van der Waals Adsorption - Physisorption

1. A relatively low value for the heat of adsorption
2. Readily and completely reversed

Chemical Adsorption - Chemisorption

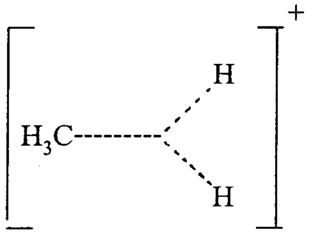
1. Heats of adsorption, an order of magnitude higher than those for physisorption (a chemical bond formed)

2. Reactions between (physisorbed) gas-phase molecules and reactive centers on the surface (active sites)

The terms carbocations is used to call include carbonium and carbenium ion. The definitions of carbonium and carbenium are varies such as

Proposed by Olah see, Olah G.,Angew. (Olah see, Olah G., Angew. Chem. Intl. Ed. Engl., 12, 173,1973)

1. Carbonium ion - The whole thing in the parenthesis with a positive charge outside, which is a five coordinated spicies (penta-coordinated intermediate species)



2. Carbenium ion (Classical carbonium) H_3C^+ - Trivalent state of the carbon atom bearing a positive charge (An sp^2 - hybridized, electron deficient central carbon atom, which in the absence of constraining skeletal rigidity or steric interference, has a planar configulation with an empty p-orbital perpendicular to the plane of the sp^2 bonds.).

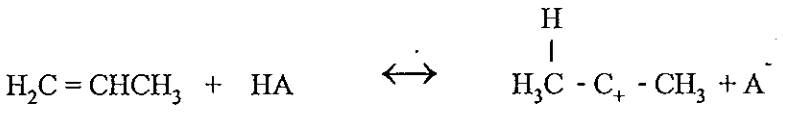
A decision made by International Union of Pure and Applied Chemistry, IUPAC in 1974 (Satterfield, N.C., 1991)

1. Carbonium ion-This term is reserved for a penta-coordinated structure by analogy to "superacids" in homogeneous catalysis.

2. Carbenium ion- Strictly, it is defined as a cation in which the charged atom is carbon.

The Formation of Carbocations.

1. H^+ of the catalyst reacts with unsaturated hydrocarbons (to accept a proton)

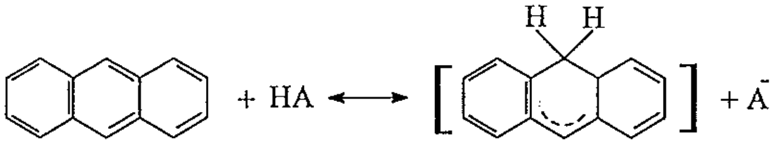


$$H_2C = CHCH_3 + HA \leftrightarrow H_3C - \overset{\overset{H}{|}}{C_+} - CH_3 + A^-$$

(olefins)

(weak base)

Usually the secondary carbocations are formed (not the primary, because the secondary is more stable than the primary).



(aromatics)

(proton acceptor)

2. From a paraffin

A hydride ion (H^-) is adstracted from a paraffin.

$RH + HA \leftrightarrow R^+ + A^- + H_2$ or

B-acid

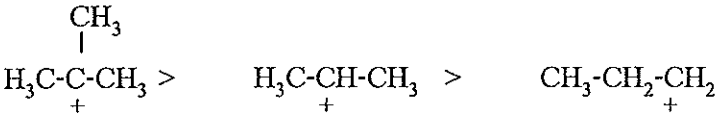
$RH + L \leftrightarrow LH^- + R^+$

L-acid

A new carbocation is formed by a hydride transfer through the interaction of a carbocation with a saturated hydrocarbon.

$$R^{+} + R_1H \longleftrightarrow RH + R_1^{+}$$

The relative stability of carbocation is



$$H_3C\text{-}\overset{\overset{CH_3}{|}}{\underset{+}{C}}\text{-}CH_3 > H_3C\text{-}\underset{+}{C}H\text{-}CH_3 > CH_3\text{-}CH_2\text{-}\underset{+}{C}H_2$$

Tertiary Secondary Primary

2.4.3 Mechanisms of Hydrocarbon Cracking Reactions.

There have been two mechanisms proposed based on the concept of carbocations. The concept was deduced from the theories relating the function of eletrons, bond energy, etc. These theories have long been proven to be correct.

2.4.3.1 Mechanism Involving The Formation of Carbenium Ion Intermediates

1. The intial step (The emergence of carbenium ions)

$$\underset{\text{Olefin}}{R_1\text{-}CH{=}CH\text{-}R_2} + \underset{\text{B-site}}{HA} \rightarrow \underset{\text{Carbenium ion}}{R_1\text{-}CH_2\text{-}\overset{+}{C}H\text{-}R_2 + A^{-}}$$

$$\underset{\text{Paraffin}}{R_1\text{-}CH_2\text{-}CH_2\text{-}R_2} + \underset{\text{L-site}}{L} \rightarrow \underset{\text{Carbenium ion}}{R_1\text{-}CH_2\text{-}\overset{+}{C}H\text{-}R_2 + LH^{-}}$$

2. Propagation step (hydride transfer)

$$\underset{\text{Carbenium ion}}{R_1\text{-}CH_2\text{-}\overset{+}{C}H\text{-}R_2} + \underset{\text{Paraffin}}{R_3\text{-}CH_2\text{-}CH_2\text{-}R_4} \rightarrow \underset{\text{Paraffin}}{R_1\text{-}CH_2\text{-}CH_2\text{-}R_2} + \underset{\text{Carbenium ion}}{R_3\text{-}CH_2\text{-}\overset{+}{C}H\text{-}R_4}$$

The carbenium ion can react with a neutral paraffin molecule via hydride transfer, which in turn undergoes β-scission.

3. Cracking step (β-scission)

$$R_3\text{-}CH_2\text{-}\overset{+}{C}H\text{-}R_4 \xrightarrow{\beta\text{-scission}} CH_2{=}CH\text{-}R_4 + \overset{+}{R_3}$$

Carbenium ion Olefin Carbenium ion

The carbenium ion can also undergo β-scission, C-C bond cleavage at the β-position to the carbon atom carrying the positive charge, is a mono-molecular reaction leading to formation of a smaller olefin and a smaller carbenium ion.

4. Termination of the chain reaction.

The carbenium ion loses a proton to the catalyst and is converted to an olefin

$$CH_3\overset{+}{C}H\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}R \longrightarrow CH_3CH{=}CH\text{-}CH_2\text{-}CH_2\text{-}R + H^+ \text{, or}$$

Carbenium ion Olefin proton

The carbenium ion picks up a hydride ion from a donor (e.g. coke) and is converted to a paraffin.

$$CH_3\overset{+}{C}H\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}R + H^- \longrightarrow CH_3CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}R$$

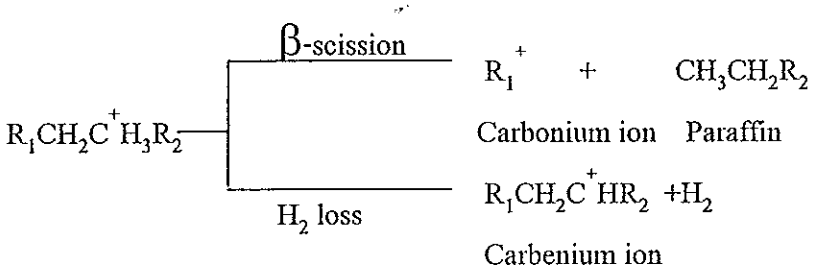
Carbenium ion Hydride ion (from coke) Paraffin

2.4.3.2 Mechanism Assumes The Formation of Penta-Coordinated Carbonium Ions Intermediates

This is a new monomolecular reaction path for paraffin cracking. The reaction takes place at higher temperatures (>500°C) via penta-coordinated carbonium ions intermediates favored by low hydrocarbon partial pressure, as well as by zeolites with high constraint indexes (ZSM-5)

$$R_1CH_2CH_2R_2 + HA \leftrightarrow R_1CH_2\overset{+}{C}H_3R_2 + A^-$$

Paraffin B-acid site Carbonium ion



$$R_1CH_2\overset{+}{C}H_3R_2 \xrightarrow{\beta\text{-scission}} \overset{+}{R_1} + CH_3CH_2R_2$$

Carbonium ion Paraffin

$$R_1CH_2\overset{+}{C}H_3R_2 \xrightarrow[H_2 \text{ loss}]{} R_1CH_2\overset{+}{C}HR_2 + H_2$$

Carbenium ion

2.4.4 Catalytic Cracking Reactions of Hydrocarbons.

2.4.4.1 Paraffins Decomposed to Smaller Paraffins and Olefins.

$$C_{16}H_{34} \leftrightarrow C_8H_{16} + C_8H_{18} \quad ; \quad P's \leftrightarrow O's + P's$$

The produced paraffin (C_8H_{18}) will continue this kind of decomposition (crack) to yield even smaller paraffins and olefins. Larger molecules of paraffins are easier to crack and reaction rate for isoparaffins are higher than normal paraffins.

2.4.4.2 Olefins Decomposition and Other Reactions.

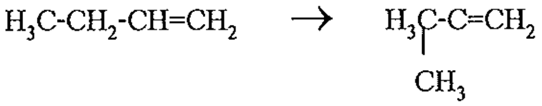
1) Decomposition to two smaller olefins.

$$O's \rightarrow O's + O's$$

Decomposition reaction rate of olefins is much higher than that of paraffins.

2) Isomerization.

2.1 Structural change-skeletal isomerization of molecule



$$H_3C\text{-}CH_2\text{-}CH{=}CH_2 \rightarrow H_3C(CH_3)\text{-}C{=}CH_2$$

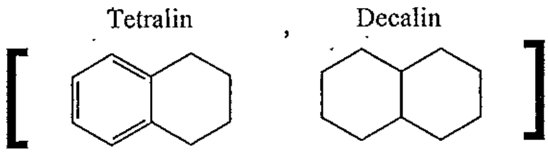
2.2 Double bond shift

$$H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH{=}CH_2 \rightarrow H_3C\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH_3$$

3) Hydrogen transfer

3.1 Naphthene + Olefin → Aromatics + Paraffins

or naphthene-aromatics, like



Hydrogen will transfer from naphthene to olefin

Olefin → Paraffin (saturation)

Naphthene → Polynuclear aromatics........→ coke

3.2 Two olefins → Paraffin + Diene

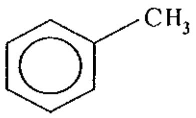
$2C_6H_{12} \rightarrow C_6H_{14} + CH_3CH{=}CH{-}CH{=}CHCH_3$

(hexene) (hexane) (hexadiene)

4) Aromatization - dehydrocyclization.

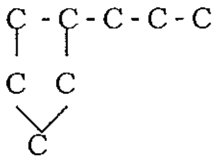
$$\text{Olefin} \xrightarrow[\text{Dehydrogenation}]{\text{Cyclization}} \text{Aromatics}$$

$CH_3CH_2CH_2CH_2CH{=}CHCH_3 \longrightarrow$



2.4.4.3 Naphthenes Cracked to Give Olefins.

- Ring broken to give olefins



$\longrightarrow$ C - C - C -C = C - C - C - C

- The produced olefins then perform reactions as stated aboved.

- The chain attached to the ring also can undergo cracking itself (if the attached chain is longer).

- Isomerization of the 5-ring naphthenes (with a side-hydrocarbon chain attached) to give a 6-ring naphthene.

- Hydrogen transfer

$$\text{5-member ring naphthenes} \xrightarrow{\text{Isomerization}} \text{6-member ring naphthenes}$$

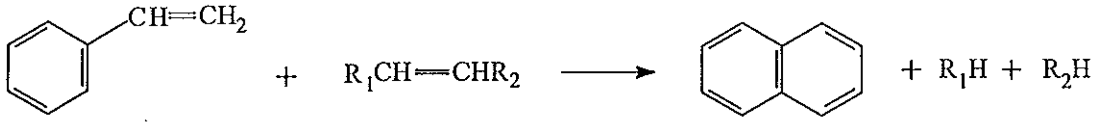
$$\xrightarrow{\text{Dehydrogenation}} \text{Aromatics}$$

- The decomposition rate is higher for naphthenes because the presence of tertiary carbon atom which is similar to the isoparaffins.

2.4.4.4 Aromatics

- The aromatic ring is very stable under catalytic cracking conditions (benzene, naphthalene).

- The rupture of the c-c bond for side-chain attached to the ring is easily broken. The detached side-chain can undergo scission to yield small molecules of olefins, but cracking rate of polynuclear aromatics is rather slow. The main reaction of polynuclear aromatics is condensation which leads to condensed-ring aromatics and eventually to convert to coke while the olefins become saturated by the released hydrogen in the reaction (paraffins)



(Condensation through olefin dehydrocyclization)

The main reactions of paraffins, olefins, naphthenes, and aromatics and their products in catalytic cracking as stated above are summarized in Table2-5 where

P's	=	Paraffins
O's	=	Olefins
N's	=	Naphthenes
A's	=	Aromatics

Table 2-5 Main reactions in catalytic cracking

$$\text{P's} \xrightarrow{\text{Cracking}} \text{P's} + \text{O's}$$

$$\text{O's} \left\{ \begin{array}{l} \xrightarrow{\text{Cracking}} \text{O's} + \text{O's} \\ \xrightarrow{\text{Cyclization}} \text{N's} \\ \xrightarrow{\text{Isomerization}} \text{iso- O's} \xrightarrow{\text{H Transfer}} \text{iso-P's} \\ \xrightarrow{\text{H Transfer}} \text{P's} \\ \xrightarrow[\text{Condensation, Dehydrogenation}]{\text{Cyclization}} \text{Coke} \end{array} \right.$$

$$\text{N's} \left\{ \begin{array}{l} \xrightarrow{\text{Cracking}} \text{O's} \\ \xrightarrow{\text{Dehydrogenation}} \text{Cyclo-O's} \xrightarrow{\text{Dehydrogenation}} \text{A's} \\ \xrightarrow{\text{Isomerization}} \text{N's with different rings} \end{array} \right.$$

$$\text{A's} \left\{ \begin{array}{l} \xrightarrow{\text{Side-chain cracking}} \text{Unsubstituted A's} + \text{O's} \\ \xrightarrow{\text{Tranalkylation}} \text{Different alkyl-A's} \\ \xrightarrow[\text{Condensation}]{\text{Dehydrogenation}} \text{Polyaromatics} \xrightarrow[\text{Condensation, Dehydrogenation}]{\text{Alkylation}} \text{Coke} \end{array} \right.$$

Chapter 3

Experimentation

3.1 Feedstocks and Catalysts

- Feedstocks

In this research, 2 sources of feedstocks were used, the standard gas oil from RIPP (boiling range 235~337 °C) and the redistilled diesel oil from Fang refinery (boiling range 248~339 °C). The diesel oil from Fang refinery is too heavy (boiling range 241~380°C) and not suitable for analysis by column of Gas chromatograph used in this research. Therefore, it was redistilled to remove heavy fraction. Hydrocarbon compounds usually decompose at the temperature about 345 °C (1 atm) and the final boiling point of the experimental feedstock is also in this range. The reduced pressure distillation was performed (see the method in appendix A).

- Catalysts

Catalysts used in this experiment were listed in Table 3-1

3.2 Equipment and Materials

1. Deionized water
2. Ethanol:CH_3CH_2OH
3. Standard normal dodecane (n-$CH_3(CH_2)_{10}CH_3$)
4. Ice bath and glass receiver for liquid product from MAT unit
5. Quartz and Glass wool
6. Rubber tube
7. Porcelain ring
8. Crucible

9. Desiccator
10. Nitrogen gas (OFN Grade, Purity 99.99%for GC and Regular Grade for MAT unit)
11. Hydrogen gas (Regular Grade)
12. Air (Regular Grade)

3.3 Instrumentations

1. Hydrothermal Aging Unit, Model CLY-1 (see appendix A)
2. Microactivity Test (MAT) Unit, Model WFS-1D (see appendix B)
3. Gas Chromatograph (GC-14 BPF, SHIMUSHU) and Integrater (HP3295,Hellet-Packard)
4. Gas Chromatograph-Mass spectrometer, Model Series II plus GC-HP5972 series Mass selective detector, Hellet-Packard
5. Brunauer-Emmett-Teller (BET), Model ASAP 2010
6. X-ray Fluorescence Spectrometer (XRF), Model PW2400, Philips
7. Differential Thermal Analyzer (DTA), Model DTA7, Perkin Elmer
8. Refractometer, Model No.BT25, ATAGO
9. X-Ray Diffractometer (XRD) Model X'Pert-MPD, Type 3040/00NC, Philips
10. Distillation unit
11. Viscometer
12. Balance, Model TOLEDO PB153, Metler

3.4 Test methods and Test Conditions

3.4.1 Microactivity Test Method and Test Condition

Catalyst sample reacted with gas oil in the fix-bed reactor of the Microactivity Test Unit and product oil or syncrude was collected in a glass receiver and thereafter was analyzed by the Gas Chromatograph (see full details of method in appendix C)

Condition of MAT unit

Catalyst loading:	5	g.
Oil weight:	1.56±0.01	g.
Catalyst/Oil	3.2	
Weight hour space velocity (WHSV):	16	hr^{-1}
Feeding rate:	1.337	g/min
Feeding time:	70	sec.
Reactor temperature:	460±1	°C
Purging time:	700	sec.

Liquid produced from MAT unit was then analyzed by the Gas Chromatograph

Condition of Gas Chromatograph (GC)

Column (Pack Column): OV-I (Methylsilocane)

Detector: Flame Ionize Detector (FID)

Carrier Gas: Nitogen (Purity 99.99%,OFN)
flow rate 35-40 ml/min.

Combustion gas: Hydrogen, flow rate 40 ml/min

Auxilliary gas: Air, flow rate 400 ml/min

Temperature of vaporization chamber (injector): 280 °C

Temperature of detector chamber: 280 °C

Temperature of column chamber: raises from 35 °C to 80 °C with a rate of 15 °C /min, then raising from 80 °C to 235 °C with rate of 8 °C /min, hold at 235 °C for 10 min.

