經濟部暨所屬機關因公出國人員報告書
（出國類別：參加亞洲煉油技術(ARTC)研討會）

報告書

出 國 人：服務機關：中國石油公司
職務：主 任 廠 長
姓名：林俊雄 朱少華
出國地點：馬來西亞
出國期間：90年3月5日至3月10日
報告日期：90年5月8日

一、出國任務：

一)參加 ARTC 煉油技術研討會，並發表論文。

二)參加 EXXON-MOBIL 燃料與滑油技術會議。

三)拜訪新加坡 SPC 石油公司。

二、拜訪紀要：

日期	地點	工作內容
90.3.5	高雄(台北)→新加坡	啟程
3.6	新加坡、吉隆坡	上午拜訪新加坡 SPC 油公司，下午赴吉隆坡
3.7	吉隆坡	參加 EXXON-MOBIL 燃料與滑油技術會議
3.8 至 3.9	吉隆坡	參加 ARTC 煉油技術研討會，並發表論文
3.10	新加坡→高雄(台北)	返程

三、工作概述：

一)拜訪新加坡 SPC 石油公司

先拜訪本公司駐新加坡代表梅加禮先生，渠為充份配合掌控承租油輪業務，以利各煉廠規劃所需原油，如期從中東、西非等地運達國內，確實非常忙錄，一切運作良好，並在渠安排下一同赴 SPC 石油公司拜訪，並蒙許萬興和胡兆禎二位副總經理和何文輝企劃經理等人接待下知悉該公司業務，據許副總稱，該公司日煉量為 27 萬桶，係由當地 SRC 和荷蘭 SHELL 及英國 BP 等三家油公司，共同合資建立，各持 40:30:30 比例股權，總共資金產值計為 27 億美元。惟目前 BP 公司想抽回資金，放棄持股，因此正詢問有興趣者接手，並告知此項訊息。若本公司有意可設法把 BP 持有 8 億美元股權，壓低至 3 至 4 億美元供參考。據悉其背景係因目前煉油加工毛利降低至每桶一塊美元左右，主要是該公司油品皆以外銷為導向，如銷至印度、日本等國，可是最近印度在 Reliance 工業區興建煉油廠，導致進口量銳減，以及韓國油品傾銷至日本等地，結果造成煉油廠毛利降低；另據胡副總稱，該公司目前與本公司仍有業務關係，即從本公司每年購買四千噸柏油及八萬噸 Bunker Oil，轉銷亞洲市場。衷想，本公司面對國內油品自由開放進口，過剩油品需速訂定外銷策略，如 SPC 油公司係以外銷為導向並業已建立良好之油品銷售網路和信息，應可考慮與該公司合作共同打開油品銷售網，並請駐新加坡單位協力評估配合。

二)參加 EXXON-MOBIL 燃料與滑油技術會議

本研討會主要是該兩公司去年合併後，各把該公司以前持有煉油技術，包括燃料(EXXON 擁有)，和滑油(MOBIL 擁有)等技術，正式對外公開介紹並提供有興趣公司參考。

1)在燃料方面：

主要針對全球各國未來汽、柴油及燃料油等油品，所訂環保規範日嚴，如汽油中硫含量，目前美國為 500PPM、加州 30PPM、歐洲共同市場 150PPM 、日本 100PPM、及韓國 200PPM 等；而 2 至 5 年內需降為：美國 30PPM(2006)，加州 15PPM(END2002)、歐洲共同市場(EU)50PPM(2005)、日本 30 至 50PPM(2005)等。另外汽油中不飽合煙含量亦加限制，美國 25VOL%、加州 4VOL%、歐洲 18VOL%、日本未定、韓國 23VOL%等。故各油公司面對上述兩項環保法令限制下，必須規劃配置新的加氫處理裝置，並且避免加氫過當致辛烷值降低所造成之損失及操作成本最低原則下等，作最適調整。EXXON-MOBIL 即藉著此研討會介紹三個相關技術供參考。

(1)SCANFINING：可將媒裂汽油硫含量降至 10PPM，而 RON 僅受些微損失，已有工業化製程。

(2)OCTGAIN：可將媒裂汽油硫含量降至 10PPM，而 RON 未受損失，本製程 EXXON 已操作六年，壓力為 600PSI，C_5^+產率 80 至 97%，且兼產 LPG。

(3)硫酸烷化製程：主要係 iC_4 與 $C_4^=$和 $C_5^=$等之烷化反應，相對降低不飽和烷煙量，和 $C_5^=$ 引起 RVP 過高困擾，台塑六輕烷化工場就採該製程。

2)在滑油方面：

目前全球製造基礎油技術，雖已演進由傳統溶劑法 GROUP I(包括溶劑脫芳香煙和脫臘、脫柏油)，晉昇至完全觸媒法 GROUP II、III(包括氫裂和加氫異構化脫臘等)。MOBIL 公司具有以上生產技術，且配合業者要求，在市場導巷下，亦可採用溶劑和觸媒種混合法。因兩者各有優劣點，故本公司擬於桃園廠興建日產 5000 桶潤滑基礎油工場，則朝媒裂法，可資參考。

三)參加 ARTC 研討會並發表論文

1)本項研討會類似美國 NPRA 煉油技術研討會性質，因此與會人員包括從事煉油業的策略規劃、管理、技術、建造與操作等專家與會，計約 180 至 200 會員。遍佈來自亞洲、中東、歐洲、美國等地區，大陸亦派一團人員與會且發表論文。本項會議主題主要包括如下：

(1)全球主要地區汽、柴油品近 1 至 5 年內環保規範及趨勢因應

主要將汽、柴油硫含量降至 10 至 15PPM，成為乾淨綠色油品(GREEN PRODUCTS)，確是煉油公司一大挑戰，大家思考、交換如何調整因應。

(2)面對環保要求，最新發展煉製技術

主要係針對各汽、柴由品摻配餾份中，引起污染較顯著部份，作最適處理，如汽油中硫含量主要來自媒裂汽油部份；而柴油亦來自媒裂 LCO 油料等。故各技術提供公司，皆朝此方向發展，提供煉油業者，作需求選擇，以降低無利潤環保投資費用。

(3)煉油工業如何投入較少投資，獲取較高利潤、策略及實例

如 JGC 提出工場用地最適規劃利用，約可節省區域內及區域外用地達一半左右；以及 KBC LP 軟件技術與日本 KAO 油公司合作實例。以上兩項實例本公司三煉廠可資參考。

2)發表論文

主要是針對本公司面對民營化和國內油品市場開放等轉變環境下，未來必需與外界地區接觸更為緊密，除了業務人員前往接洽外，亦要宣傳讓外界地區認識本公司在煉油技術程度上是很高，設施及位置均良好，可資合作如委煉並行推廣。

(1)發表題目為「A CASE STUDY：Detection of the coking temperature of crude oil by thermal analysis for use as an operating guide in the vaccum unit」如附