Sample injection volume: 1 μl

Catalyst samples and feedstocks which were tested by MAT were listed in Table 3-2

3.4.2 Hydrothermal Treatment Procedure and Test Condition

The fresh catalysts before evaluation by the MAT unit, must be deactivated (normally by high temperature steam aging) to decrease activity of the test catalysts. In this work the deactivation performed by hydrothermal aging unit model CLY-1 manufactured by RIPP (see full details of the equipment in appendix B).

The conditions of hydrothermal treatment were listed in Table 3-3 .

3.4.3 Thermal Treatment Procedures and Test Condition

Hydrothermal aged catalysts (4 hrs.,100% steam, 800 °C) of Gong-Y and Lanet-35 were used to compare the effect of thermal and hydrothermal deactivation. The procedures are as follows,

1. Dried the samples in a furnace at a temperature about 110-120 °C for 1 hr and cooled down in a desiccator;
2. When the temperature of the furnace was 800 °C, place the samples in the furnace for a duration of the desired time before taking them out and cooling down in the desiccator. The conditions of thermal treatment were listed in Table3-4.

3.4.4 Unit Cell Size Determination

Fresh, hydrothermally and thermally treated catalysts were determined for its unit cell size (USC) by a X-ray diffractometer (XRD) according to ASTM D-3942 (see appendix D).

3.4.5 Surface Area Determination

Fresh, hydrothermally and thermally treated catalysts were determined total surface area (SA) by Brunauer-Emmelt-Teller (BET). These results were analyzed by Department of Chemical Engineering, Khonkan University.

Table 3-1 Catalysts used in experiments

Catalyst	Treatment	Source
A	fresh	Thai oil company Ltd., Co.
B	fresh	Thai oil company Ltd., Co.
C	fresh	Thai oil company Ltd., Co.
D	fresh	Thai oil company Ltd., Co.
E	fresh	Thai oil company Ltd., Co.
3A	fresh	RIPP
Gong-Y	fresh	RIPP
Lanet-35	fresh	RIPP
3A	hydrothermal aged(4hrs.100%steam 800 ^{o}C)	RIPP
CRC-1	hydrothermal aged(4hrs.100%steam 800 ^{o}C)	RIPP
F-EQ	Equilibrium catalyst	Thai oil company Ltd., Co.
G-EQ	Equilibrium catalyst	Star petroleum refining
H-EQ	Equilibrium catalyst	RIPP
I-EQ	Equilibrium catalyst	RIPP
CRC-1-EQ	Equilibrium catalyst	RIPP
MZ3-EQ	Equilibrium catalyst	RIPP
OD-EQ	Equilibrium catalyst	RIPP
RHZ-300-EQ	Equilibrium catalyst	RIPP

Table 3-2 Catalysts and feedstocks tested by MAT unit

Catalyst	**Treatment**	**Source of Feedstock**
CRC-1(aged ready from RIPP)	4 hrs., 100%steam 800°C	RIPP
3A (aged ready from RIPP)	4 hrs., 100%steam 800°C	RIPP
3A	4 hrs., 100%steam 800°C	RIPP
A4	4 hrs., 100%steam 800°C	RIPP &Fang
A6	6 hrs., 100%steam 800°C	RIPP &Fang
A8	8 hrs., 100%steam 800°C	RIPP &Fang
A12	12 hrs., 100%steam 800°C	RIPP &Fang
A17	17 hrs., 100%steam 800°C	RIPP &Fang
B4	4 hrs., 100%steam 800°C	RIPP &Fang
B6	6 hrs., 100%steam 800°C	RIPP &Fang
B8	8 hrs., 100%steam 800°C	RIPP &Fang
B12	12 hrs., 100%steam 800°C	RIPP &Fang
B17	17 hrs., 100%steam 800°C	RIPP &Fang
C4	4 hrs., 100%steam 800°C	RIPP &Fang
C6	6 hrs., 100%steam 800°C	RIPP &Fang
C8	8 hrs., 100%steam 800°C	RIPP &Fang
C12	12 hrs., 100%steam 800°C	RIPP &Fang
C17	17 hrs., 100%steam 800°C	RIPP &Fang
D4	4 hrs., 100%steam 800°C	RIPP &Fang
D6	6 hrs., 100%steam 800°C	RIPP &Fang
D8	8 hrs., 100%steam 800°C	RIPP &Fang
D12	12 hrs., 100%steam 800°C	RIPP &Fang
D17	17 hrs., 100%steam 800°C	RIPP &Fang
E4	4 hrs., 100%steam 800°C	RIPP &Fang
E6	6 hrs., 100%steam 800°C	RIPP &Fang
E8	8 hrs., 100%steam 800°C	RIPP &Fang
E12	12 hrs., 100%steam 800°C	RIPP &Fang
E17	17 hrs., 100%steam 800°C	RIPP &Fang

Table3-2 (Continue)

Catalyst	**Treatment**	**Source of Feedstock**
Gong Y(Hy) 4	4 hrs., 100%steam 800°C	RIPP &Fang
Gong Y(Hy)6	6 hrs., 100%steam 800°C	RIPP &Fang
Gong Y(Hy) 8	8 hrs., 100%steam 800°C	RIPP &Fang
Gong Y(Hy) 12	12 hrs., 100%steam 800°C	RIPP &Fang
Gong Y(Hy)16	16 hrs., 100%steam 800°C	RIPP &Fang
Gong Y(T)4	0 hrs., 0%steam 800°C	Fang
Gong Y(T) 6	4 hrs., 0%steam 800°C	Fang
Gong Y(T) 8	6 hrs., 0%steam 800°C	Fang
Gong Y(T)12	8 hrs., 0%steam 800°C	Fang
Gong Y(T) 16	12 hrs., 0%steam 800°C	Fang
Lanet 35(Hy) 4	4 hrs., 100%steam 800°C	RIPP &Fang
Lanet 35(Hy) 6	6 hrs.,100%steam 800°C	RIPP &Fang
Lanet 35(Hy) 8	8 hrs., 100%steam 800°C	RIPP &Fang
Lanet 35(HY) 12	12 hrs., 100%steam 800°C	RIPP &Fang
Lanet 35(HY) 16	16 hrs., 100%steam 800°C	RIPP &Fang
Lanet 35(T) 4	0 hrs., 0%steam 800°C	Fang
Lanet 35(T) 6	4 hrs., 0%steam 800°C	Fang
Lanet 35(T) 8	6 hrs., 0%steam 800°C	Fang
Lanet 35(T) 12	8 hrs., 0%steam 800°C	Fang
Lanet 35(T) 16	12 hrs., 0%steam 800°C	Fang
F-EQ	Equilibrium catalyst	RIPP &Fang
G-EQ	Equilibrium catalyst	RIPP &Fang
H-EQ	Equilibrium catalyst	RIPP &Fang
I-EQ	Equilibrium catalyst	RIPP &Fang
RHZ-300	Equilibrium catalyst	RIPP &Fang
MZ-3-EQ	Equilibrium catalyst	RIPP &Fang
CRC-1-EQ	Equilibrium catalyst	RIPP &Fang

Table3-3 The conditions of hydrothermal treatment

Catalyst	Treatment time(hrs.)	Temperature(°C)	% steam
A4	4	800°C	100
A6	6	800°C	100
A8	8	800°C	100
A12	12	800°C	100
A17	17	800°C	100
B4	4	800°C	100
B6	6	800°C	100
B8	8	800°C	100
B12	12	800°C	100
B17	17	800°C	100
C4	4	800°C	100
C6	6	800°C	100
C8	8	800°C	100
C12	12	800°C	100
C17	17	800°C	100
D4	4	800°C	100
D6	6	800°C	100
D8	8	800°C	100
D12	12	800°C	100
D17	17	800°C	100
E4	4	800°C	100
E6	6	800°C	100
E8	8	800°C	100
E12	12	800°C	100
E17	17	800°C	100
Gong-Y(Hy) 4	4	800°C	100
Gong-Y(Hy) 6	6	800°C	100
Gong-Y(Hy) 8	8	800°C	100
Gong-Y(Hy) 12	12	800°C	100
Gong-Y(Hy) 16	16	800°C	100
Lanet-35(Hy) 4	4	800°C	100
Lanet-35(Hy) 6	6	800°C	100
Lanet-35(Hy) 8	8	800°C	100
Lanet-35(Hy) 12	12	800°C	100
Lanet-35(Hy) 16	16	800°C	100

Table 3-4 The conditions of thermal treatment

Catalyst	**Treatment Time (hrs.)**	**Temperature (^{o}C)**	**Steam (%)**
Gong-Y(T)4	0	-	-
Gong-Y(T)6	2	800	0
Gong-Y(T)8	4	800	0
Gong-Y(T)12	8	800	0
Gong-Y(T)16	12	800	0
Lanet-35(T)4	0	-	-
Lanet-35(T)6	2	800	0
Lanet-35(T)8	4	800	0
Lanet-35(T)12	8	800	0
Lanet-35(T)16	12	800	0

Chapter 4

Results and Discussion

4.1 Preparation of MAT Feedstock from Fang Gas Oil (Diesel Oil)

According to RIPP Method 92-90 Standard method for microactivity test,feedstock for testing of microactivity of FCC catalysts in the laboratory is a type of LGO (a straight-run light gas oil, boiling range 235-337 °C), produced by a refinery in Tianjin (China) originated from Dagang (an oil field near Tianjin) crude and then refined, tesed and characterized by RIPP.

In this work, it is aimed to use Thai LGO for the experiments to determine the difference between Thai and RIPP feedstocks and investigate for the possibility to use Thai LGO as the feedstock for the microactivity testing in the future.

The product diesel oil from Fang Refinery is also a straight-run distillate (VGO, vacuum gas oil, boiling range 241~380 °C). As the end point of its boiling range is 380°C, which heavier than 350°C, the heavy ends would cause loss of function (separation) of GC column, because after catalytic cracking reaction, the heavy-end products would adhere on the surface of the packing-the fixed phase coated with fixed liquid of the GC column.

Therefore, a simplified vacuum distillation unit (see Figure A-1) was installed to redistill the Fang VGO to collect fraction at about the same boiling range as of the RIPP feedstock. The method is to use the GC column of the MAT unit to control the end point of the distillate, This method was proved to be successful as can be seen from the GC chromatograms (Figure 4-1, 4-2) and the analyzed data from the experiments.

Table 4-1 Properties of Fang diesel oil (received from Fang refinery)

Properties	**Results**
Flash point, °C	>110
Viscosity, cst	5.38
Pour point, °C	+20
Gravity, °API @16.5°C	39.4
Color ASTM	1.0
Boiling range, °C	241~380

Table4-2 Properties of RIPP gas oil and Fang gas oil (redistilled)

Properties	**Gas Oil**	
	RIPP	**Fang (redistilled)**
Boiling range, °C	235~337	248~339
Viscosity@40°C, cst	4.0	4.4
Refractive index@20°C	1.470	1.459
Sulfur content, %wt.(XRF)	0.061	0.089
Specific gravity@15.5°C	0.845	0.820
Conradson carbon content,%wt	0.12	0.01
° API gravity@15.5°C	36.6	41.1
Ni, ppm (ICP-MS)	1.04	0.70
V, ppm (ICP-MS)	1.69	1.24

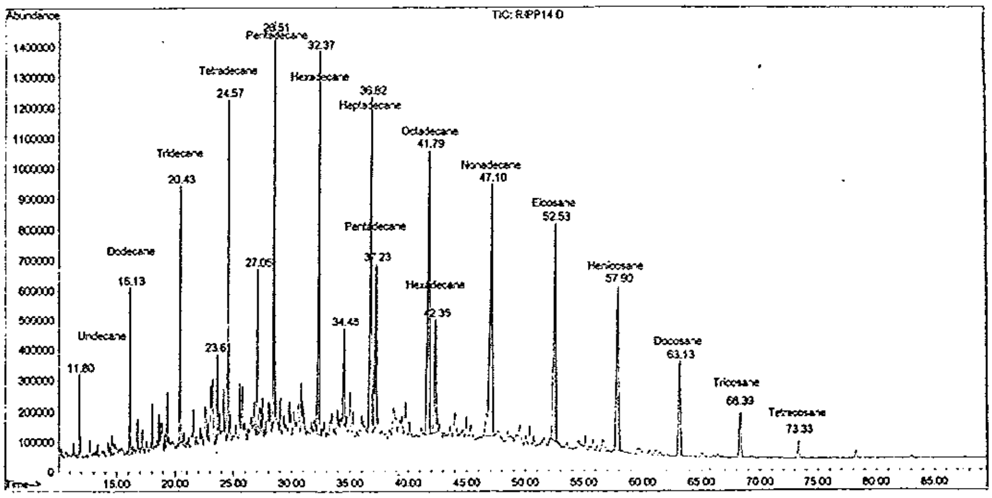


Figure 4-1 Chromatogram of RIPP standard gas oil

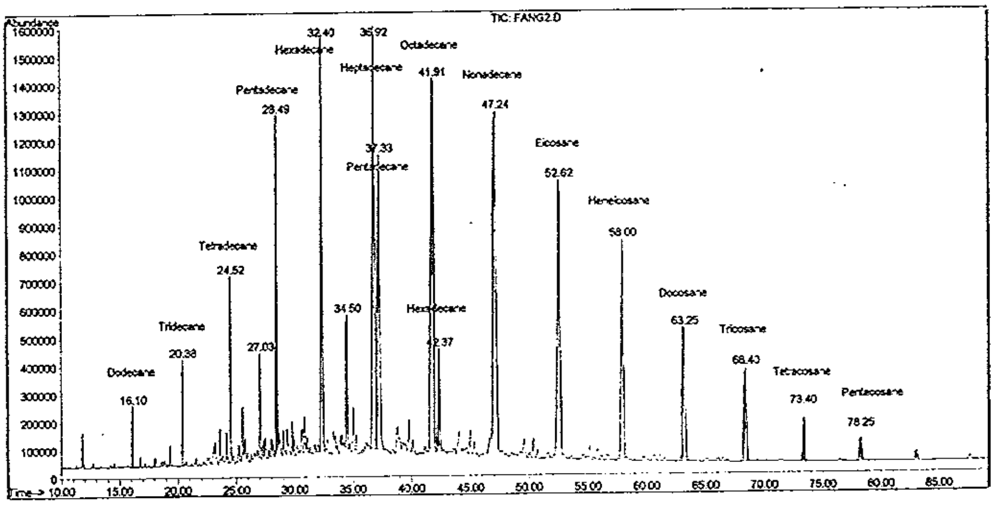


Figure4-2 Chromatogram of Fang gas oil (redistilled)

The boiling range of Fang gas oil is slightly higher than that of the RIPP gas oil. The chromatogram of Fang gas oil gave the first peak at $C_{12}$and final peak at C_{25}. As for RIPP gas oil, the first and final peaks are at C_{11} and C_{24} , respectively

Viscosity of Fang gas oil is a little higher than that of RIPP gas oil. It approved that may be lower in the fraction of aromatic.

Refractive index of Fang gas oil is a little lower than that of RIPP gas oil, This indicates that its aromaticity may be lower.

Sulfur content of Fang gas oil is 0.089 and that of RIPP gas oil is 0.061. Usually, sulfur content plays a minor role in unit conversion and yields but some sulfur in the form of aromatics do not convert to gasoline. It becomes predominantly cycle oil, depending on side-chain length, and also produces fuel gas. This tends to lower conversion and reduces maximum yields.

Specific gravity of Fang gas oil was found to be lighter than that of RIPP gas oil.

From the properties and chromatograms of RIPP and Fang gas oil, we can see that these two are similar

In this work we successfully in redistilled even through there was no existing analysis equipment to help us identify the boiling range of the products and this can be attributed to our scientific thinking.

4.2 Repeatability Tests for MA Measurements

This is to lay the basis of characterizing the measured data to make sure if the differences, if any, are significant (in a mathematical sense) or not.

Through repeated measurements under otherwise identical conditions and data processing, we can make sure that our obtained data reflect only the differences caused by the samples, and this is the purpose for us to do the measurements. So we need to carefully control the test conditions to be very stable and repeatable. The meaning of repeatability tests is to make sure that the sample pretreatments, the fluctuations of test conditions (parameters control like temperature, catalyst loading, reaction time, feed weight, reaction pressure) and the operator's skill are qualified for the testing

The results for repeatability tests are listed in Table4-3

Table 4-3 Repeatability tests of MA measurements

NO.	MA(%wt)	NO.	MA(%wt)
1	65.1	16	66.8
2	66.1	17	67.2
3	66.9	18	67.8
4	65.2	19	65.0
5	67.2	20	64.4
6	66.6	21	68.8
7	66.2	22	65.4
8	68.2	23	68.8
9	66.0	24	67.5
10	65.7	25	65.6
11	66.4	26	68.7
12	73.2	27	64.7
13	68.5	28	70.3
14	67.5	29	67.8
15	67.3	30	66.0
	$\bar{X}$=67±2.0	SD=1.8	

These data are processed by statistical method (near Gaussian distribution, use t-test method) to obtain the MA average of 67, standard deviation of 1.8, and 95% confidence limit (95% C.L.) of 67±2.0

From the data obtained, we can see that the sample treatment and process parameters control are repeatable for measuring catalyst microactivity (MA) of around 60-75 which is the average level of activity in FCC units. And this helps us to rate the microacitvity that if MA difference of two catalysts is within 2.0, then we can say that these two are at the same activity level.(might be a little bit difference, but too small to be detected, so in statistics "not significant")

Some comments with process parameters control of MA measurements

1. Catalysts sample should be dried before doing the experiments;

2. Weight of catalyst is 5.00 g., and the variation not beyond ± 0.01 g, because it would affect the cat/oil ratio;

3. Reactor temperature should be within $460\pm1^{\circ}$C ,it has effect to heat of reaction;

4. Position of thermocouple should be in the middle of the catalyst bed length;

5. The liquid product receiver should be immersed into the ice bath (ice -NaCl mixture to keep the temperature at 0°C);

6. Calibrate the oil injection every day to ensure the average weight does not change and no bubble in the syringe;

7. Sampling technique for GC analysis;

   - Rinse the syringe several times with ethanol and sample;
   - No bubbles in the syringe by withdrawing and injecting the sample many time;
   - When injecting sample, press start botton of GC and the integrator immediately.