結果被與會者肯定，如巴基斯坦油公司執行副總 RAZI 先生，當面評語為論文最佳發表者，並來函要求演講文稿。發表後 ARTC 並經調查，來函回應本項發表備受與會者評價甚高。希能提供明年續辦，本項會議之建議與地點初步回應建議在台北。

（2）此外大林廠朱廠長另安排推薦於四月份本公司「重油脫硫技術研討會」，再作發表，結果亦備受參與同仁肯定，對設計與操作提供最適參考資料，尤其是加氫處理和媒裂最適溫度選擇。因工程設計公司僅提供操作範圍，而對其提昇操作裂解度會產生何種影響及理由皆未敘述，本論文可把上述資訊作一整体詳述。

四、結論與建議

一)新加坡 SPC 油公司，具有以外銷為導向行銷網，本公司除柏油、船用高硫燃油等二種油品與該公司有建立業務合作關係外，應可擴大至柴油等過剩油品外銷業務上，以增加外銷管道。

二)EXXON-MOBIL 燃料與滑油技術經驗

面對油品環保新規範，值得更實地去接觸瞭解，以資參考和因應油品無國界行銷策略。

三)亞洲 ARTC、與歐美 ERTC 及 NPRA 煉油技術會議，性質相近，係一從事煉油業者交換經營策略、技術和操作等經驗國際主要會議，值得本公司每年選派人員與會，以獲取重要相關資訊，其效益應是正面。

A case study：Detection of the Coking Temperature of Crude Oil by Thermal Analysis for use as an Operating Guide in the Vacuum unit

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Abstract

By thermal analysis method including TG、DTA and DSC, the coking temperature data of the crude oil (AH、KC、IL、OM、DJ、Nkossa)，reduced crude and vacuum residue can be easily detected. It shows three kinds of thermal behavior such as no weight loss, temperature rising and exothermic reaction occur at the same temperature range 370℃ to 390℃. The above phenomena are similar to the coking reaction and being considered as the coking temperature of the crude oil.

A corresponding test is further performed to trace the composition change for 1 to 3 ring aromatics. It shows that at the coking temperature the content of 1-2 ring aromatics decreases and 3 ring aromatics increases. The mechanism is similar to aromatic condensation reaction.

The above results are well used to improve the yield of VGO and control the penetration point of vacuum residue for asphalt purpose in vacuum unit.

Keyword：Crude Oil, Coking Temperature, Thermal Analysis, Exothermic reaction

1.Introduction

The motivation of this research is come from the suggestion of the plant site Taoyuan Refinery (TOR) . It has two topping unit (100,000 B/D x 2) to treat high sulfur (2.0wt$^+$%) and low sulfur crude (1.0wt%-) respectively. The bottom cut of the high sulfur crude or reduced crude is further treated by a vacuum unit (36,000 B/D) to reCOVER much more distillate. and the residuum directly as asphalt uses. The LVGO, HVGO, SWO and 85~100 penetration asphalt (AC-10) are its main products as Fig.1. Due to the market demand new high grade asphalt (AC-20) ,so there is a team needed to find out the following data:

1) What is the coking or carbonization temperature of the selected crude oil and its heavy components and how to measure it?
2) What is the mechanism of the coking formation and how to avoid it?

Basically, the coking or carbonization behavior of Hydrocarbon belongs to the polymerization of reactive components in the crude oil or reduced crude. Hydrocarbon polymerization is a new bond formation which will show certain characteristics during reaction such as no volatile weight loss and exothermic relatively. But oppositively for the cracking phenomena is belong to the bond cleavage and will show weight loss with its cracked volatile part and endothemic effects. Distillation is mainly by heat as separating agent. Therefore by the same function of thermal analysis including TG, DTG, DTG, DSC and corresponding bench test might be combined together to make that study.

This report is to show its results and further applications for the related unit as a reference.

2.Experimental

(1) Materials

- Six whole crude oil slates include two high sulfur i.e. AH, KC (2wt%$^+$ S) , two medium sulfur i.e. IL, OM (1.0~2.0wt% S) and two low sufur Djeno, Nkossa (1.0wt%$^-$ S) . Their principal characteristics are given in Table 1.
- Two high sulfur-reduced crude and its vacuum unit products, such as LVGO, HVGO and asphalt are taken to make further study.

(2) Methods

- Thermal analysis

Simultaneous TG-DTG-DTA-DSC measurements were conducted in a TGA 2950TA instrument and high temperature DSC-404 NETZSCH analyses interfaced with data acquisition and processing system. Samples Size of crude and its derivatives are taken about of 7~14mg. Pyrolysis experiments were carried out under 99.995% pure nitrogen at a flow of 100cc/min with heating rate of 10℃ per minute over the temperature range 25~700℃.

- Bench scale test

An autoclave of Parr 4842 model with 350c.c. capacity was served as a pyrolyzer for the reduce crude. The reaction temperature kept at 330~350℃ and under 1kg/cm^2 N_2 pressure.

The composition of reduced crude and its derivatives were analyzed by TLC-FID Iatroscan model MK-5. For the cracked gases were analyzed by GC.

Table 1 The main physical properties of crude oil and its reduced crude in TOR

Name	API,60°F	S wt%	C.C.R. wt%	wt% at TBP400℃
AH	27.5	2.92	7.9	41
KC	30.5	2.55	5.8	50.5
IL	33.1	1.53	3.50	56
OM	34.2	1.01		52
Djeno	28.0	0.29		40.5
Nkossa	49.1	0.025		67.2
AH-RC	14.8	3.30		22.4
IL-RC	15.3	3.17		25
Asphallt (AC-10)	5.9			0.5

3.Results and Discussion

(1) AH crude oil and its heavy parts thermal behavior

- Fig.2 shows the TG and DTG curves of AH high sulfur crude. For the relationship of weight loss with heating temperature, there are two maximum weight loss rate peaks temperature , one at 0.2811% /℃ or 225.36℃, the other at 0.2842% /℃ or 427.92℃ respectively. For the first one, it means by physical vaporization of light ends such as naphtha and some distillate. The second peak is by chemical further decomposition or cracking of some unstable heavy ends to become volatile light parts.

Correspondingly, there are also two no weight loss plateau at 363.39℃ and 500℃ respectively. The first temperature (363.39℃) means the chemical reactive components in the feed crude such as olefins polymerization or aromatics condensation. But there are usually no olefin components in the crude, so the condensation of aromatics is related. The second temperature (500℃) gives much higher aromatics condensation to become solid coke.

- Fig.3 shows the DSC curve of AH crude. For the endo and exo enthalpy change with temperature variation, there are three plateau : 371.3 (endo to exo), 483.0 (exo to endo) and 527.3 (endo to exo) ℃. It means at those temperature range, there are in series occurring chemical reaction to generate much more amount reaction heat in the system than the regular heat needed. Basically the New bond formation will generate the reaction heat or called exo thermal reaction such as condensation, polymerization or coking. Connection the new bond formation at 371.3℃ with the no weight loss phenomena at 363.39℃ in Fig. 2 together, the two temperatures are very closely. It might explain at that temperature interval the reaction behavior belongs to the aromatics condensation reaction with dehydrogenation. Therefore the weight loss effect of hydrogen to the system seems not very sufficient and nearly keeping constant. So based on the above occurring behavior, the temperature interval could be assigned as the so-called coking temperature or the primary coking temperature of the AH crude oil.