4.3 Hydrothermal Treatment Testing

Table4-4 Hydrothermal aging -MA test results, %wt

Catalyst	**Parallel measurements**		**Average**
Cat.3A	**No.1**	**No.2**	
Aged by RIPP	31.64	32.75	32.2
Aged by PSU	33.90	32.63	33.3

This will prove that we can perform the aging treatment at the same severity as RIPP did. So we can compare our data of aging on the same basis with RIPP. Although the above measurements are not the real repeatability test, but they have proved our operation and the test conditions are stable and give us the confidence that these tests are reliable. Indeed, to find the repeatability of the hydrothermal treatments we may need it almost 30 times like MAT testing but we did not have enough fresh catalyst to do like MAT testing.

Some comments with process parameters control of hydrothermal treatment

1. Position of thermocouple should be in the middle of the catalyst bed length;
2. The temperature gradient through the catalyst bed should not exceed 4 °C.

4.4 A Comparison of RIPP and Fang Feedstock for MAT

Gas oil from Fang (redistilled) and RIPP standard gas oil were used to test hydrothermal treated and equilibrium catalysts to compare the results of cracking between these two feedstocks.

The results were listed in Tables 4-5 to 4-6 and Figures 4-3 to 4-9

Table 4-5 Comparison of RIPP and Fang feedstocks for MA (Hydrothermal aging cataylsts)

		MA (%wt) at various treatment times					
Catalyst	**Feedstock**	**4 hrs.**	**6 hrs.**	**8 hrs.**	**12 hrs.**	**16 hrs.**	**17 hrs.**
Gong-Y	RIPP	73	69	67	61	59	-
	Fang	72	64	63	56	55	-
Lanet-35	RIPP	76	64	62	52	45	-
	Fang	77	57	54	44	34	-
A	RIPP	68	63	62	56	-	54
	Fang	68	60	57	52	-	49
B	RIPP	69	64	61	56	-	51
	Fang	68	59	58	53	-	43
C	RIPP	71	62	58	54	-	45
	Fang	71	63	59	51	-	44
D	RIPP	71	69	65	55	-	52
	Fang	69	68	64	52	-	48
E	RIPP	77	68	64	62	-	56
	Fang	77	68	62	59	-	54

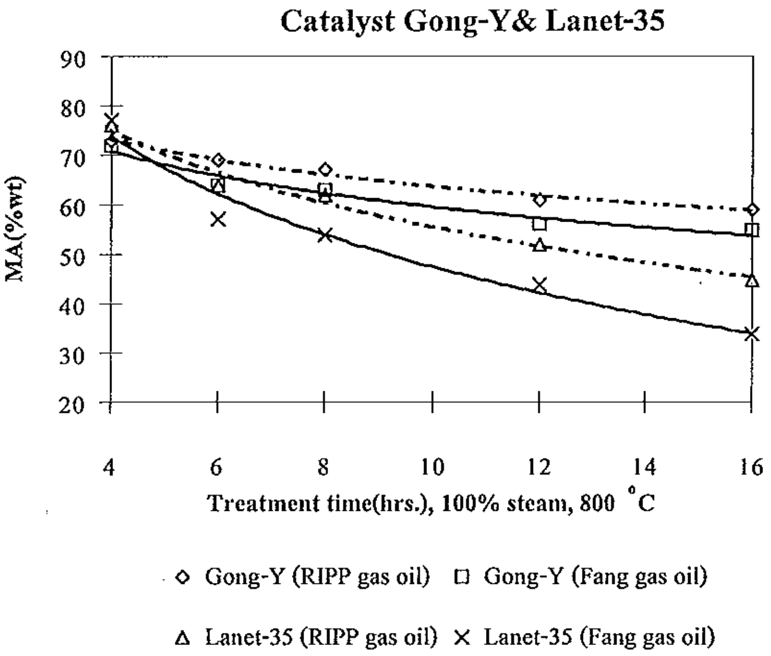


Figure 4-3 Comparison of RIPP and Fang feedstocks for MA for catalyst Gong-Y and Lanet-35 (- - -for RIPP gas oil, ----- for Fang gas oil)

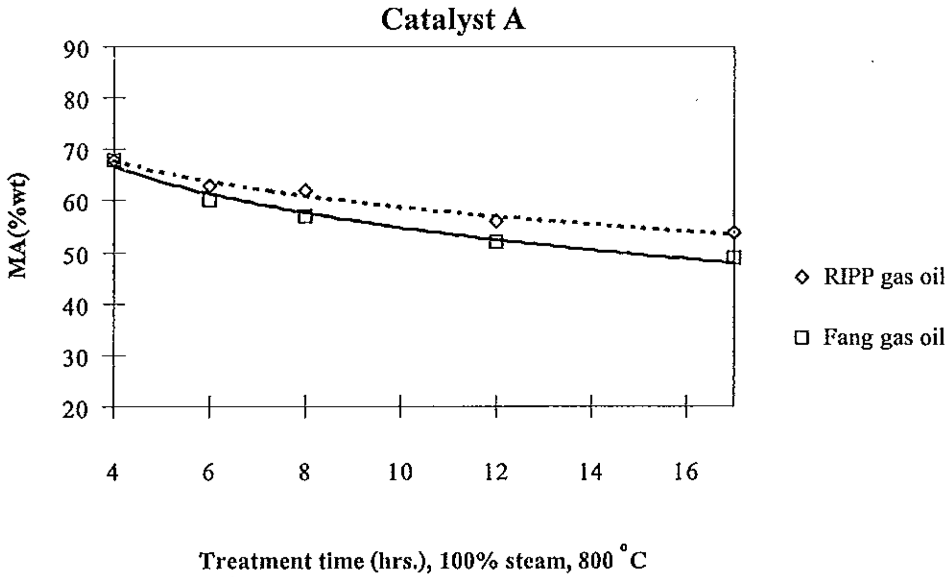


Figure 4-4 Comparison of RIPP and Fang feedstocks for MA for catalyst A

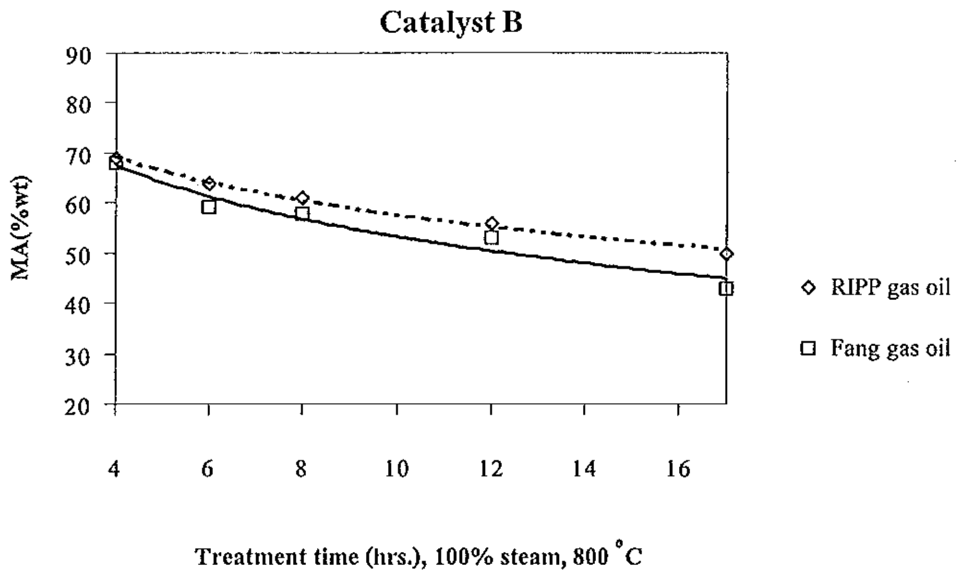


Figure 4-5 Comparison of RIPP and Fang feedstocks for MA for catalyst B

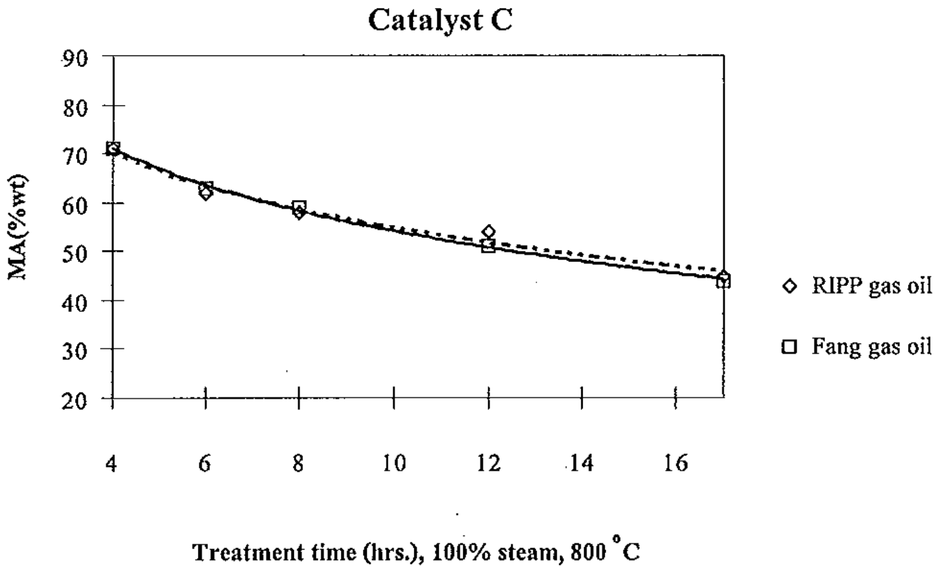


Figure 4-6 Comparison of RIPP and Fang feedstocks for MA for catalyst C

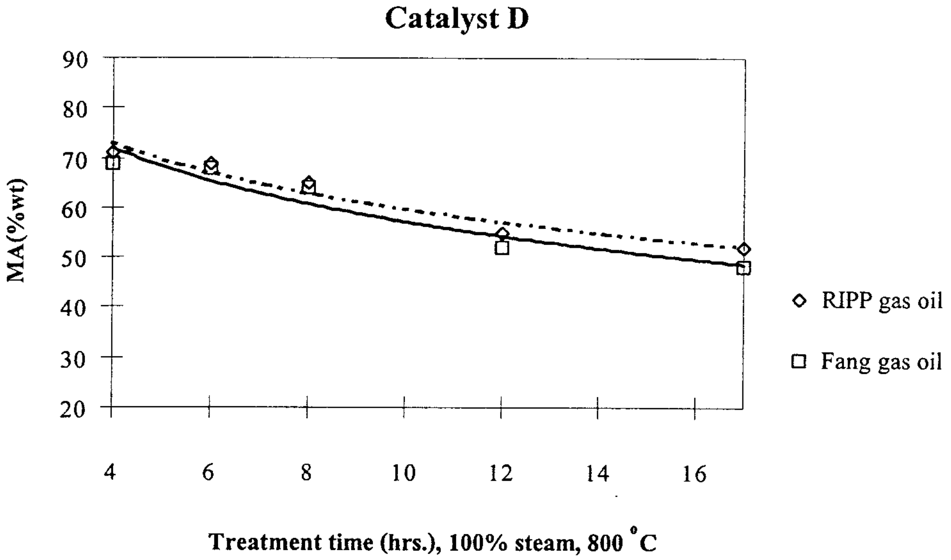


Figure 4-7 Comparison of RIPP and Fang feedstocks for MA for catalyst D

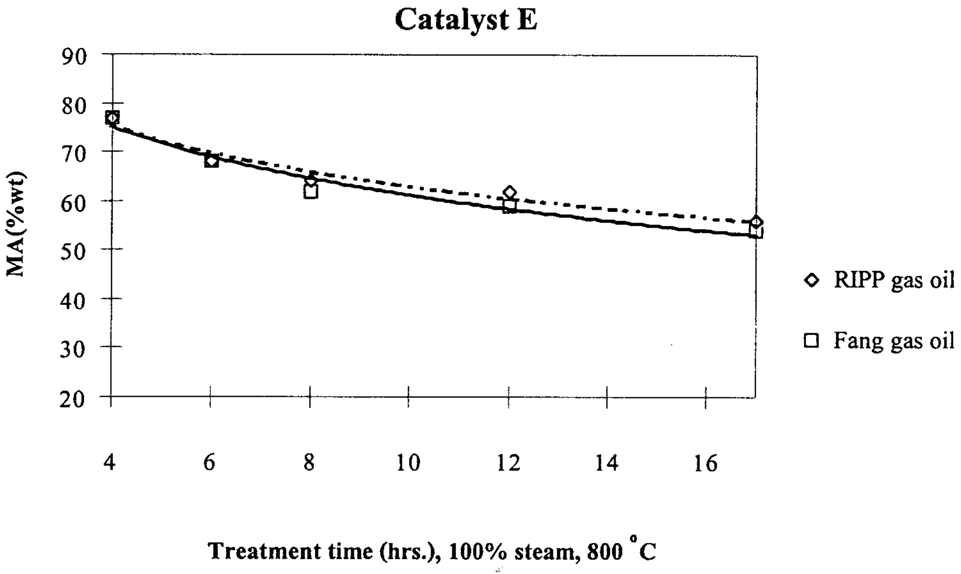
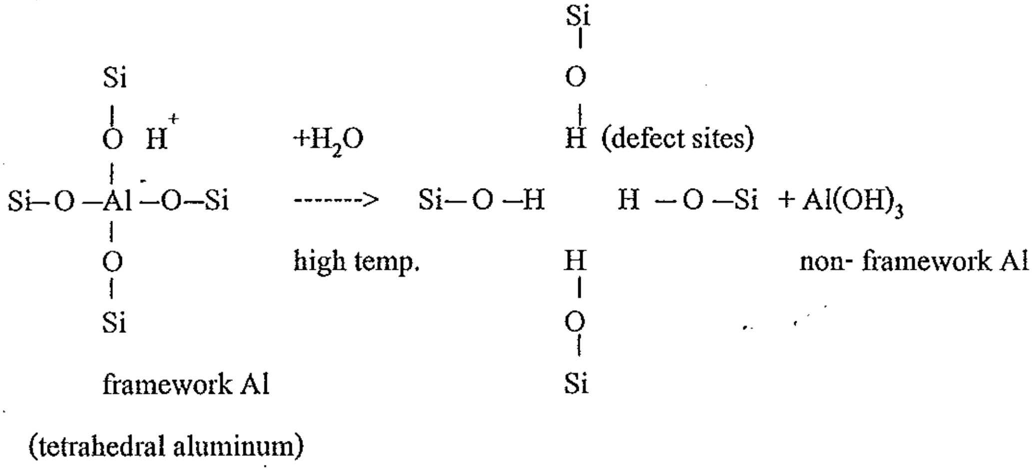


Figure 4-8 Comparison of RIPP and Fang feedstocks for MA for catalyst E

During high temperature steaming (hydrothermal treatment), zeolite is dealuminated by hydrolysis of Al atoms in the zeolite framework that cause USC, SA loss and subsequently MA decrease.



Gong- Y (REY type catalysts) and Lanet-35 (REHY-USY type catalyst) are also dealuminated by hydrolysis of Al atoms. the Lanet-35 shows its characteristics featured as USY type catalysts, under high temperature steam is more prone to deactivate. As for Gong-Y, the RE occupied the cationic positions in the framework of Y zeolite which perform some restraining effects on hydrolyzing reaction, so the REY catalysts usually shows higher activity under hydrothermal condition.

Dealumination of Y zeolite is retarded by exchange rare-earth. Fully rare-earth exchanged zeolite retains aluminum to a greater extent than partially rare-earth exchanged zeolite (REHY), so Gong-Y shows higher stable than Lanet under 4-16 hrs. hydrothermal treatment

Figures 4-3 to 4-8 present results between MA with hydrothermal times for Fang and RIPP feedstock. MA decreased when treatment times increased. Most of catalysts show the same (or a little difference) MA at 4 hrs. of treatment for 2 feedstock. But, when the severity of treatment grows higher, like longer time of treatment in this work, the MA drop grows bigger for Fang feedstock than for RIPP feedstock for some catalysts. So, crackability depends on catalysts and feedstocks.

Table 4-6 MA results by using RIPP and Fang feedstocks for equilibrium catalysts

Catalyst.	**MA (%)**	
	RIPP gas oil	**Fang gas oil**
F-EQ	65	63
G-EQ	59	56
H-EQ	61	60
I-EQ	67	64
RHZ 300	57	48
MZ-3 EQ	68	64
OD-EQ	66	63
CRC-1-EQ	70	69

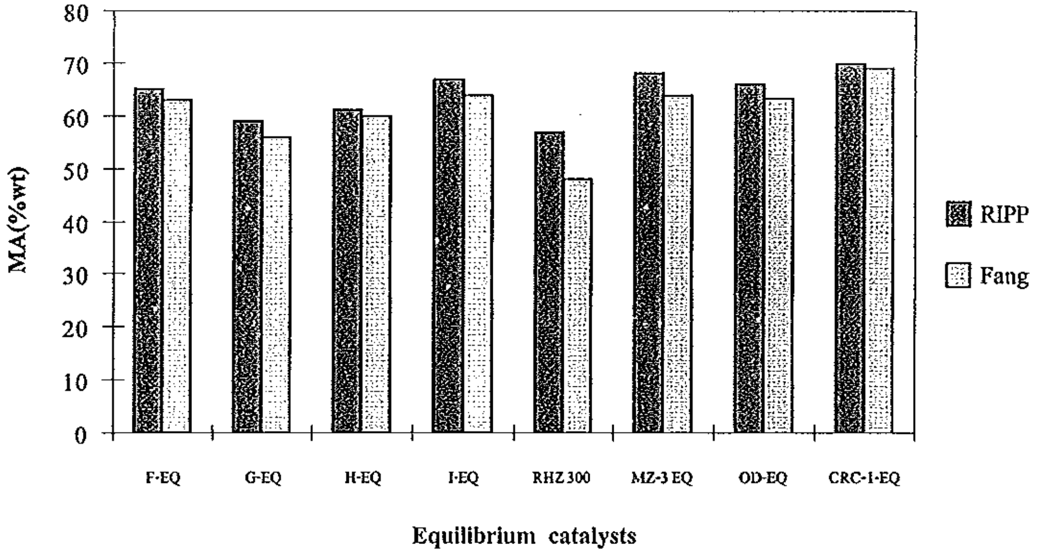


Figure 4-9 Microactivity (MA) results by using RIPP and Fang feedstocks for equilibrium catalysts

For E-cats, in Table 4-6 and Figure 4-9, RIPP feedstock is easier to crack than Fang feedstock. The difference for using RIPP feed as compared to Fang feed for highest MA (CRC-1) is 1 and lowest MA (RHZ300) is 9. So, the MA drop is smaller for the catalysts of higher activity.

4.5 Evaluation of Fresh FCC Catalysts

Table 4-7 Properties of fresh catalysts A, B, C, D, E

Properties	**Catalyst**				
	A	**B**	**C**	**D**	**E**
Chemical properties, %wt					
Al_2O_3	35.4	42.2	48.5	40.7	38.3
RE_2O_3	1.6	1.3	2.0	0.9	1.6
Na_2O	0.31	0.41	0.33	0.26	0.37
SiO_2	61	55	45	56	56
P_2O_5	0.13	0.1	0.13	0.63	0.5
K_2O	0.22	0.15	0.14	0	0.11
CaO	0	0	0.17	0	0
TiO_2	1.9	2.1	1.5	1.7	1.4
Fe_2O_3	0.8	0.8	1.1	0.7	0.7
SO_3	0	0	2.7	0.32	0.36
Cl	0	0	0.11	0	0
BaO	0	0	0	0.29	0
Physical properties					
Total surface area m^2/g	239	254	172	239	191
U.C.S (Fresh cat), Å	24.55	24.64	24.54	24.58	24.59
I/I_0 (Fresh cat)	0.18	0.19	0.15	0.19	0.23
U.C.S (800 °C/4h), Å	24.26	24.25	24.30	24.25	24.30
I/I_0 (800 °C/4h)	0.10	0.11	0.09	0.15	0.15
DTA collapse temp. °C	1002.7	995.7	986.8	990.1	988.4

Table4-7(Continue)

Properties	**Catalyst**				
	A	**B**	**C**	**D**	**E**
Microactivtiy, LGO feed,%wt (800 °C/4hrs. C/O 3.2)					
MA	68	69	71	71	77
Micro-reactor evaluation,%wt. (800 °C/4hrs.,Shengli VGO feed, C/O 4)					
Gas	11.1	12.7	12.4	13.8	14.9
Gasoline	60.7	61.3	61.9	61.5	63.1
LCO	17.9	16.5	16.0	15.7	13.1
HCO	8.3	6.3	6.5	6.3	5.0
Coke	2	3.2	3.2	2.7	3.9
Conversion	73.8	77.2	77.5	78.0	81.9
Gasoline + LCO	78.6	77.8	77.9	77.2	76.2
Gas composition, %wt(Based on feed)					
Hydrogen	/	/	/	0.1	0.1
Methane	0.2	0.3	0.3	0.3	0.4
Ethylene	0.3	0.4	0.4	0.4	0.5
Ethane	0.2	0.3	0.3	0.3	0.3
Propylene	3.1	3.5	3.3	3.7	3.6
Propane	0.3	0.3	0.3	0.3	0.4
Butylenes	3	3.5	3.2	3.8	3.3
i - Butane	3.4	3.8	3.9	4.3	5.2
n - Butane	0.5	0.6	0.6	0.7	1.0

Table4-8 Properties of fresh catalyst Gong-Y and Lanet-35

Properties	**Catalysts**	
	Gong-Y	**Lanet-35**
Chemical properties, wt%		
Al_2O_3	26.4	53.5
Na_2O	0.18	0.32
RE_2O_3	2.5~2.8	0.78
Fe_2O_3	0.47	1.1
Physical properties		
SA, m^2/g	204	160
PV, ml/g	0.57	0.35
ABD, g/ml	0.44	0.79
Particle size, wt%		
0-40 μm	21.6	21.6
0-80 μm	78.5	73.1
0-149μm	95.0	96.9
APS μm	68.4	74.1
Unit cell size, Å(Fresh)	24.68	24.49
Unit cell size, Å (4 hrs,100%steam, 800 °C)	24.39	24.28
DTA, Collapse temp , °C	1014.15	996.48
Microactivity, %wt (LGO feed)		
800 °C/4 hrs. (Fixed bed)	73	76
790 °C/17hrs (Fluidized-bed)	70	/

Table4-8 (Continue)

Properties	**Catalyst**		
	Gong-Y		**Lanet-35**
Micro-reactor evaluation ,VGO(%wt)	Fluidized-bed		Fixed-bed
	790 °C/17hrs		800 °C/4 hrs
Cat/Oil	5 .0	3.5	4.0
Gas	14.6	12.0	13.1
Coke	3.3	2.6	3.5
C_5-204 °C	55.0	50.0	62.0
204-330 °C	18.2	21.1	15.4
204 °C+ CONV	72.9	64.4	78.0
>330 °C	8.9	14.5	7.0
Gas components, wt%			
Ethylene	0.46	0.39	/
Propylene	3.42	2.87	/
Butylenes	2.52	1.95	/
i-Butane	3.19	2.74	/

Data for properties of fresh catalysts properties data are useful and helpful in catalyst evaluation and in FCC unit operation. Take DTA collapse temperatures an example, the collapse temperature of catalyst B to E from Thai oil refinery and Catalyst Lanet-35 from RIPP are a little lower than 1,000 °C as for catalyst A and Gong-Y show a little higher than 1,000 °C DTA collapse temperature can be a reference for considering the thermal stability of catalysts.

The fresh catalysts need to be deactivated (normally by hydrothermal treament) first to decrease the fresh activity of test catalysts. Hydrothermal is much more severe than thermal, so in laborytory practice we usually use hydrothermal (aging) as an artificial means to obtain accelerated deactivation of catalysts to simulate the structure aging and deactivation in real FCC units, thus we can obtain the information about deactivation in a shorter (realistic) time. This is the meaning of the so-called "simulation"

Table4-9 Microactivity testing of hydrothermal-treated catalysts with RIPP feedstock

Treatment time (hrs.)	MA(%wt)						
	A	B	C	D	E	Gong- Y	Lanet-35
4	68	69	71	71	77	73	76
6	63	64	62	69	68	69	64
8	62	61	58	65	64	67	62
12	56	56	54	55	62	61	52
16	-	-	-	-	-	59	45
17	54	50	45	52	56	-	-

Table4-10 Unit cell size of hydrothermal-treated catalysts

Treatment Time (hrs.)	Unit Cell Size (Å)						
	A	B	C	D	E	Gong -Y	Lanet-35
0	24.55	24.64	24.54	24.58	24.59	24.68	24.49
4	24.26	24.25	24.30	24.25	24.30	24.39	24.28
6	24.25	24.27	24.27	24.24	24.23	24.40	24.19
8	24.25	24.27	24.22	24.26	24.24	24.36	24.20
12	24.24	24.26	24.23	24.26	24.26	24.35	24.20
16	-	-	-	-	-	24.33	24.18
17	24.25	24.26	24.22	24.26	24.24	-	-

Table4-11 Total surface area of hydrothermal treated catalysts

Treatment time(hrs.)	Total surface area (m^2/g)						
	A	B	C	D	E	Gong-Y	Lanet-35
0	239	254	172	239	191	204	160
4	136	164	131	166	168	128	125
6	127	165	119	163	156	122	86
8	125	143	113	152	134	112	80
12	111	148	94	131	132	105	53
16	-	-	-	-	-	105	53
17	99	119	82	130	128	-	-

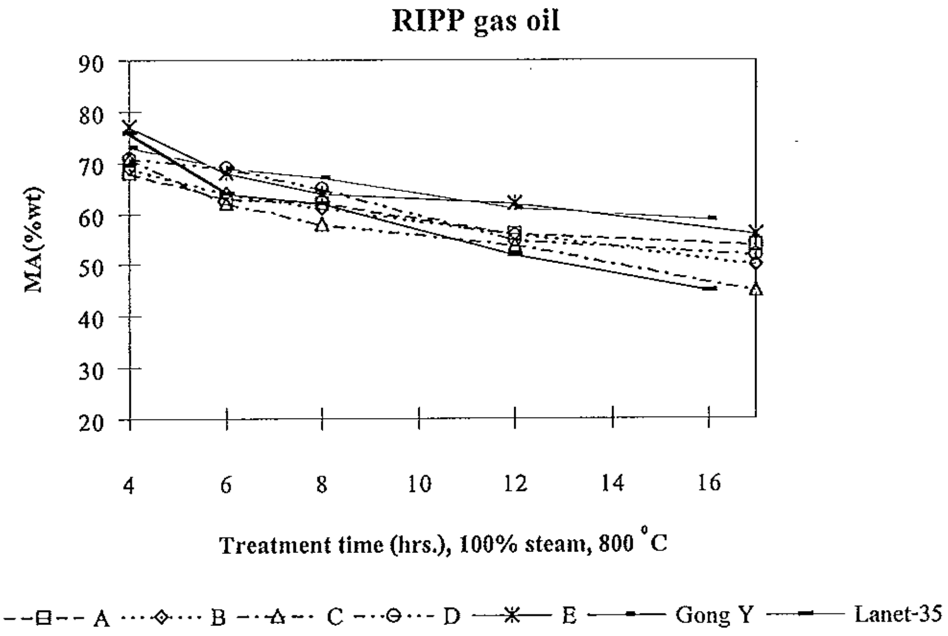


Figure 4-10 Microactivity (MA) of hydrothermal treated catalysts with RIPP feedstock

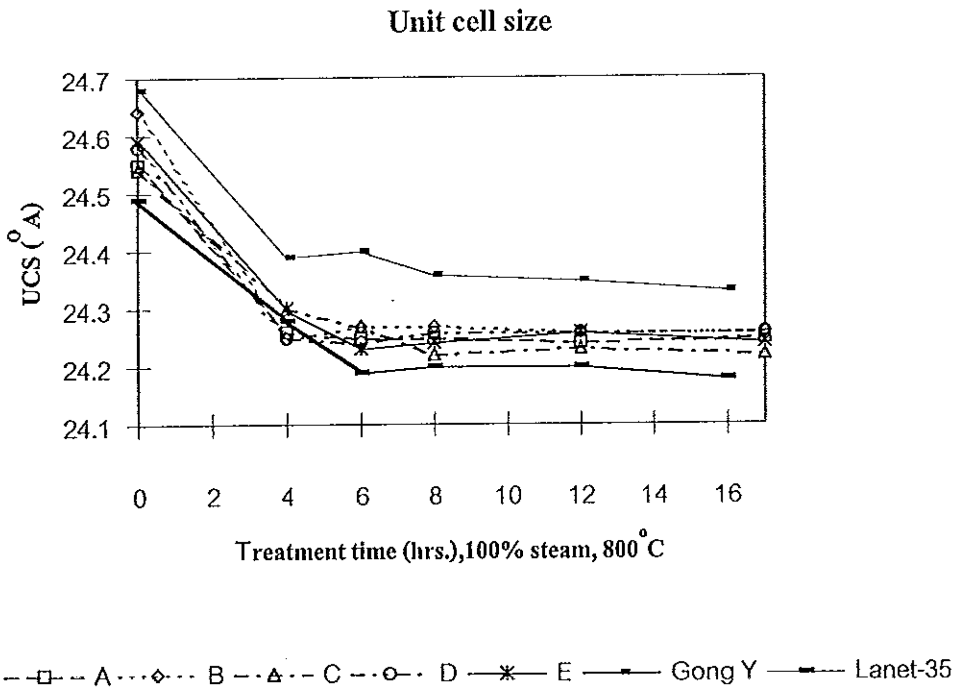


Figure 4-11 Unit cell size (UCS) of of hydrothermal treated catalysts

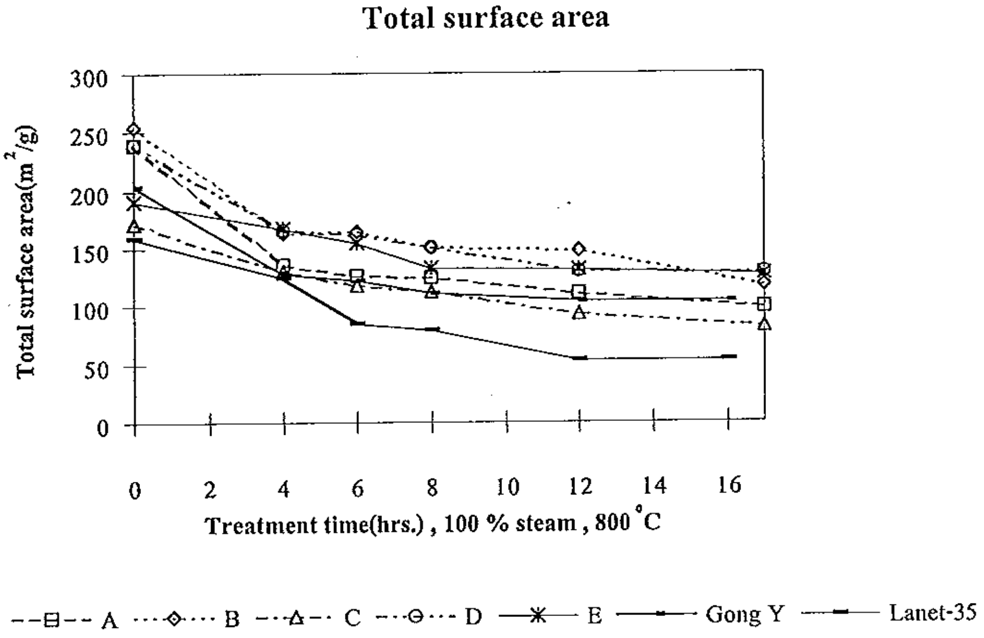


Figure 4-12 Total surface area (SA) of hydrothermal treated catalysts

If the goal of treatment is to target only the unit cell size, then it might be concluded that one steaming severity is needed. What this approach overlooks is that it does not account for expected changes in MA or total surface area. Figure 4-11 shows that an equilibrated unit cell size (USC) for catalyst Lanet-35 can be obtained at about 6 hrs. of steaming at 800^{0}C, 100% steam; but as presented in Figure4-10 and 4-12, the MA and total surface area will continue to change with treatment time proceeds. The UCS of catalyst A through E equilibrated in the same range and Lanet-35 equilibrated at the lowest. Gong-Y had the highest equilibrated UCS. For MA of all catalyst also show in the same trend as UCS. Gong-Y shows the highest MA and Lanet-35 shows the lowest MA at 16 hrs. of hydrothermal treatment.

Testing fresh catalysts only one severity condition provides not enough information to compare each type of catalysts because it can not know the stability of catalysts. In FCC unit, to maintain catalytic activity, fresh catalyst is added to the unit with different rate; it is so-called "make up rate". So information with stability of each type of catalysts is one guideline in consider the make up rate in FCC unit. In Figure 4-10 catalyst C shows higher MA than catalyst A at 4 hrs. of treatment otherwise when treatment time is increased especially at 17 hrs. MA of catalyst A is higher than catalyst C that is because the decay rate of catalyst C is higher than catalyst A. So to maintain activity level, make up rate of catalyst C should be higher than catalyst A. The result of this kind of aging tests can provide very useful information to consider the make up rate of fresh catalyst for a FCC unit.

4.6 Evaluation of Equilibrium Catalysts

Table4-12 Properties of equilibrium catalysts

Properties	**Equilibrium catalysts**							
Activity	**F**	**G**	**H**	**I**	**RHZ300**	**MZ-3**	**OD**	**CRC-1**
MA	65	59	61	67	57	68	66	70
C.F.	/	1.9	/	/	/	/	/	/
G.F.	/	6	/	/	/	/	/	/
Chemical properties								
Al_2O_3, wt%	35.0-37.0	39.3	36.7	37.6	42.0	23.0	/	41.9
Na, wt%	0.23-0.25	0.29	0.37	0.59	/	/	/	0.30
Fe, wt%	0.48-0.52	0.51	0.53	0.52	/	/	/	0.42
SO_4, wt%	/	/	<0.2	<0.2	/	/	/	0.2
C, wt%	0.30-0.60	0.03	/	/	/	/	/	/
V, ppm	500-550	4,355	/	/	2,300	/	/	400
Ni, ppm	560-600	2,277	500	400	3,900	/	/	4,300
Cu, ppm	25-50	21	<50	<50	/	/	/	46
Sb, ppm	0	743	/	/	/	/	/	/
Fe, ppm	/	/	/	/	6,900	/	/	6,000
RE_2O_3, wt%	1.0	1.1	<0.5	0.8	/	23.0	/	2.8
Physical properties								
S.A. (m^2/g),BET	110-120	121	132,169*	120,157*	63	120~130	/	97
P.V.(cc/g),H_2O	0.23-0.26	0.32	0.33	0.31	0.22	0.30~0.35	/	0.25
A.B.D.(g/cc)	0.88-0.92	0.88	0.78	0.81	0.91	/	/	0.89
USC , Å	24.28	24.24	24.22	24.24	24.31	24.42	24.22	24.51
Particle size(micron)								
0-20,wt%	0-2	1	/	/	/	/	/	/
0-40,wt%	3-5	13	/	/	7	/	/	/
0-80,wt%	38-43	72	/	/	66	/	/	/
APS (micron)	80	65	/	/	68	68	/	/

* Langmuir method

The equilibrium catalyst evaluation is to test the equilibrium catalyst properties on routine basis which includes many items usually done by the catalyst manufacturer at a frequency of every one or two weeks to test a sample and send the data back to the refinery. The data generated by the testing when properly understood are very useful to refinery operation.

As a general rule, the equilibrium catalyst data are mainly useful to identify changes or trends in catalyst properties over a period of time, thus can lead the refinery to change the policy of using catalyst (catalyst type or catalyst make up rate) or to change the processing conditions which would improve the performance and profitability of the FCC unit.

Equilibrium catalyst F is used in Thai Oil Company, LTD. Equilibrium catalyst G is used in Star Petroleum Refinery. Equilibrium catalyst H, I, RHZ-300, MZ-3, OD, CRC-1 were received from RIPP. The MA of these catalysts lies in the range of 57-70 (when tested with RIPP gas oil). Data shows that FCC units of Thailand are operating at a MA level of equilibrium catalysts of 60-65.