  Following the same reaction behaviors, the second temperature interval between maximum weight loss rate 429.9℃ and exo to endo temperature 483℃ might be thought as the primary cracking temperature The temperature interval between 500℃ (no weight loss) and 527.3℃ (endo to exo) might be thought as the secondary coking temperature of higher aromatic rings condensation of the crude oil to generate much more reaction heat released. Then it will become completely coking of the feed crude.
- Fig 4 shows the TG and DTG curve of AH reduced crude. There are two maximum weight loss rate stages at 276.0℃ (0.3429%/℃) and 435.7℃ (0.3802%/℃) respectively. The first temperature 276℃ means the vaporization of the distillate such as gas oil cut and a litter bit higher than225.6

℃ fig.2. The second one at 435.7℃ is also caused by decomposition or cracking of heavy parts to become volatile components.

Correspondingly, there are also two no weight loss plateaus at 372.08℃ (0.2426%/℃) and 500℃. Both temperatures locate at same range as its original crude. The reason is the reduced crude still retained its non-distilled heavy parts.

- Fig.5 shows the DSC curve of AH reduced crude for the endo and exo enthalpy change with temperature, there are also existing three plateau: 401.2 (endo to exo), 459.1 (exo to endo) and 511.6 (endo to exo) ℃, It meams at those temperature range some ractions occurring. The first endo to exo temperature 401.2℃ is corresponding to the first no weight loss temperature 372.1. The second exo to endo temperature 459.1℃ is the same respond to maximum weight loss peak 435.7℃ and the third endo to exo temperature 511.6℃ is responded to the second no weight loss temperature 500℃. It proves the dehydrogenation and further polymerization showing the same reaction mechanism model.
- Fig. 6 shows the TG and DTG of LVGO from AH reduced crude. There is only one maximum weight loss rate at 200.69 ℃ (1.058%/℃) to respond the vaporization of some distillate in it. When the temperature further rising to 300℃, there is almost completely evaporated and the heavy part retained very small. The no weight loss temperature is around at 320 ℃.
- Fig. 7 shows the DSC curve of LVGO. There are two temperature range at (343.6℃ and 378.4℃) or 362℃ to change the heating behavior from endo to exo reaction for the retained small amount heavy part. It means the LVGO coking temperature is around at 362℃.
- Fig. 8 shows the HVGO'S TG and DTG curve. There is also only one maximum weight loss rate at 291.58℃ (0.8167%) Then after 350℃, the heavy part is only retained very small amount. The no weight loss temperature is around at 350℃.
- Fig. 9 shows the DSC curve of HVGO. There are two temperature range 416.8~451.6℃ and 533.2℃ for the endo to exo. It means the condensation temperature is started around at 411℃.

- Fig. 10 shows the TG and DTG curve of asphalt. The maximum weight loss rate at 400.1℃ (0.7321%). For the no weight loss temperatures are at 350℃ and 500℃.
- Fig. 11 shows the DSC curve of asphalt. There are two endo to exo temperature ranges, one 320℃, the other at 502℃ to 554.8℃, and one exo to endo temperature at 457.5℃. From the coking behavior phenomena, the asphalt's primary coking or condensation on temperature is at 335℃, then cracking at 400~435℃, finally the secondary coking temperature at 502 ℃.
- Fig. 12 shows the TG and DTG of LSFO (S 0.43wt%) from reduced crude for further hydroprocessing by RDS Unit. There are two maximum weight loss rate peak at 259.12℃ (0.3853%/℃)and 429.21℃(0.3210%℃). Correspondingly, there are also two no weight loss plateau at 372.08℃ (0.2323%/℃) and 500℃ .Comparing with its original feed Fig. 4, all are shown the same temperature patterns. It means the sulfur content don't have any effects to the coking behavior temperature variation.
- Fig. 13 shows the DSC of LSFO. There are two endo to exo temperature range at 407℃ and 503℃ respectively and one exo to endo temperature at 459.1℃. To compare with its feeding fig. 5, all temperature patterns are the same. It further means the reduced crude keeping the same with LSFO. So it could be used as the guide for RDS operation temperature guide.

(2) Thermal behavior of Djeno and Nkossa low sulfur crude

- Fig. 14 shows the TG and DTG crude of Djeno low sulfur crude (0.29wt%). There are two maximum weight loss rate at 256.52 ℃ (0.3082%) and 440.90℃ (0.3688%℃). The first one represents the physical evaporization of light ends in the crude such as naphtha and kerosene cuts. The second one means the decomposition or cracking of heavy parts to become volatile light parts. Correspondingly ,for the smaller or no weight loss temperatures are founded at 364.29℃ (0.2040%℃) and 500℃ respectively. Comparing with Fig. 2, AH high sulfur crude (2.92wt%)TG and DTG curve, both show the close maximum weight loss rate and no weight loss temperature ranges. It means the sulfur differences giving no effect to the coking temperatures.

- Fig. 15 shows the DSC curve of Djeno crude . For the endo to exo changing temperatures, there are distributed at 419.2℃, 503.2℃ and 540.4℃ . Those temperature ranges are almost the same as AH crude.
  vacuum unit.
- Fig. 16 shows the TG and DTG curves of Nkossa low sulfur crude (0.025wt%). There is one maximum weight loss rate at 104.61 (0.558%/℃) . It means the crude posses major amount of light ends such as naphtha, kerosene and diesel cut. Under 300℃ all those distillate are almost vaporized out and only retained small heavy part below 10wt%. So there is not shown the second maximum weight loss rate due to cracking under higher temperature. For the no weight loss rate., there are shown two platuo at 409.7℃ and 500℃ likely step change. It means the heat generation from the polymerization of small heavy parts not quite obviously.
- Fig. 17 shows the DSC curve of Nkossa crude . For the endo and exo changing temperature, it was founded at 475℃ and 492.4℃. From the above data, the coking temperature of Nkosaa crude is expected at 409~500℃.

The related feed and products thermal characteristic of vacuum unit in TOR are shown in Table 2.

Table 2.Thermal analysis of crude oil, reduced crude and asphalt

Name	API.60°F	S wt%	Condensation temperature, °C DTA (EXO)	 DSC (EXO)	 DTG (Const wt	Cracking temperature, °C DSC (ENDO)	 DTG (max wt loss
AH	27.9	2.85	346-383	371-383	363-380	483	429
KC	32.5	2.66	345-377.2	370-412	375		456
IL	33.8	1.35	341-375	340-375	370		454
OM	36.3	0.79	391	395	390		444
TY-Crude (IL 74vol%	32.8	1.88	339-369	378-405	378		456
TOR-RC (IL)	15.3	3.17	372-404	375-405	372		460
TOR-Asphalt (IL)	5.9	4.62	378-410	350-405	387		
Djeno	28.0	0.29		419	364	419	440

Nkossa	49.1	0.025		475	409		492
TOR-RC (AH)	15.3	3.30		401	372	401	435
TOR-Asphalt (AH)	5.9			335	350		400

(3) Bench test

This pyrolysis test is to further elucidate the composition variation of the reduced crude with temperature. The selected temperature ranges are at 330~350 ℃ followed the coking temperature measurement from DTG and DSC. Table 3 shows the temperature effect v.s. product aromatic type distribution of reduced crude. The cracked gases yield is 1.2wt/% (330℃) , 1.3 wt% (340℃) ,1.5 wt% (350℃) For their composition is mainly H_2 and C_1,C_2,C_3, C_4,H_2S, CO_2 etc.,Table 4.

H_2 content is kept at 2~3 ,Mol.%. It shows two important phenomenon, one is the cracking reaction very slightly, the other is the mechanism belong to dehydrogenation. This results explain the no weight loss information from TG,DTG test properly.

Table3. Temperature effect vs product aromatic type distribution of TOR's reduce crude (under 1kg/cm2 N2 initial pressure)

Run NO.	Feed	TOR-330	TOR-340	TOR-350	asphalt
Reaction time, minute	0	30	30	30	
Reaction temperature, °C		330	340	350	
Product yield, wt%					
liquid		98.6	98.5	98.4	
gas		1.2	1.3	1.4	
Liquid product composition, wt%					
saturates	28.8	30.1	27.3	26.7	9.3
aromatics (1 & 2 ring)	15.6	15.1	15.7	14.5	11.3
aromatics (3+ ring)	34.7	35.7	36.3	37.8	38.8
polars	20.9	19.1	20.7	21.0	40.6
Total recovery, wt%		99.8	99.8	99.8	

Table 4.Temperature effect vs cracked gases composition of TOR's reduce crude (under 1 kg/cm2 N2 initial Pressure 30 minutes)

Run No.	TOR-330 (17/19)	TOR-340 (17/15)	TOR-350 (17/171)
Reaction temperature ℃	330	340	350
Gas field wt%	1.2	1.3	1.5
Gas composition mol%			
H2	0.14	0.29	0.46
C1	0.94	1.79	3.12
C2	0.96	1.21	1.61
C2=	0.50	0.45	0.21
C3	0.31	0.93	1.19
C3=	0.21	0.34	0.46
C4 (n+iso)	0.19	0.46	0.79
C4=	0.11	0.28	0.67
C5 (n+iso)	0.23	0.45	0.92
C0	0.20	0.29	0.30
C02	0.40	0.78	0.62
H2S	0.17	1.02	0.67
N2	93.0	87.0	84.3
C6+	2.65	4.69	4.62

Fig. 18 shows the variation of liquid products composition at 350 ℃and under 1kg/cm^2 N$_2$ initial pressure. For the saturates part, its content is about 6.2wt% decline with time . But for the mono- and di-ring aromatics, it drops seriously to 22%. Correspondingly the tri ring and higher aromatic is increasing to 26wt%. It manifests 1~2 ring aromatic decreasing by dehydrogenation to become tri-ring aromatics by condensation, at the coking temperature.

(4) Mechanisum of the coke formation

Based on the above results, the coking mechanism of reduced crude is proposed as following:

Fig. 19 the coking mechanism of reduced crude

$$\text{Crude oil} \xrightarrow[370^{\circ}\text{C}]{\text{Condensation Reaction}} \text{Asphalt} \xrightarrow[520^{\circ}\text{C}]{\text{Polymerization}} \text{Coke}$$

Reduced Crude 1-2ring aromatics	3-ring aromatic $+H_2$	PNA $+H_2$ etc.
Heat of Reaction=	exo	exo

(5) Plant Site Application

Based on the coking temperature data, the vacuum unit becomes much more flexible to produce the two grade AC-10 and AC-20 asphalt. Their operation condition are as following Table 5.

Table 5 The Performance of Vacuum Unit at TOR

●Asphalt Grade	AC-10(85～100)	AC-20(50～70)
●Feed API 60°F	14.8	14.7
●Feed rate, B/D (kl/hr)	22,000(150)	18,300(120)
●Conditions :		
Vacuum,mmHg		
TOP	10.7	8.24
Flash Zone	24.4	19.1
Temperature,°c		
Furnace outlet	368	382
Flash zone	357.5	371.9
●Product,yield wt%		
LVGO	13.3	18.3
HVGO	39.7	39.2
SWO	2.6	5.7
Asphalt	44.9	36.8
●Asphalt quality		
Penetration,25°c,100g,5sec	98	50
Viscosity,60°c poise	1115	1919

4.Conclusions and Suggestions

(1) Thermal analysis including TG-DTG-DTA-DSC is a simple and fast method to detecting the coking temperature of the crude such as AH, KC, IL,OM,DJ, Nkaossa and its heavy part and derivatives, based on the minimum weight loss rate and endo to

exo temperature data. The primary coking temperature of the above crude are 370-390℃.

(2) The coking mechanism is mainly from the aromatic condensation of mono-di ring to tri-multi ring aromatic by dehydrogenation path.

(3) In order to upgrade the utilization of the crude oil heavy parts, A suggestion is proposed to include the coking temperature data in the crude assay from the suppliers.

5.References

(1).Lewis,I.C. etc"Studies of the Conversion of Petroleum Feedstocks to Coke", Preprint,Symposiaon Chemistry of Carbonization of Petroleum Feedstocks, Los Angles,CA,Sept 25~30,1988.

(2).Albright,L.F. Crynes,B.L.,& Corcoran,W.H.ed., "Pyrolysis:Theory and Industrial Practice." Academic Press, N.Y. 1983.

(3).Bianco, A.D. etc"Thermal Cracking of Petroleum Residue Kinetic Analysis of the Reaction." Fuel,72,77 (1993).

(4).Amelia, M.A. etc "Suitablity of thermogravimetryand differential thermal analysis for characterization of pitches." Fuel,71,611 (1992).

(5).Bermejo,J.etc "Thermal behavior of extrographic fractions of coal tar and Petroleum pitches." Fuel,76,179 (1997).