4.7 A Comparison between Thermal and Hydrothermal Treatments

Table 4-13 A comparison between thermal and hydrothermal treatment for Catalyst Gong-Y

Treatment Time(hrs)	MA(%wt)	
	Thermal treatment	Hydrothermal treatment
4	72	72
6	70	64
8	68	63
12	68	56
16	67	55
	Unit cell size (Å)	
	Thermal treatment	Hydrothermal treatment
4	24.39	24.39
6	24.40	24.40
8	24.40	24.36
12	24.41	24.35
16	24.41	24.33
	Total surface area(m^2/g)	
	Thermal treatment	Hydrothermal treatment
4	128	128
6	134	122
8	133	112
12	126	105
16	132	105

Table 4-14 A comparison between thermal and hydrothermal treatment for Catalyst Lanet-35

Treatment Time(hrs)	MA(%wt)	
	Thermal treatment	**Hydrothermal treatment**
4	77	77
6	76	57
8	75	54
12	75	44
16	75	34
	Unit cell size (Å)	
	Thermal treatment	**Hydrothermal treatment**
4	24.28	24.28
6	24.27	24.19
8	24.27	24.20
12	24.28	24.20
16	24.26	24.18
	Total surface area(m^2/g)	
	Thermal treatment	**Hydrothermal treatment**
4	125	125
6	124	86
8	124	80
12	122	53
16	122	53

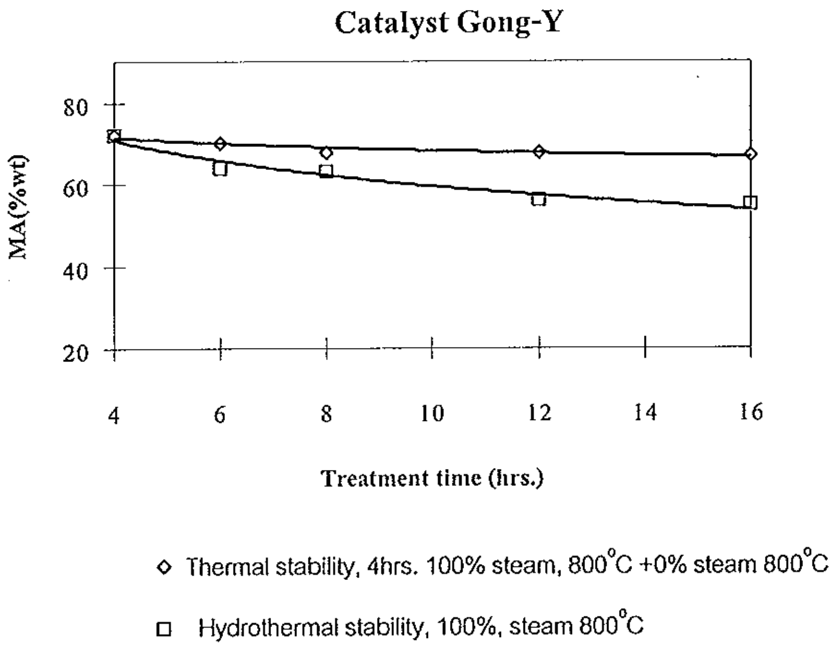


Figure 4-13 Thermal and hydrothermal stability of catalyst Gong-Y : Microactivatiy test (MA)

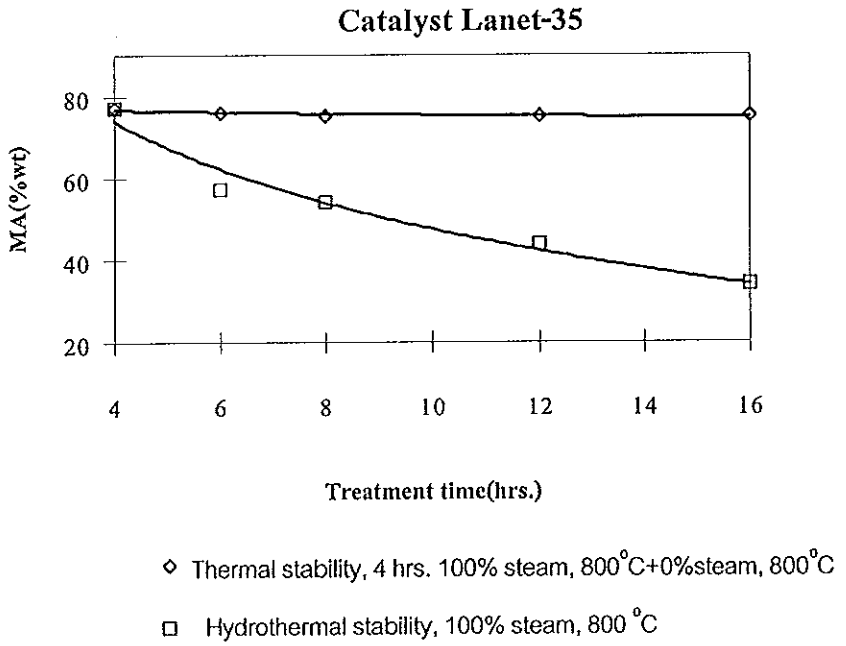


Figure 4-14 Thermal and hydrothermal stability of catalyst Lanat-35 : Microactivatiy test (MA)

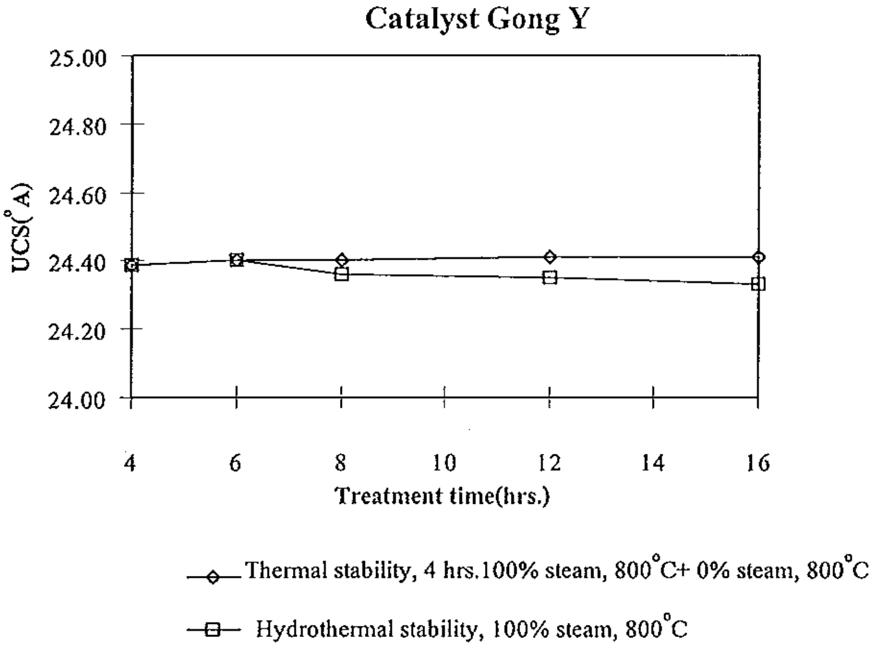


Figure 4-15 Thermal and hydrothermal stability of catalyst Gong Y : Unit cell size

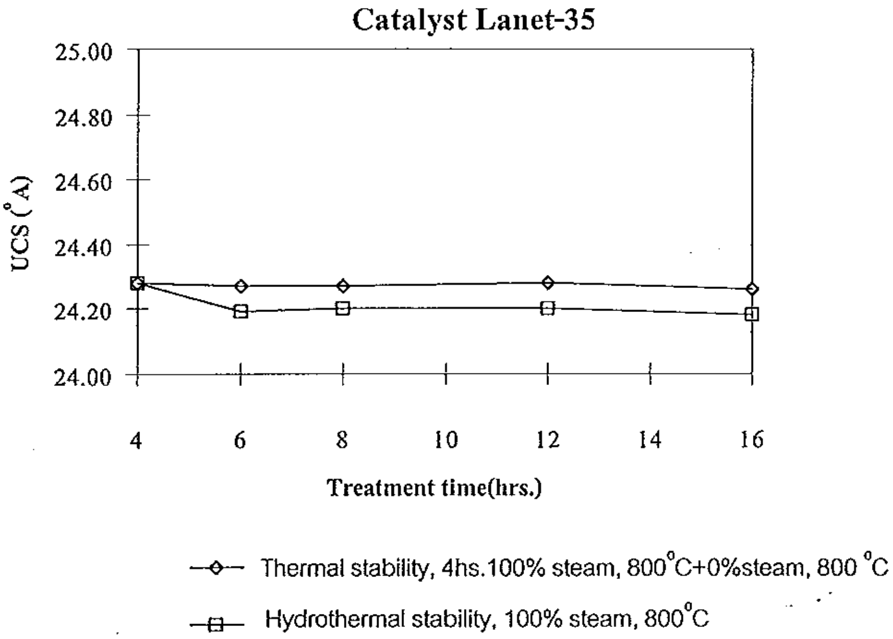


Figure 4-16 Thermal and hydrothermal stability of catalyst Lanet-35 : Unit cell size

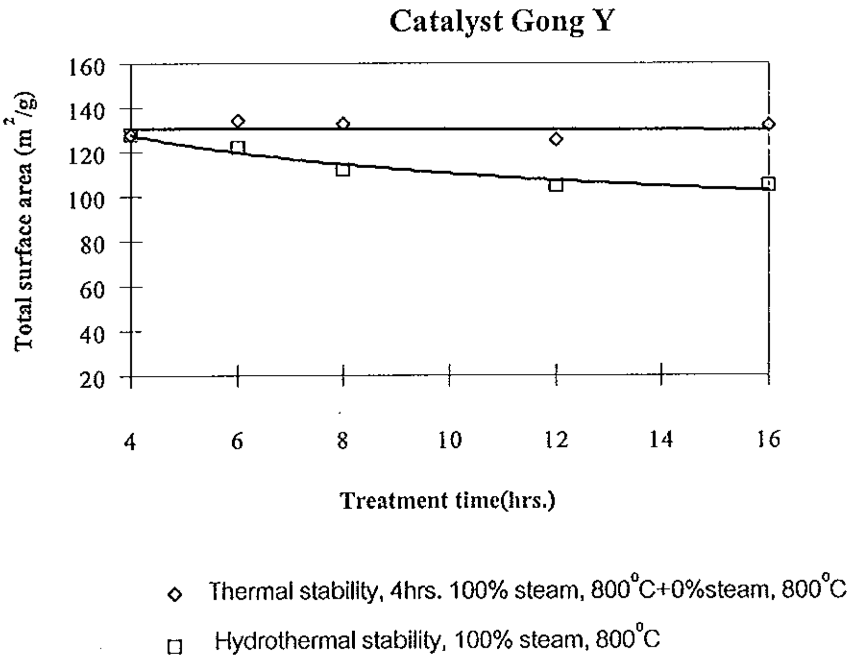


Figure 4-17 Thermal and hydrothermal stability of catalyst Gong-Y : Total surface area

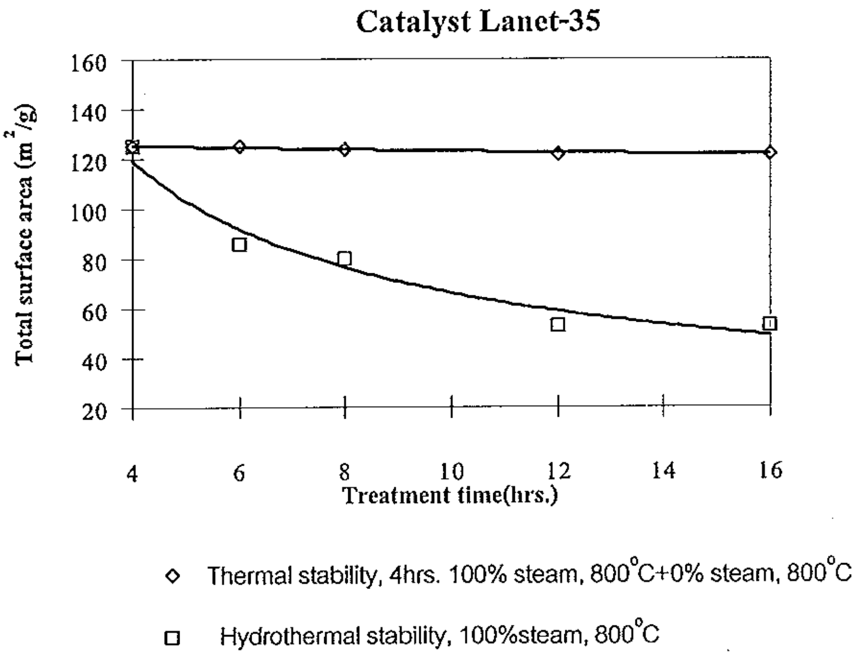


Figure 4-18 Thermal and hydrothermal stability of catalyst Lanat-35 : Total surface area

Thermal and hydrothermal aging of catalyst is a permanent deactivation. Activity loss from thermal deactivation is caused mostly by sintering. Hydrothermal deactivation results from dealumination and subsequent crystallinity (and surface area) loss, as well as pore size shifts and surface area loss in matrix.

Catalysts in FCC units were deactivated by high temperature and steaming. So in this work, it is intended to ensure that between thermal and hydrothermal deactivation, which has predominate effect to FCC catalysts.

Catalyst Gong-Y and Lanet-35 were used to compare between thermal and hydrothermal treatmet at 800 °C, 1 atm. It is proved that hydrothermal treatment is much more severe than thermal treatment as shown in Tables 4-13, 4-14 and Figures 4-13 to 4-18.

At the same temperature and pressure, stability curve of catalysts Gong Y and Lanet-35 show that catalyst are more strongly deactivated hydrothermal than thermal (the thermal deactivation equation of catalyst Gong-Y and Lanet-35 are $-3.21\ln(x)+75.6$ and $-1.47\ln(x)+78.5$, the hydrothermal deactivation equation of catalyst Gong-Y and Lanet-35 are $-12.3\ln(x)+87.9$, $-28.7\ln(x)+113$, respectively; where x is times) and from the unit cell size (USA) and total surface area (SA), which the caused of deactivation of catalysts, are also shown that hydrothermal deactivation is severe than thermal deactivation .These results were the same as mentioned by Letzch, W.S., Ritter, R.E. and Vaughan, D.E.W. (1976)

Note: In thermal deactivation, conditions used were 4 hrs.,100% steam 800°C then to heat at 800°C 2, 4, 8, 12 hrs., respectively.

Chapter 5

Conclusion

The microactivtiy test unit (Model WFS-1D) can do measurements of MA for FCC catalysts, the data can be compared to RIPP's measurements.

The hydrothermal aging test unit (Model CLY-1) can do aging treatments of various severities to investigate the tendency of MA (and/or other properties) change of catalysts under thermal together with steam atmosphere conditions. This can be a means for detecting or simulating the changes in some extent (mostly structural without metal contamination) of catalysts under FCC unit operations (especially at regeneration).

Department of Chemical Engineering, Prince of Songkla University started to study with MAT and hydrothermal aging units in its preliminary work on evaluation of FCC fresh catalysts and also E-Cats.

In this work we successfully conducted redistillation of Fang gas oil without existing analysis equipment to help us identify the boiling range of products. Repeatability for MA measurements of catalyst CRC-1 obtained the average of 67, standard deviation of 1.8, and 95% confidence limit of 67±2.0 . Testing of hydrothermal treatment also proved that we can perform the aging treatment at the same severity as RIPP did.

Catalyst Gong-Y(REY) shows higher stability than Lanet-35 (REHY-USY) under hydrothermal treatment in the range of 4-16 hrs. and has higher UCS and total SA than Lanet-35. The difference in crackability of 2 feedstocks depends on different catalysts and feedstocks. When the severity of treatment grows higher, the activity, total surface area and unit cell size of catalysts all decreased, as for UCS equilibrated at about 6 hrs. under hydrothermal treatment at 800 °C, 100% steam.

Two of the FCC units of Thailand are operating at the MA 60-65.

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Appendix

Appendix A

Preparation of Feedstock for MAT from Fang Gas Oil

The end point of Fang gas oil is 380 °C which is heavier than the feedstock that RIPP now using for MAT tests (235~337°C), so it was redistilled to as light as standard RIPP feedstock by using a simplified vacuum distillation unit.

Procedure of Distillation under Reduced Pressure.

A.1 Dehydration of Diesel oil

1. Dry $CaCl_2$ in furnace with temperature about 110 °C for 8 hrs. and let it cool in descicater.
2. Mix $CaCl_2$ 10-15 g. with diesel oil 300 ml.
3. Stir the mixture about 30 min. then separate $CaCl_2$ from diesel oil by filtration

A.2 Distillation Diesel Oil under Reduced Pressure

1. The equipment was set up as shown in Figure A-1

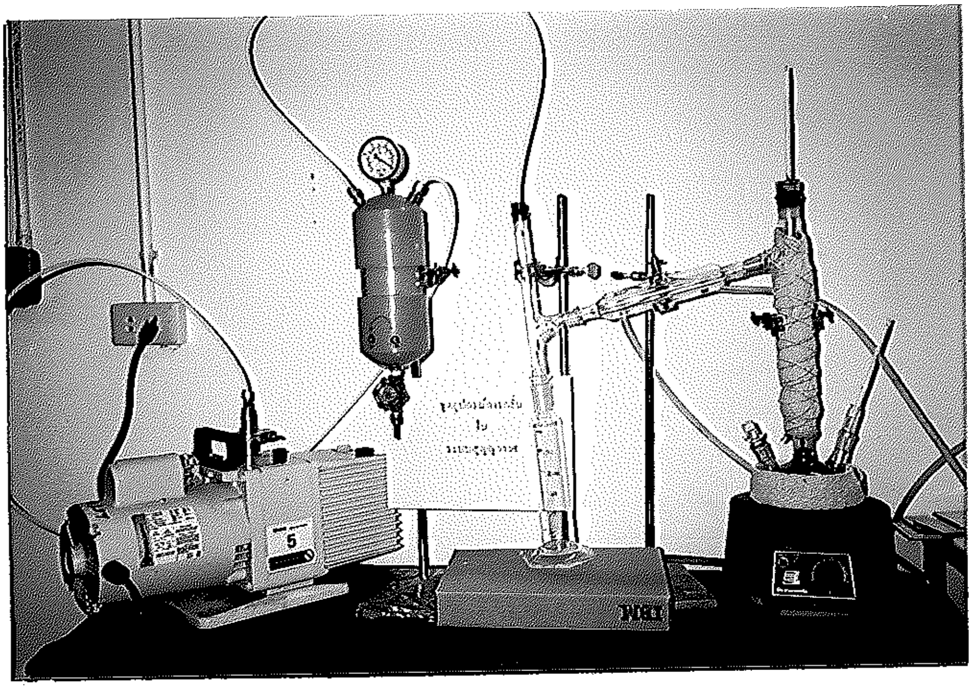


Figure A-1 Simplified vacuum distillation unit

2. Cover the column by insulator to prevent heat loss.

3. Open vacuum pump and decrease pressure to the minimum value of vacuum gauge.

4. Check leak of unit.

5. Close vacuum pump, pour about 300 ml of diesel oil and glass beads in boiling bottle

6. Open vacuum pump and decrease pressure to -27 inch. Hg (72.4 mmHg) then the sample is heated

7. Decrease the pressure a little to -29 inch Hg and increase the temperature a little until the liquid temperature reaches about 250 °C, and the temperature of the effluent (distillate) reaches about 229 °C

8. Collect the distillate to analyze by GC

A.3 Analysis of Distillate with Gas Chromatograph.