	Feed	LVGO	HVGO	Slop Waxy Oil	Asphalt
API	15.8	30.5	21.1	12.9	5.9
Flow rate (kg/hr)	228,640	41.590	78,580	6.480	102.000
Flow rate (BPSD)	36,000	7,200	12,820	1.000	14.980

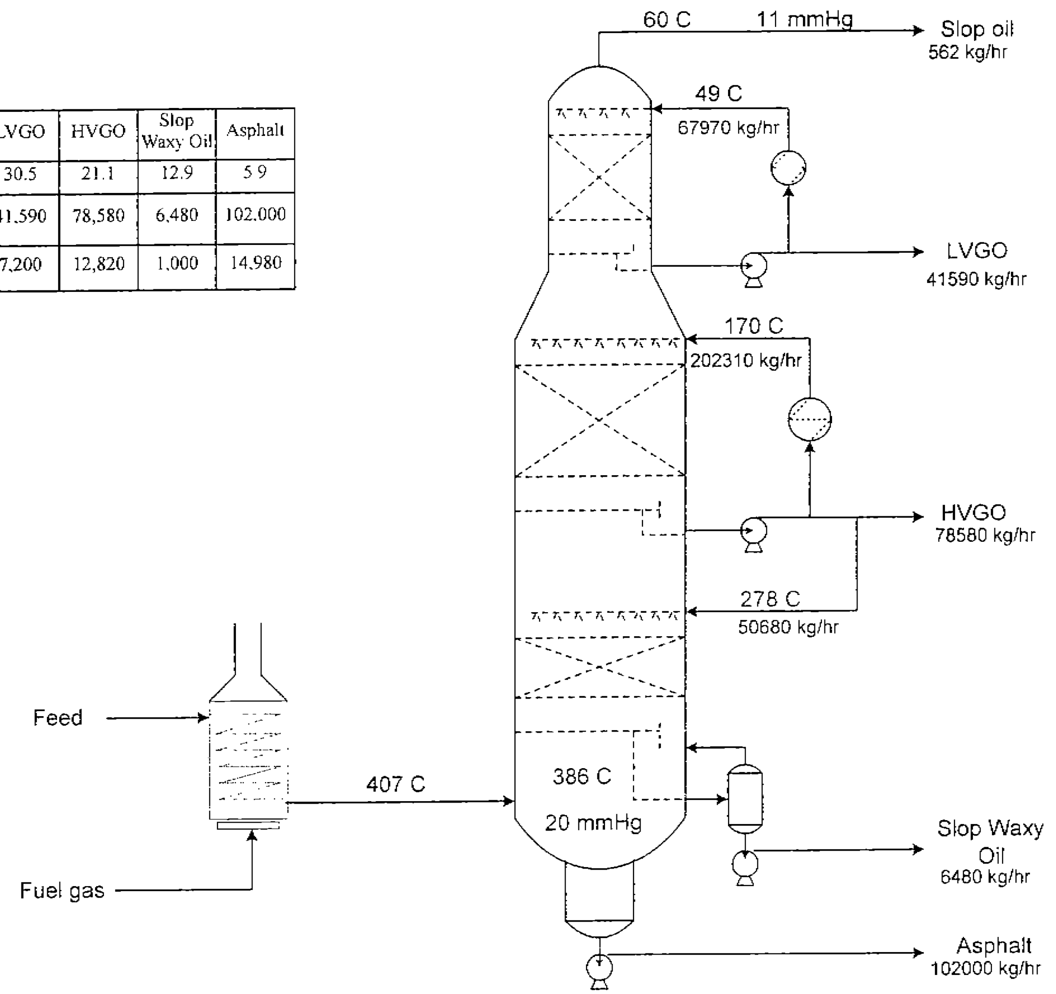
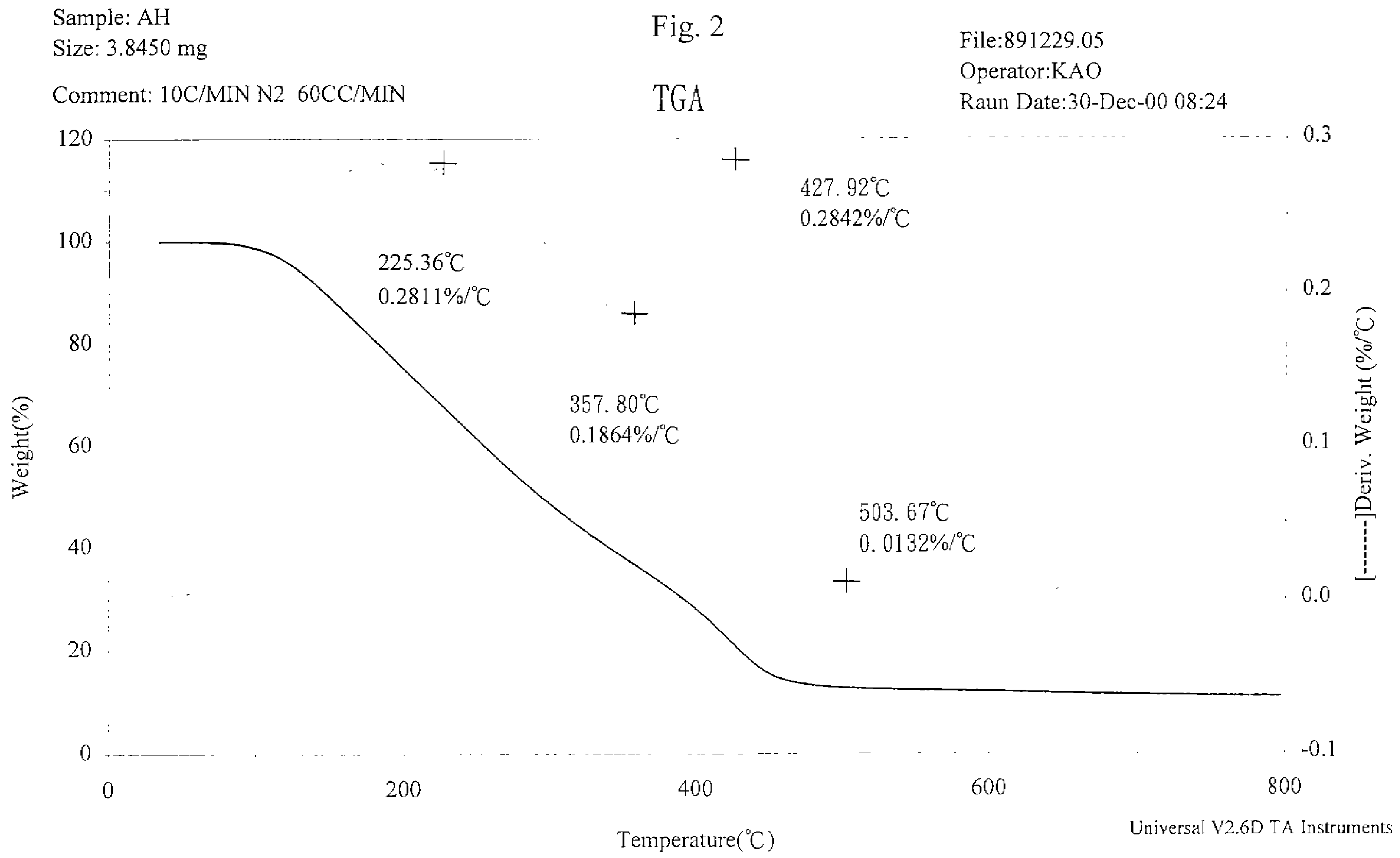


Fig 1 Process Flow Diagram of Vacuum Distillation Unit in Taoyuan Refinery,CPC

Fig. 2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Size: 3.8450 mg
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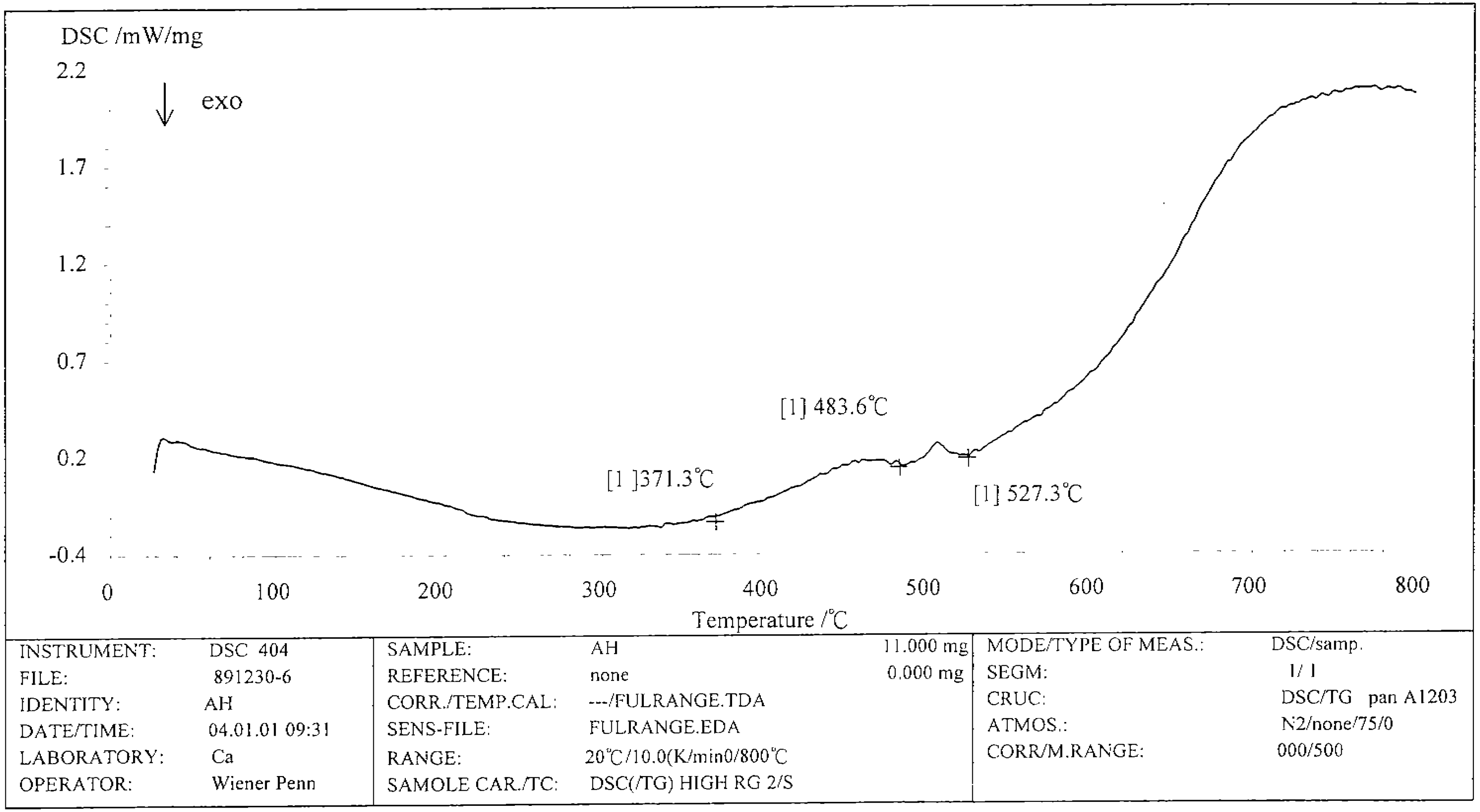
TGA
File:891229.05
Operator:KAO
Raun Date:30-Dec-00 08:24
225.36℃
0.2811%/℃
357. 80℃
0.1864%/℃
427. 92℃
0.2842%/℃
503. 67℃
0. 0132%/℃
Weight(%)
120
100
80
60
40
20
0
0
200
400
600
800
Temperature(℃)
[-------]Deriv. Weight (%/℃)
0.3
0.2
0.1
0.0
-0.1
Universal V2.6D TA Instruments

Fig. 3

NETZSCH-Ger tebau GmbH Thermal Analysis



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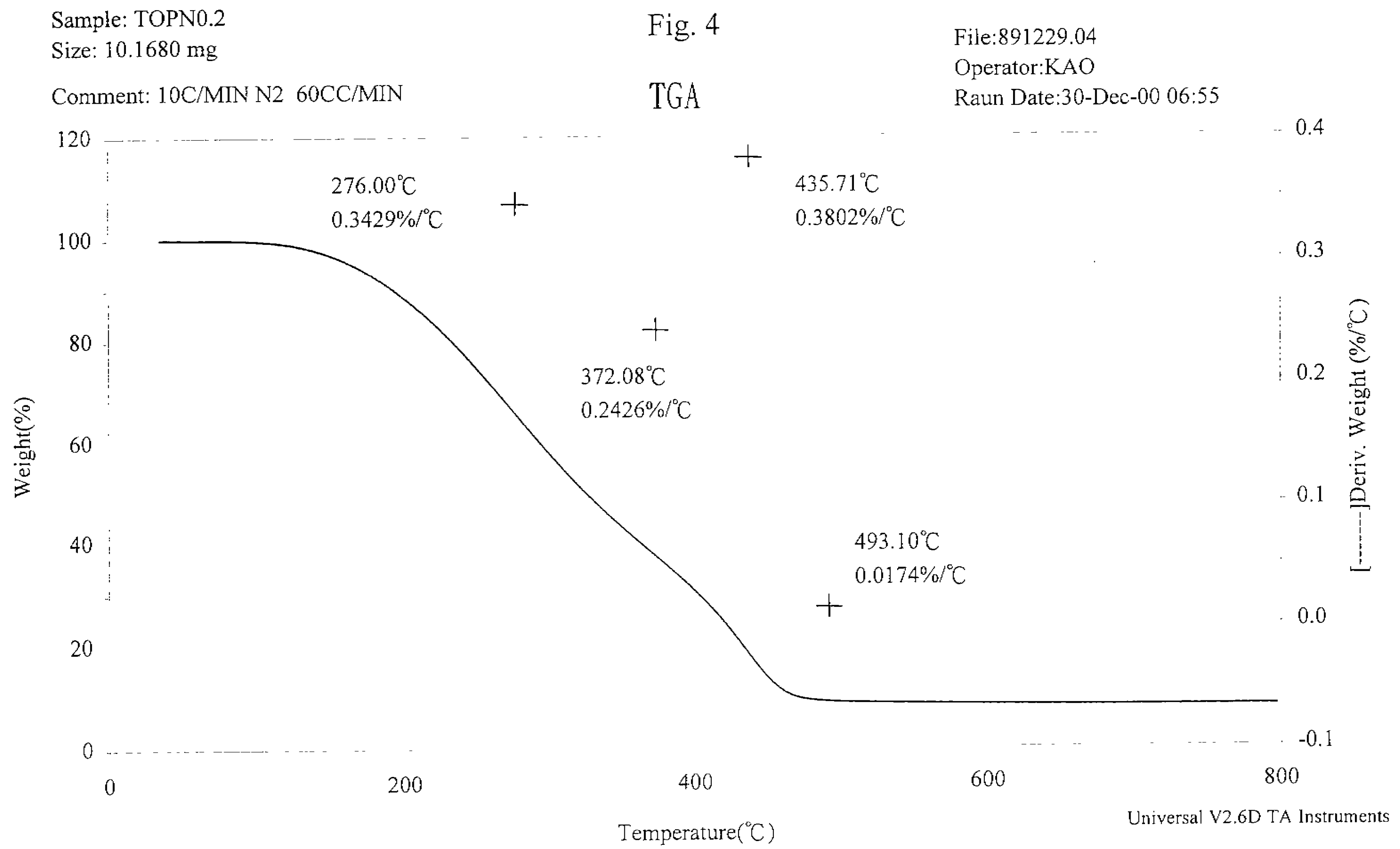
DATE/TIME:	04.01.01 09:31	SENS-FILE:	FULRANGE.EDA		ATMOS.:	N2/none/75/0
LABORATORY:	Ca	RANGE:	20℃/10.0(K/min0/800℃		CORR/M.RANGE:	000/500
OPERATOR:	Wiener Penn	SAMOLE CAR./TC:	DSC(/TG) HIGH RG 2/S			