1. Conditions of GC for analysis

   The same conditions as microactivity test (see appendix C)

2. Inject 1µl of mixture of RIPP standard gas oil and standard n-C_{12}

3. Inject 1µl of mixture of Fang distillate and standard n-C_{12}

4. Compare chromatogram of RIPP standard gas oil (LGO) and Fang gas oil (LGO)

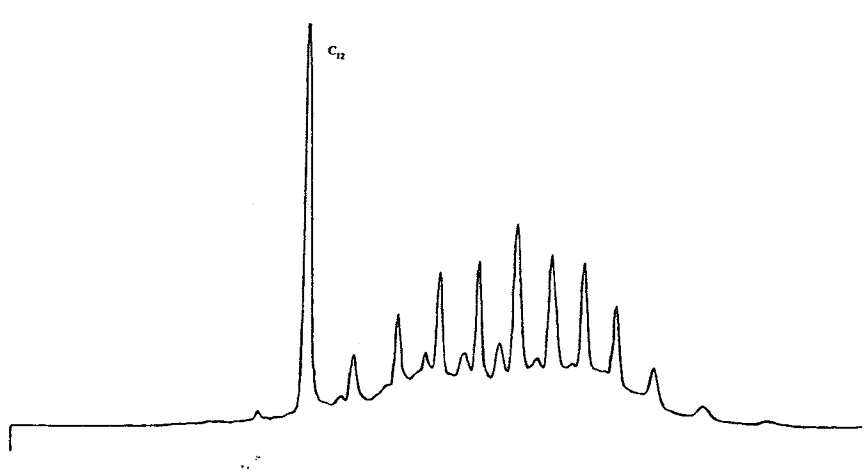


Figure A-2 Chromatogram of mixture of RIPP standard gas oil and standard n-C_{12} by Gas Chromatograph

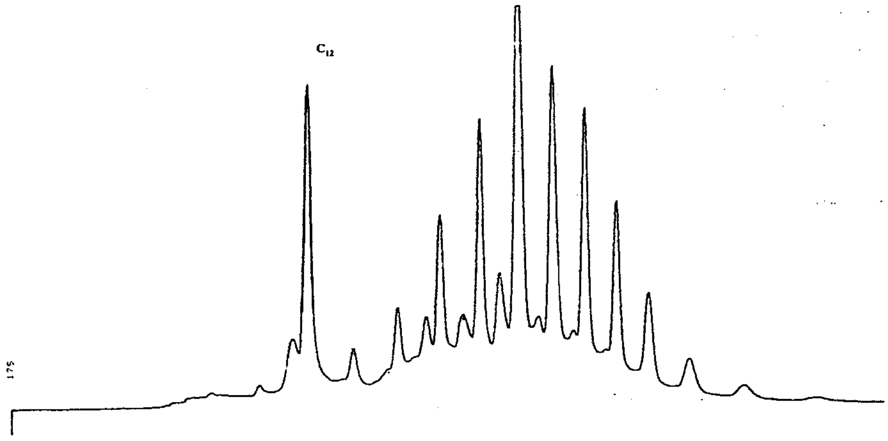
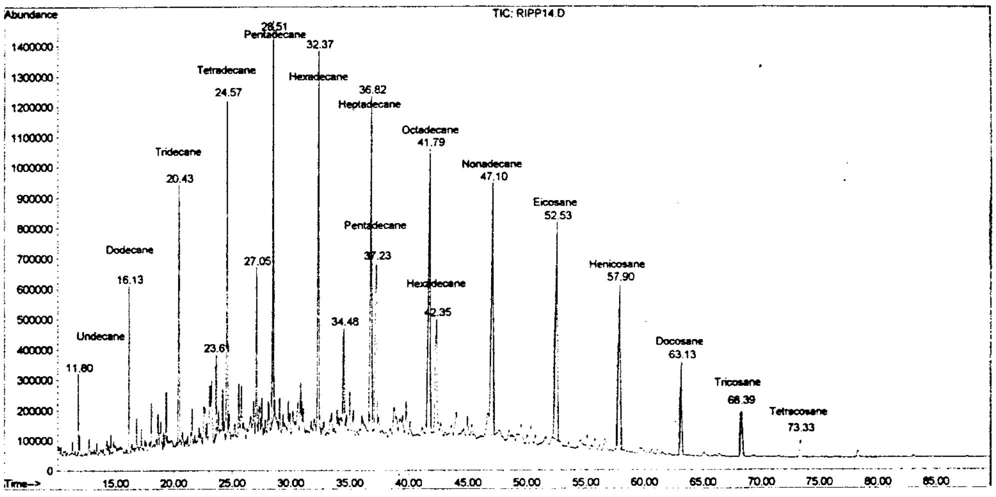


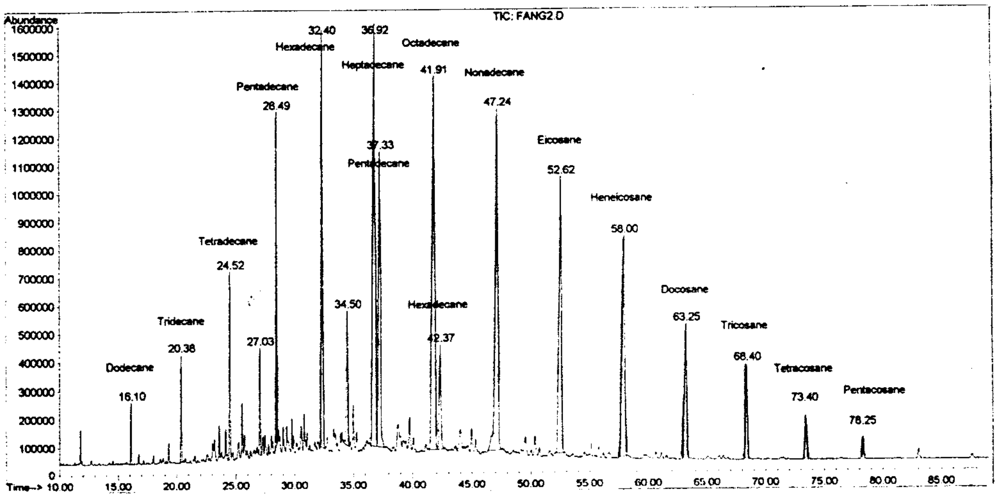
Figure A-3 Chromatogram of Fang gas oil (redistilled) and standard n-C_{12} by Gas Chromatograph



Peak#	R.T. min	Peak type	Peak height	Raw area	Corr. area	Corr.%max
1	11.80	PV	270083	10868576	10044480	9.46%
2	16.13	PV	555034	25204269	23824824	22.45%
3	20.43	PV	841392	41754627	40625781	38.28%
4	23.61	PV	293622	15650020	14178973	13.36%
5	24.57	VV	1127744	65062530	63646526	59.97%
6	27.05	VV	552776	30696342	29184949	27.50%
7	28.51	PV	1317216	84349364	82418879	77.65%
8	32.37	VV	1280457	97473872	94690842	89.22%
9	34.48	VV	353824	36773564	34196139	32.22%
10	36.82	BV	1099217	106443073	103152752	97.19%
11	37.23	PV	535832	53527262	51211815	48.25%
12	41.79	VV	943230	110029290	106136733	100.00%
13	42.35	VV	386860	47416587	44926859	42.33%
14	47.10	VV	827634	103685859	99451509	93.70%
15	52.53	BV	734041	99738102	94187913	88.74%
16	57.90	VV	554065	63708438	60669455	57.16%
17	63.13	BB	311646	32672881	30222325	28.47%
18	68.39	BB	154717	16154206	14007048	13.20%
19	73.32	BB	58528	7279748	5237965	4.94%

Figure A-4 Chromatogram of RIPP standard gas oil

by Gas chromatograph-Mass spectrometer



Peak#	R.T. min	Peak type	Peak height	Raw area	Corr.area	corr.%max
1	16.10	BV	218530	9823979	8766063	4.60%
2	20.38	BV	373663	16102649	15516574	8.14%
3	24.52	PV	655560	32255495	31447511	16.50%
4	27.03	VV	381449	20920908	19981244	10.48%
5	28.49	PV	1174104	69460911	68163707	35.77%
6	32.40	VV	1500964	131848953	129909796	68.17%
7	34.50	BV	475156	42778179	41047817	24.54%
8	36.92	BV	1497892	186626497	183803425	96.45%
9	37.33	VV	1046019	118830064	115763934	60.74%
10	41.91	BV	1328557	193440300	190574288	100.00%
11	42.37	VV	365199	41238206	39044631	20.49%
12	47.24	VV	1214976	191259054	186706993	97.97%
13	52.62	BV	983540	153525064	149559562	78.48%
14	58.00	BB	784996	107846718	104579238	54.88%
15	63.25	BV	479022	57801732	56129801	29.45%
16	68.40	BB	338076	36628823	34608624	18.16%
17	73.40	BB	158205	16509271	15100700	7.92%
18	78.25	BB	82004	9212641	7810689	4.10%

Figure A-5 Chromatogram of Fang gas oil (redistilled)

by Gas chromatograph- Mass spectrometer

Note: Chromatogram in Figure A-4 and A-5 was analyzed by Gas chromatograph-Mass spectrometer Model Series II plus GC-HP5972 series Mass selective detector, Hewlett-Packard. (GC-serial No. 3336A62208, Mass serial No.3609A03625)

Condition in analysis

Column : HP1 15m.X0.25mm.X0.25μm (Capillary column.)

Carrier gas : Nitrogen (OFN)

Injector temp. : 280 °C

Detector temp. : 280 °C

Flow rate : 1 ml/min.

Split ratio : 80:1

Injection mode : split

Inject volume : 1μl

Temperature of column chamber

- Initial temp. : 40 °C hold 1 minute
- Temp. rate I : 3 °C/min. from 40°C to 125 °C
- Temp. rate II : 1.5 °C/min
- Final temp. : 260 °C hold 3 minutes

Mass spectrometer : EI mode

Mass range : 10-450 amu

Scan rate : 2 scans/sec.

Appendix B

Hydrothermal Deactivation (by CLY-1 Hydrothermal Aging Unit)

B.1 Installation and Preparation

B.1.1 Power Supply

It is better to have a three-phase electrical power. Each L-N voltage is 220 V, AC, 20A, If the laboratory is not equipped with three-phase power supply, the three lines should be shorted in the power switch. The water pump and the recorder is lined to AC 220 V.

B.1.2 Air Supply

There has to be a air supply, its pressure is about 0.4 MPa. It can be from a pipe line or a small air compressor. On the aging unit the air pressure is adjusted to 0.3 MPa. Regulator pressure is adjusted to 0.1 MPa and the air flow is adjusted to 30 ml/min.

B.1.3 Water

The water used for aging should be deionized water. Before starting aging, the water is to be filled in the water tank to the full scale.

B.1.4 Temperature Adjustment

The furnace must have a long enough isothermal length (~10 cm.). If the isothermal length is not long enough, you can adjust the furnace temperature as following:

Fulfill the aging tube with porcelain rings or sand. Set the three temperature controller of the furnace at nearly 800 ^{o}C, start heating and air stripping. When the temperature are stable, start water pump at a rate of 25 ml/hr. After 40 min. gradually adjust the three temperature controllers for the furnace until the isothermal length reaching its maximum at 800^{o}C

B.2 Aging Procedure

B.2.1 Load Catalyst

The catalyst is to be loaded in the middle of the isothermal section of the aging tube as follows:

1. Fill porcelain rings at the bottom of the aging tube up to the isothermal section (about 17 cm. from the bottom). And at its top, put some broken rings, the thickness is about 1-2 cm.
2. Put a quartz cotton layer of about 1-2 cm on its top.
3. Better to fill 40 ml. catalyst inside the tube.
4. Put a quartz cotton layer of about 1-2 cm. thick on the top of the catalyst bed.
5. Fill some broken porcelain chips in.
6. Fill the tube with porcelain rings.
7. Put the tube in the furnace and line up.

B.2.2 Pre-Air Stripping and Start Heating.

1. Open the air-in valve on the unit panel, adjust the air pressures to 0.3 Mpa, regulated pressure be 0.1 MPa, and adjust the air flow to 30 ml/min.
2. Turn the "power" switch on.
3. Set the heating time for 2 hrs.
4. Set the aging time for 4, 6, 8, 12, 17(16) hrs., respectively.
5. Set the alarm time at aging time minus 1 min.
6. Push the button "heat" to start heating
7. Turn on pump power and set pump rate at 0.41 ml/min

B.2.3 Start Hydrothermal Aging

When the aging temperature stays at 800 ^{o}C for about 10-20 minutes, push the "start" button to start aging. (Use water-pump to start pump water, water valve open and the air valve close, and aging time start going on automatically)

B.2.4 Post Air Stripping

When the aging time has passed, the water-pump stops, water valve closed and the air valve opened automatically by LOGO, the post air stripping begins.

B.2.5 Finish

After about 10 minutes post air stripping, you can turn off the power and close the air supply, take out the aging tube and cool it down in the air, and then take out the catalyst and separate it from porcelain rings.

Figure B-1 Hydrothermal aging unit

Appendix C

Microactivity Test (by WFS-1D Microactivity Test Unit)

There are two parts in the test system: test unit (MAT unit) and gas chromatography set.

C.1 MAT Unit

In this thesis we use MAT unit model WFS-1D produced by Research Institute of Petroleum Processing, SINOPEC. WFS-1D is designed according to the standard method developed by RIPP and mainly used to test the activity index of cracking catalyst. The standard test method of cracking catalyst microactivity index in China is RIPP 92-90, the conditions are:

Standard feed gas oil : Straight-run light gas oil, boiling range of 235-337 °C

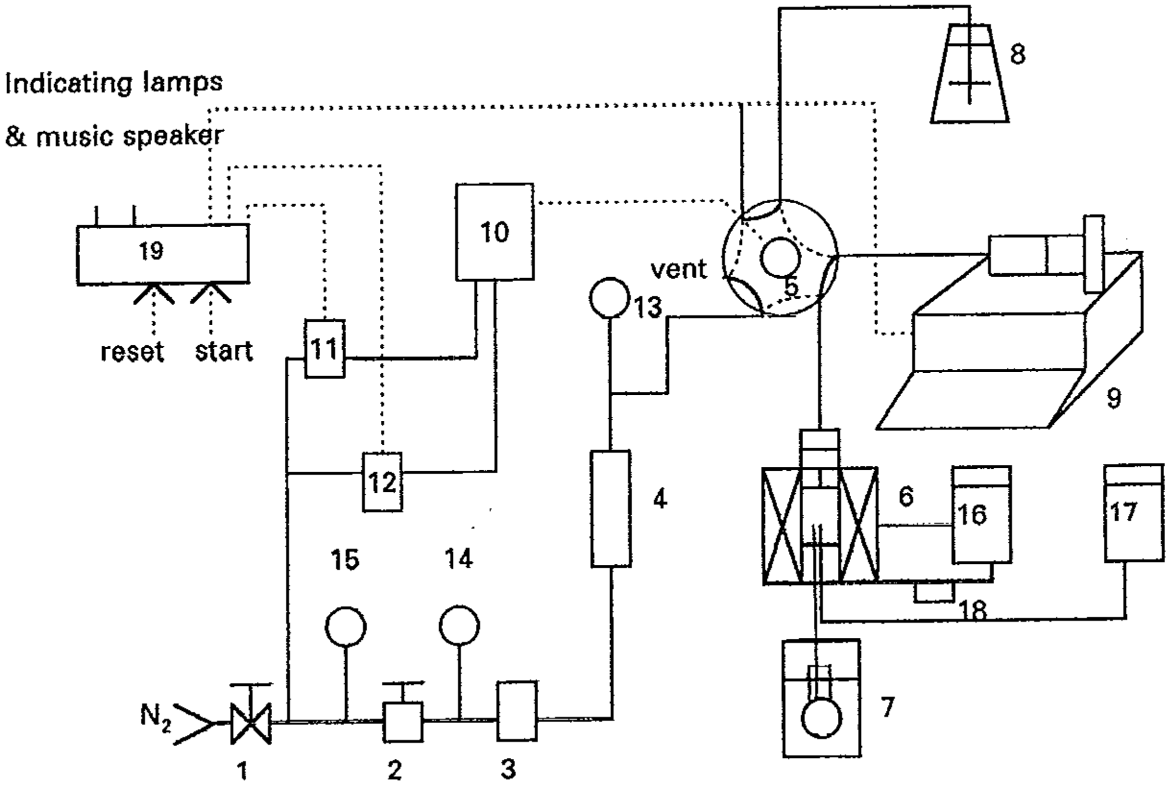
Reaction temperature : 460±1 °C

Feed oil weight : 1.56±0.01 g

Feeding time : 70 sec.

Post stripping time : 10 min.

Stripping nitrogen flow-rate : 20-30 ml/min.



1: valve 2: pressure regulator 3: flow regulator 4: rotary flow meter

5: six-port valve 6: reactor & heater 7: ice bath & collect bottle 8: feed oil bottle

9: injection pump 10: six-port valve driver 11: solenoid valve 12: solenoid valve

13: reaction pressure gauge 0-0.16 MPa 14: regulated pressure gauge 0-0.4 MPa

15: inlet pressure gauge 0-0.16 MPa 16: temperature controller (furnace)

17: temperature monitor (reactor) 18: solid relay

19: programmable logic controller

Figure C-1 The process diagram of MAT unit.

C.1.1 Reaction and Collection System

The system includes the reactor, the heating furnace, the condenser well and the collecting bottle. The reactor is the heart of the reaction system where the reaction takes place. The screw bar is at the reactor's upper section, around which the feed oil is vaporized. Under the bar there is a isothermal section, the length is about 7 cm. where the catalyst is to be loaded. At the bottom, liquid product is collected in receiver bottle by pass through a long needle that is joined with the receiver bottle by rubber tube, the bottle is immersed in the condense well filled with ice and water. A medical syringe needle sticks into the rubber tube, through it the cracking gas exits.

C.1.2 Feed Oil Injection System

This includes the injection pump, the six-ways valve and the feed oil bottle. It is used to smoothly inject 1.56±0.01 g. feed oil into the reactor within 70 sec.

C.1.3 Stripping System

It includes the pressure regulator, the gas-flow regulator, pressure gauge and rotary flow-meter. The function of this system are:

1. Pre-stripping: The nitrogen stripping before oil injection can ensure the catalyst is in the nitrogen atmosphere and water-free

2. Post-stripping: After oil injection the nitrogen stripping can get residual oil in the tuber into reactor and strip out all reaction production from reactor.

C.1.4 Measurement and Control System

The system includes the temperature controllers, the solenoid valves and the programmable logic controller(PLC). the two temperature controllers are the same, one indicates the catalyst bed temperature, the other one a controls temperature of the furnace. They are intelligent controllers produced by Shimandan (Shimudzu), Japan, with PID self tuning, automatic cold conjunction temperature compensation, thermocouple linearisation and deviant correction. Due to unique of the furnace manufacture technology, the reactor has more than 7 cm. long isothermal catalyst bed with only one heater.

The PLC controls the injection pump and the six-port valve. The operating procedures are as follows (refer to Figure C-1):

1. Preparation step: If the nitrogen source is supplied, when the power switch turns on the PLC will draw the six-port valve to the position shown by the dotted lines. That is the pre-stripping.

2. Oil injection step: After the reactor bed temperature has stabled, push the "start" button, then the six-ways valve will turn to the position shown by the solid lines, the syringe plug goes forward, the feed oil is injected into the reactor through the six-ways valve.

3. Oil suction step: After 70 seconds of oil injection, the six-ways valve turns back to the dotted lines position. Then post-stripping begins and syringe plug goes backward, the feed oil is sucked into the syringe from the feed oil bottle.

4. Squeezing step: When the oil-suction has lasted for 70 seconds the syringe plug goes forward again for 20 seconds to squeezing out gas bubbles.

5. Post-stripping: When post-stripping lasts about 10 min. the speaker song music, the system goes back to the preparation step again. In order to keep the syringe plug always stay at a certain position, only in this period the reset button is enable.

C.2 PC Work Station (Option)

C.2.1 Functions

PC work station is designed to work with WFS-1D to change and save test parameters, remote control, print report, display the history or real time trace of process variables. It is linked to the test unit through a serial communication card, but the test unit can work independently.

C.2.2 Operations

C.2.2.1 Start up

1. Enter Windows 3.11
2. Double click Group WFS-1D
3. Double click the icon WFS-1D of the group
4. Input the operator's name and click "OK" then go into the working window

C.2.2.2 Operations in the main working window:

1. To change the temperature controller's parameter: There are two temperature controllers. The upper one is used to indicate the reaction temperature, the lower one is used to control the furnace's temperature. The set value can be changed on it's window, click "SV" to send it to the controller. The PID parameters can be changed by click the "PID", click the PID diagram blank place can close the PID window.

2. To change the operation time parameters: there is operation time table on the right of the main working window. The feeding time (T1), sucking time (T2), preparing time (T3) and purging time (T4) all can be changed. The ranges are:

$0 \leq 1 \leq 150s$

$T1 \leq T2 \leq T1+30s$

$T3 = T2 - T1$ (s)

$T4 \leq 991 - T1$ (s)

After they are set or changed, click "OK" then click "SEND" , these parameters can be send to PLC of the test unit.

C.2.3 Commands

There are several command blocks at the main working windows button:

1. "RUN" : begin to run.
2. "RESET" : to reset the system.
3. "EXIT" : to quit from the main working window.
4. "SAVE" : to save the parameters onto the system's hard disk.
5. "LOAD" : to load the parameters from the system's hard disk.
6. "QUIT" : to quit from the WINDOWS.
7. "CALCULATOR" : to use system's calculator.
8. "REPORT" :to print test report. Each report can contain two test reports.

According to the prompt input parameters, and then click "OK", the computer can calculate out the needed parameters, and then click "PRINT" and the report can be print out. Click "EXIT" to quit from the window.

9. “TRACE” : to display the temperature’s trace. In this window there are several command blocks.

- “HISTORY” : to display history traces, the test number can be selected by click “SELECT” and “TIME”
- “SET SCALE” :to set the temperature’s scale by input the minimum / maximum temperature.
- “EXIT” : to quit from this window.

C.3 Gas Chromotography Set and Integrator

The G.C. is Shimudzu GC - 14B, the intergrator is Shanghai HP 3295. For the use of detecting cracking catalyst microactivity index, the conditions in analysis are

Carrier gas : nitrogen (OFN), flow rate: 35 - 40 ml / min

Combustion gas : hydrogen, flow rate: 40 ml / min

Auxilliary gas : air, flow rate: 400 ml / min

Temperature of vaporization chamber (injector): 280 ^{o}C

Temperature of detector chamber : 280 ^{o}C

Temperature of column chamber : rises from 35 ^{o}C to 80 ^{o}C by rate of 15 ^{o}C / min., then rises from 80 ^{o}C to 235 ^{o}C by rate of 8 ^{o}C / min, hold at 235 ^{o}C for 10 min.

Sample injection volume : 1μl

Range : set to 10^{2}

The recommended integrator’s parameters are:

Attenuation : 8

Half - peak width: 0.04 min. after 1.5 min. changes to 0.16 min.

Use Integrate function 14 to sum up all the peak areas (%wt) before C12 (including C12). It is the cut point of gasoline and feed oil (gas oil or diesel oil). Use integration function 5 to set the base line horizontally.

C.4 Preparation Before Operation

C.4.1 Reactor's Temperature

In order to have the reactor's catalyst bed temperature correctly indicated, its thermocouple should be calibrated regularly (half or one year) with standard or recently calibrated thermocouple and standard differential potential meter. The deviation value should be input into the temperature controller.

The catalyst bed temperature of the reactor should be controlled at 460 ± 1 °C. It can be obtain by adjusting the furnace temperature controller's set value.

C.4.2 Tested Catalyst

In order to have the test catalyst correctly weighted, before load it into reactor it should be dried in oven for an hour at 110 - 120 °C.

C.4.3 Feed Oil

Heavy oil isn't suitable for this apparatus.

C.4.4 Feed Oil Weight Calibration

In order to have a correct injected oil weight, it is suggested to calibrate the weight every day before experiment. The method is to insert the joint to a small bottle, then push the " start" button, when the squeezing step has finished, push the " reset" button and weigh the bottle. If the oil weight is not 1.56 ± 0.01 g, adjust the pump's speed and calibrate again.

Example Calibration of the feed pump.

Feed oil: standard gas oil (RIPP)

Flow rate ml/ min	1.52	1.52	1.52	1.52	1.52	1.52	1.52
Measured Value (g)	1.569	1.571	1.563	1.557	1.556	1.556	1.559
average = 1.562 g							

C.4.5 Material Balance Test

In this test the cracking gas is not collected and the coke deposit is not detected either, so in practice test the material balance is not done. The material balance test here is like this: Instead of using catalyst, use quartz sand to do the same process as with catalyst, weight the collected oil, it should be more than 98% of the injected feed.

Example Blank test for checking liquid recovery

Feeding amount (g)	1.562	1.562	1.562	1.562
liquid Recovery (g)	1.547	1.567	1.558	1.537
Balance (loss, g)	0.015	- 0.005	0.004	0.025
% recovery	99.0	100.32	99.7	98.4

C.5 Operation Steps

1. Adjust the gas tank pressure to 0.30 - 0.35 MPa and then turn on the power switch, WFS - ID goes stripping status automatically.
2. Put some quartz fiber at the reactor's bottom, weight 5 g. of catalyst and load it into the reactor. Put the reactor into the furnace and link it to the six-port valve.
3. Link the collect bottle to the reactor with rubber tube and then put the bottle into the ice-water well.
4. When the reactor's temperature has stabled for 5 min., push the " start " button then the unit work in automatic for injection, suction, squeezing and post-stripping. After 10 minutes stripping, the speaker sings music indicating that the test has finished.
5. Take off the collect bottle and wipe out the water on the bottle, weigh the bottle and note down the collected oil weight, put it in a refrigerator for G.C. analysis
6. Take out the reactor from the furnace and take out the catalyst.

C.6 Analyses of Reacted Product and Aata Disposal

The liquid product is analyzed with G.C, and then calculated the MAT with program WFS-1D

C 6.1 Find the cut point of gas oil and the gas oil:

Put a little standard n-dodecane ($CH_3(CH_2)_{10}CH_3$) into the mixture of gasoline and the standard feed oil or used only standard n-dodecane, Analyze the sample with G.C., The n-dodecane retention time is the cut pint (n-dodecane belongs to the gasoline)

C.6.2 Calculation the microactivity index:

Put weight of feed oil, weight of liquid product, gasoline area (%wt.) in program WSF-1D in report command, it will calculate the MAT index.

$$\text{Conversion (MAT)} = 100 - [(\frac{100-A}{C})\text{x}B]$$

Where:

A = Gasoline yield, analyzed by GC ,%wt

B = Liquid product from MAT, g.

C = Feed oil, g.

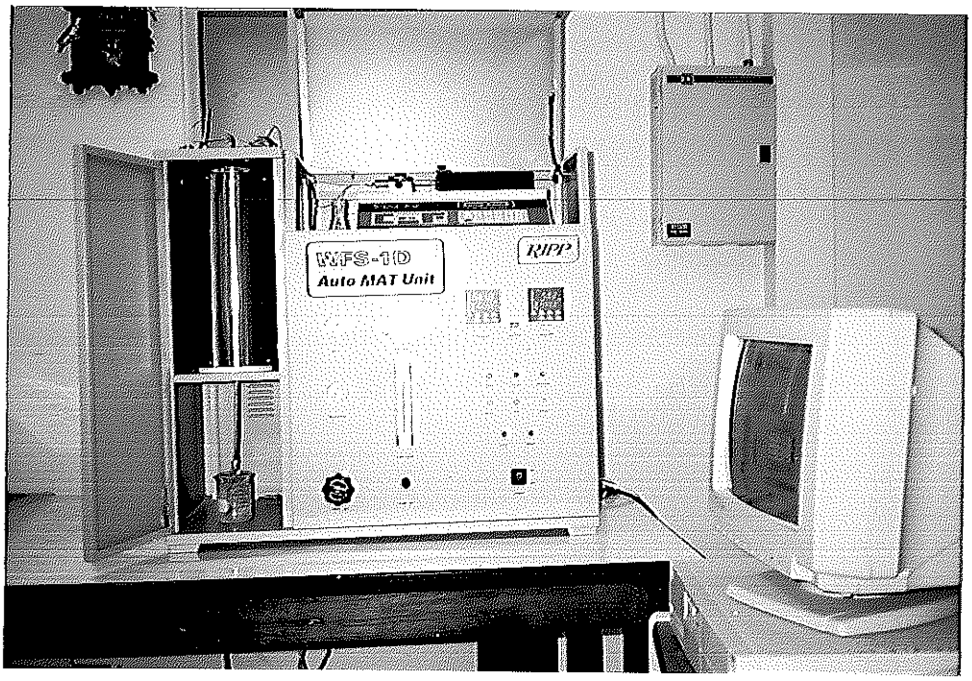


Figure C-2 Microactivity test unit

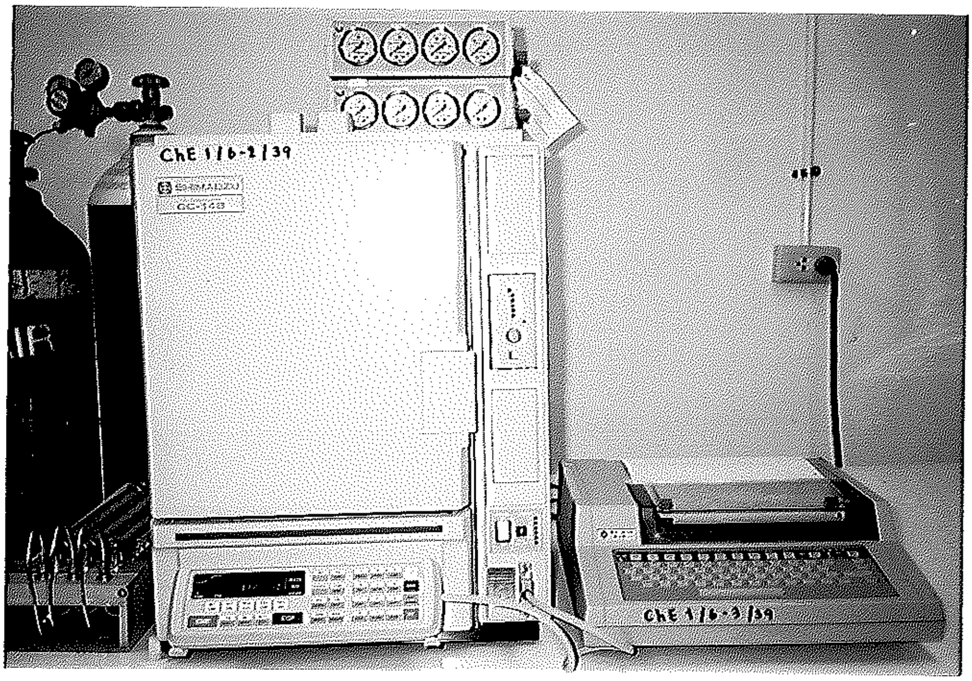


Figure C-3 Gas Chromatograph unit

Example : Find the MA (%wt) of catalyst A8

1. Gasoline cut point : Analyze the mixture of gasoline + gas oil + standard n-dodecane or pure n-dodecane with Gas Chromatograph

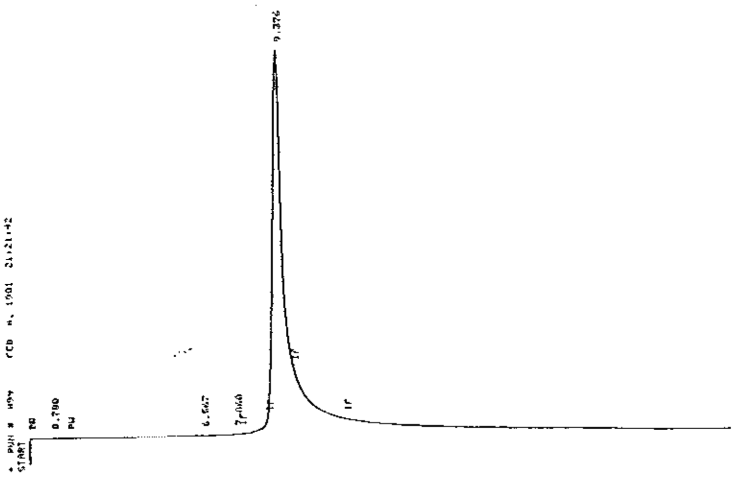


Figure C-4 Chromatogram of n-dodecane (n-C_{12})

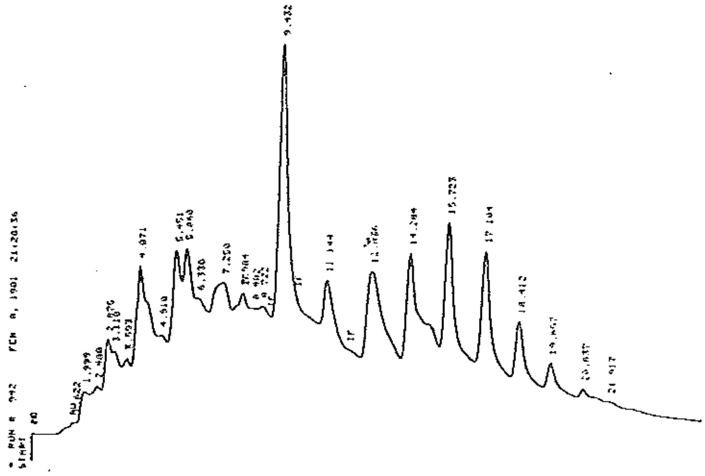
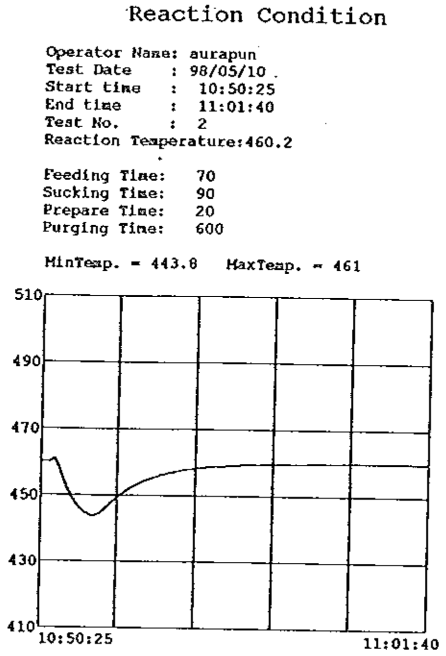