Fig. 4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Size: 10.1680 mg
Comment: 10C/MIN N2 60CC/MIN
TGA
File:891229.04
Operator:KAO
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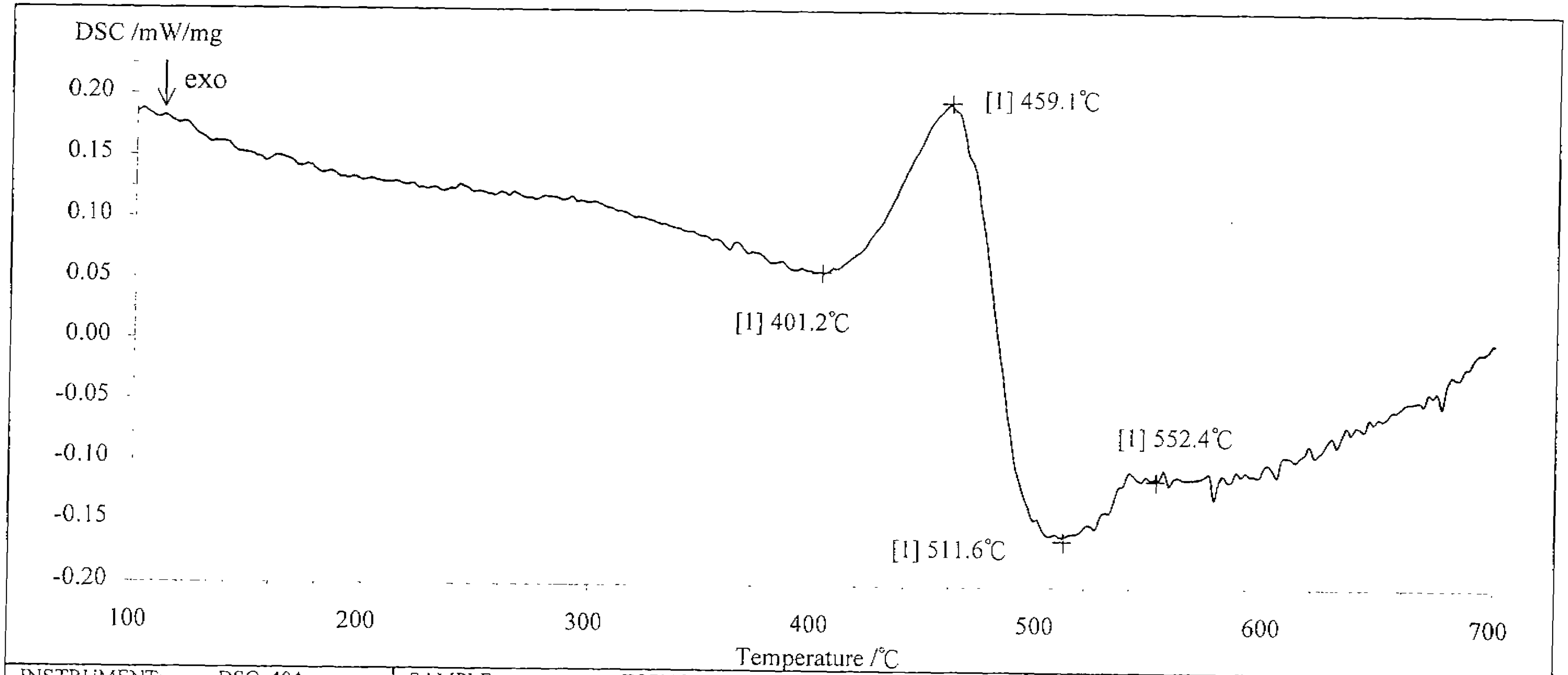
435.71℃
0.3802%/℃
372.08℃
0.2426%/℃
493.10℃
0.0174%/℃
Weight(%)
120
100
80
60
40
20
0
0.4
0.3
0.2
0.1
0.0
-0.1
[-------]Deriv. Weight (%/℃)
0
200
400
600
800
Temperature(℃)
Universal V2.6D TA Instruments

NETZSCH-Ger tebau GmbH Thermal Analysis

Fig. 5



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DATE/TIME:	03.01.01 14:22	SENS-FILE:	FULRANGE.EDA		ATMOS.:	N2/none/75/0
LABORATORY:	Ca	RANGE:	20℃/10.0(K/min0/800℃		CORR/M.RANGE:	000/500
OPERATOR:	Wiener Penn	SAMOLE CAR./TC:	DSC(/TG) HIGH RG 2/S			

Sample: LVGO
Size: 8.0260 mg
Method: Hi-Res TGA Method
Comment: 50C/MIN S=1 R=4 N2 60CC/MIN