Figure C-5 Chromatogram of mixture of gasoline+gas oil +n-dodecane (n-C_{12})

From Figure C-4,C-5 ,the retention time of gasoline cut point is about 9.4

2. Reaction of catalyst with gas oil: let catalyst A8 to react with Fang-gas oil in MAT unit



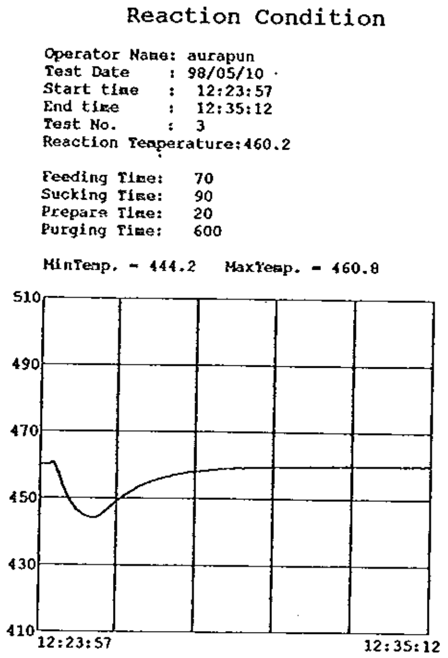
```
Reaction Condition

Operator Name: aurapun
Test Date     : 98/05/10
Start time    :  10:50:25
End time      :  11:01:40
Test No.      :  2
Reaction Temperature:460.2

Feeding Time:    70
Sucking Time:    90
Prepare Time:    20
Purging Time:    600

MinTemp. = 443.8    MaxTemp. = 461
```

Figure C-6 Temperature profile of sample A8.1



```
Reaction Condition

Operator Name: aurapun
Test Date     : 98/05/10
Start time    :  12:23:57
End time      :  12:35:12
Test No.      :  3
Reaction Temperature:460.2

Feeding Time:    70
Sucking Time:    90
Prepare Time:    20
Purging Time:    600

MinTemp. = 444.2    MaxTemp. = 460.8
```

Figure C-7 Temperature profile of sample A8.2

3.Gasoline yield (gasoline area, %wt) : Analyze liquid product from MAT unit with Gas Chromatograph

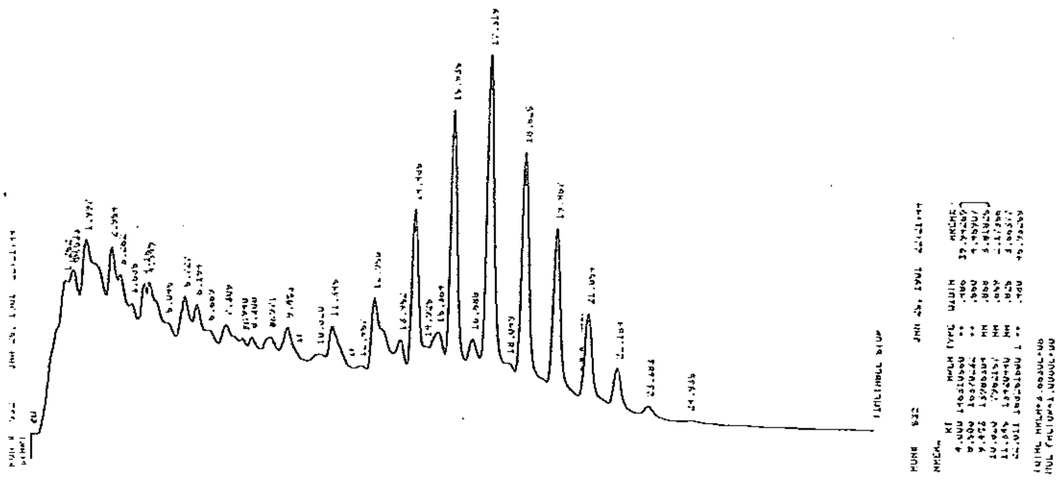


Figure C-8 Chromatogram of sample A8.1

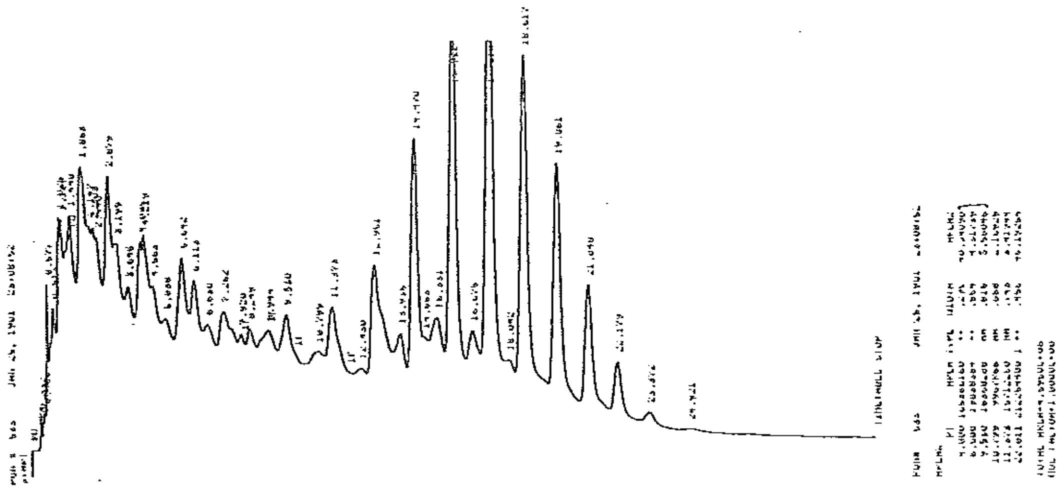
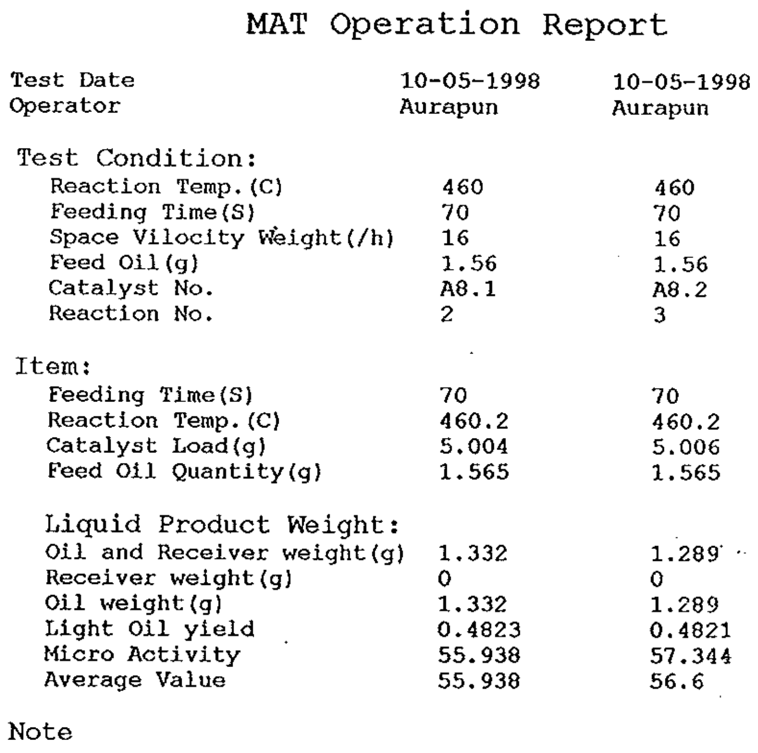


Figure C-9 Chromatogram of sample A8.2

4. Put the gasoline yield (gasoline area, %wt), liquid product yield, liquid product weight in program WSF-1D in report command.



```
                    MAT Operation Report

Test Date                          10-05-1998     10-05-1998
Operator                           Aurapun        Aurapun

Test Condition:
   Reaction Temp.(C)                  460            460
   Feeding Time(S)                    70             70
   Space Vilocity Weight(/h)          16             16
   Feed Oil(g)                        1.56           1.56
   Catalyst No.                       A8.1           A8.2
   Reaction No.                       2              3

Item:
   Feeding Time(S)                    70             70
   Reaction Temp.(C)                  460.2          460.2
   Catalyst Load(g)                   5.004          5.006
   Feed Oil Quantity(g)               1.565          1.565

   Liquid Product Weight:
   Oil and Receiver weight(g)         1.332          1.289
   Receiver weight(g)                 0              0
   Oil weight(g)                      1.332          1.289
   Light Oil yield                    0.4823         0.4821
   Micro Activity                     55.938         57.344
   Average Value                      55.938         56.6

Note
```

Figure C-10 MAT operation report.

Appendix D: Determination of The Unit Cell Dimension by X-ray Diffractometer

D.1 Appratus and Reagents

1 X-ray diffractometer

- Model X' Pert-MPD
- Scan at 0.25 $^{\circ}2\theta$/min
- Anode material : copper tube

2 Drying Oven, set at 110 $^{\circ}$C

3 Hydrator, maintain at 35% relative humidity by a saturated solution of anhydrous calcium chloride ($CaCl_2$) maintain at 23$\pm$3 $^{\circ}$C

4. Silicon powder

D.2 Procedure

1. Place 1 g. of powdered catalyst sample in the drying oven at 110 $^{\circ}$C for 1 h.

2. Blend 1 g. of powered catalyst sample with about 0.05 g. of silicon in a motar and grind until intimately mixed. Place a thin bed of the mixed sample in the hydrator for at least 16 h. Some samples may be require a longer equilibration time. Pack the hydrated sample in the diffractometer mount

3. Determine the X-ray diffratometer pattern across range from 53 to 60 $^{\circ}$ 2θ .

4. Measure the angle of the zeolite reflections at about 53.4° and 57.8 $^{\circ}$ 2θ and that of the 56.1° silicon reflection to at least two decimal places.

Note: when low intensity prevents use of these high-angle reflections, as for example with equilibrium catalysts containing rare earth elements, measure the strong zeolite reflection near 23.5, 26.9 and 31.2 and the silicon reflection at 28.443 $^{\circ}$ 2θ

D.3 Calculation

1. Correct the measured reflection angles for the zeolite by adding the correction factor to each the quantity (Calculated minus measured angle of the silicon reflection).When the silicon reflection of CuK α_1 radiation is measured, the calculated angle is 56.123 $^{\circ}$

Note: The corresponding calculated angles when lower angle reflections must be used is 28.443 ° 2θ ($CuK\alpha_1$)

2. Convert the corrected angles of reflection to d-spacing values using the equation:

$$d_{hkl} = \lambda / 2\sin\theta$$

Where:

d_{hkl} = distance between reflecting planes having the Miller indices hkl,(nmx10),and

λ = wave length of X-ray radiation which is 1.54060 °A for $CuK\alpha_1$ Note that the angle used in this calculation is only θ.

3. Calculated the unit cell dimension, *a*, of the zeolite in catalyst using the equation

$$a = \{(d_{hkl})^2(h^2+k^2+l^2)\}^{1/2}$$

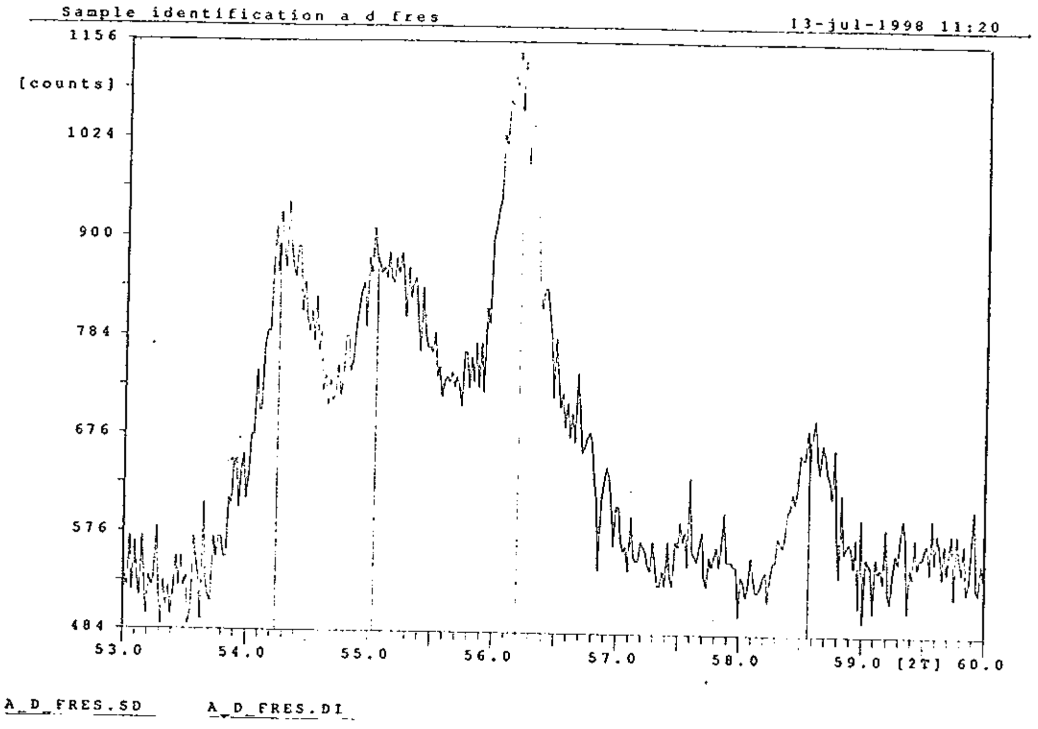
Where the sum $(h^2+k^2+l^2)$ of respective zeolite reflections has the following values

Reflection	$(h^2+k^2+l^2)$
57.8 ° 2θ	243
53.4 °	211
31.2 °	75
26.9 °	56
23.5 °	43

Note: Certain components of a catalyst matrix can interfere with individual peaks. For example, quartz may interfere with the reflection at 26.9 °. when an interference occurs, other reflections should be used in the calculation.

4. Average the valued of *a* calculated from more than one reflection.

Example Catalyst D (fresh catalyst)



```
File: C:\APDW\DATA\A_D_FRES.DI
==========================================================================
Philips Analytical                                PC-APD, Diffraction software

          D I  F I L E :

               Sample identification: a_d_fres

                       DI file name: A_D_FRES.
                    Input file name: A_D_FRES

                 Start angle [°2q]: 53.010
                   End angle [°2q]: 59.990
                Start d-value ,[Å]: 1.72606
                  End d-value  [Å]: 1.54083
           Maximum number of counts: 562

                    Anode material: Cu
                a1 Wavelength  [Å]: 1.54060
                a2 Wavelength  [Å]: 1.54439

          Intensities for FIXED slit

         Peak positions defined by: Minimum of 2nd derivative of peak
            Minimum peak tip width: 0.00
            Maximum peak tip width: 1.00
           Maximum peak base width: 2.00
              Minimum significance: 0.75
                   Number of peaks: 4

         D I F F R A C T I O N  L I N E S :

  Angle     d-value     d-value T.width  Height  Backgr. Rel.int. Signific
  [°2q]     a1 [Å]      a2 [Å]   [°2q] [counts] [counts]   [%]
 -------   ---------   --------- ------- ------- -------- -------  --------
 54.245     1.68965     1.69380   0.280     357      534    63.6      4.62
 55.040     1.66711     1.67121   0.480     342      534    60.9      3.56
 56.200     1.63542     1.63944   0.280     562      538   100.0      6.83
 58.565     1.57488     1.57876   0.320     132      548    23.5      3.76
```

Figure D-1 X-ray diffraction pattern of catalyst D-fresh

Calculation

Degrees 2θ			
Measured	Corrected	$(h^2+k^2+l^2)$	(a, Å)
54.245	54.168	211	24.576
56.200	56.123	silicon	-
58.565	58.488	243	24.579
			average 24.577

Note: the correction factor in the above calculation is {56.123 (calculated for Si) - 56.200 (measured) = -0.077 °} and is simply added to the measured angle of the two zeolite reflections.

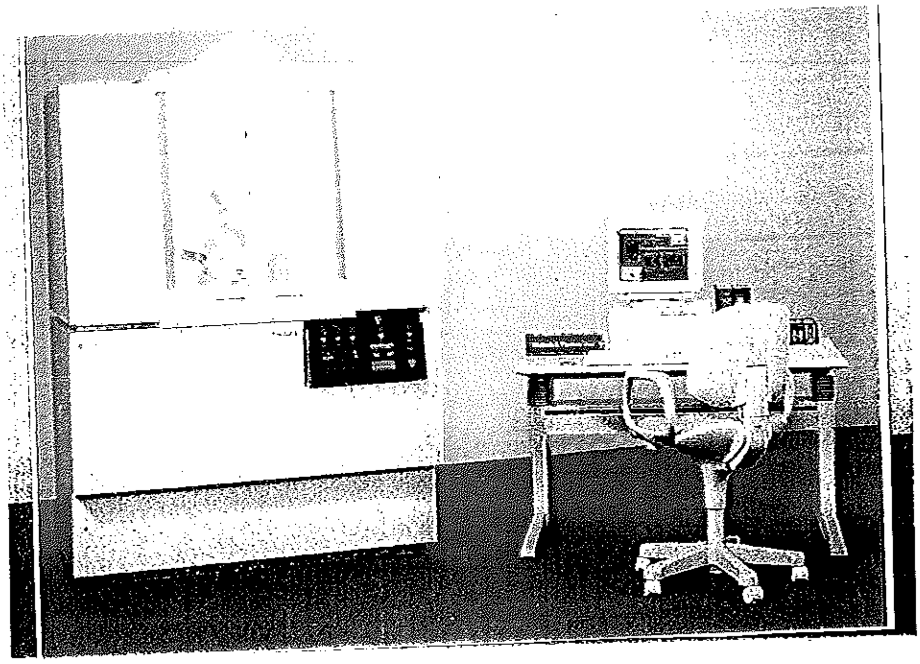


Figure D-2 X-ray diffractometer

Vitae

Name	Aurapun Angkasuwan
Birth Date	May 21, 1970

Educational Attainment

Degree	Name of Institution	Year of Graduation
B.Sc.(Chemistry)	Prince of Songkla University	1993