Fig. 6

TGA

File:891229.09
Operator:KAO
Raun Date:8-Jan-01 13:25

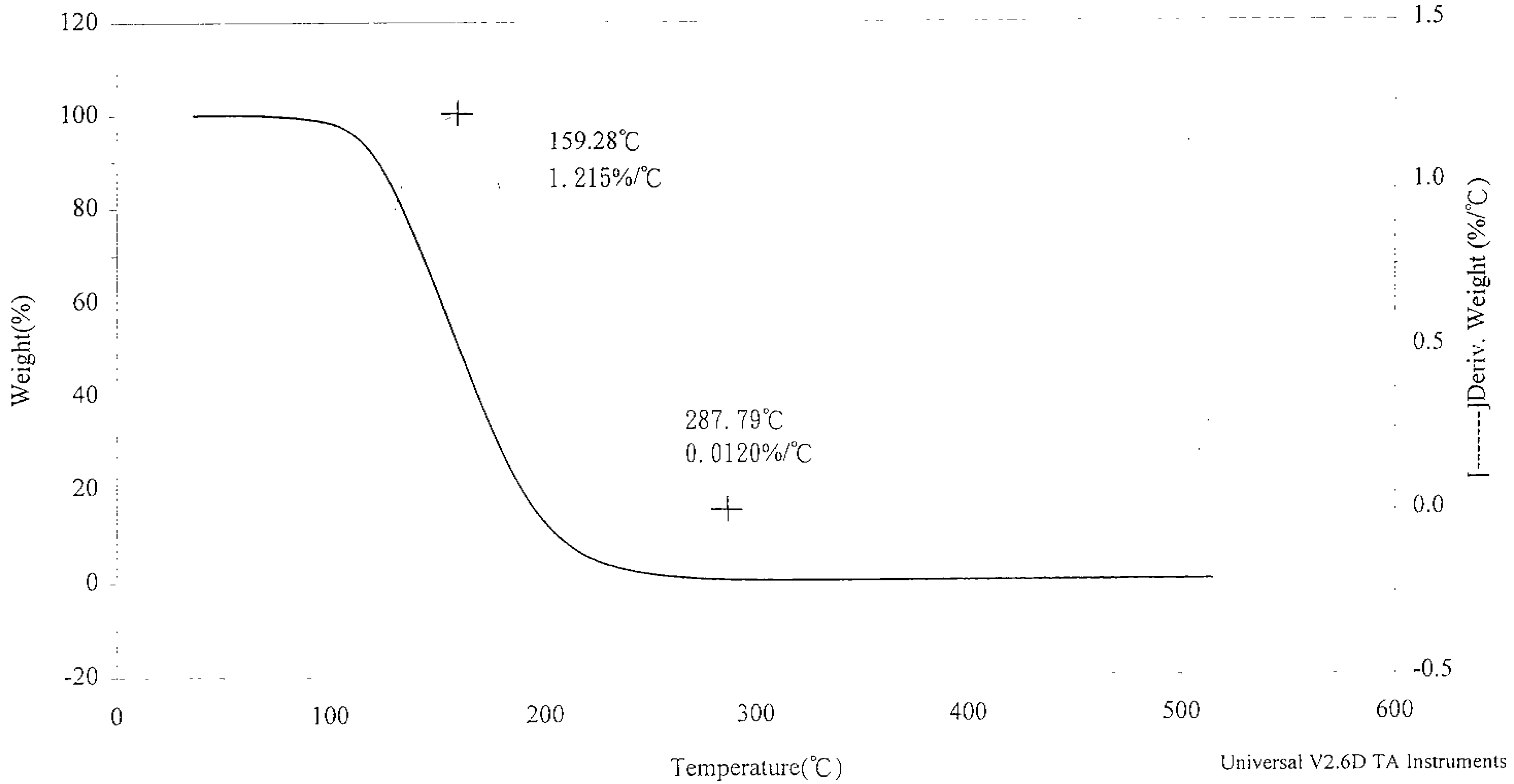
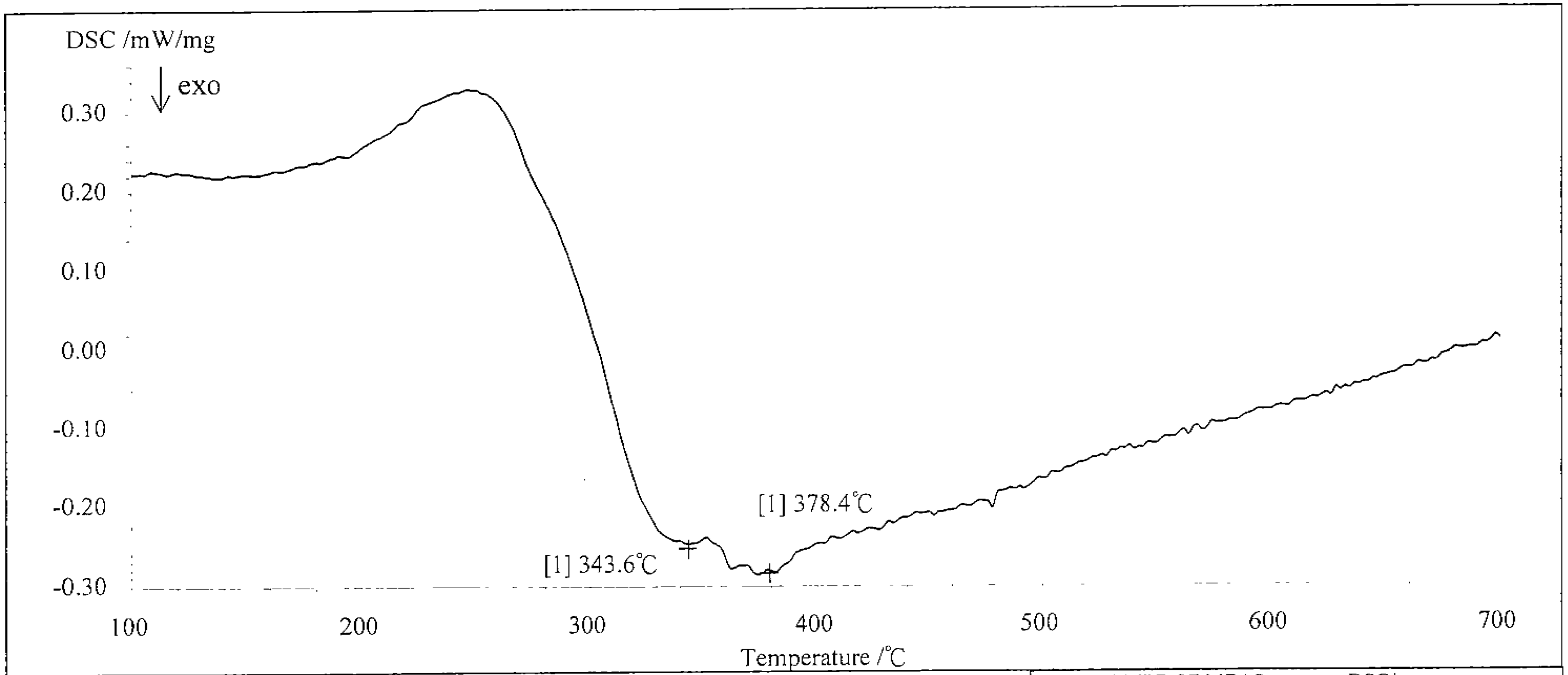


Fig. 7

NETZSCH-Ger tebau GmbH Thermal Analysis



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IDENTITY:	LVGO	CORR./TEMP.CAL:	---/FULRANGE.TDA		CRUC:	DSC/TG pan A1203
DATE/TIME:	01.01.01 14:31	SENS-FILE:	FULRANGE.EDA		ATMOS.:	N2/none/75/0
LABORATORY:	Ca	RANGE:	20℃/10.0(K/min0/800℃		CORR/M.RANGE:	000/500
OPERATOR:	Wiener Penn	SAMOLE CAR./TC:	DSC(/TG) HIGH RG 2/S			

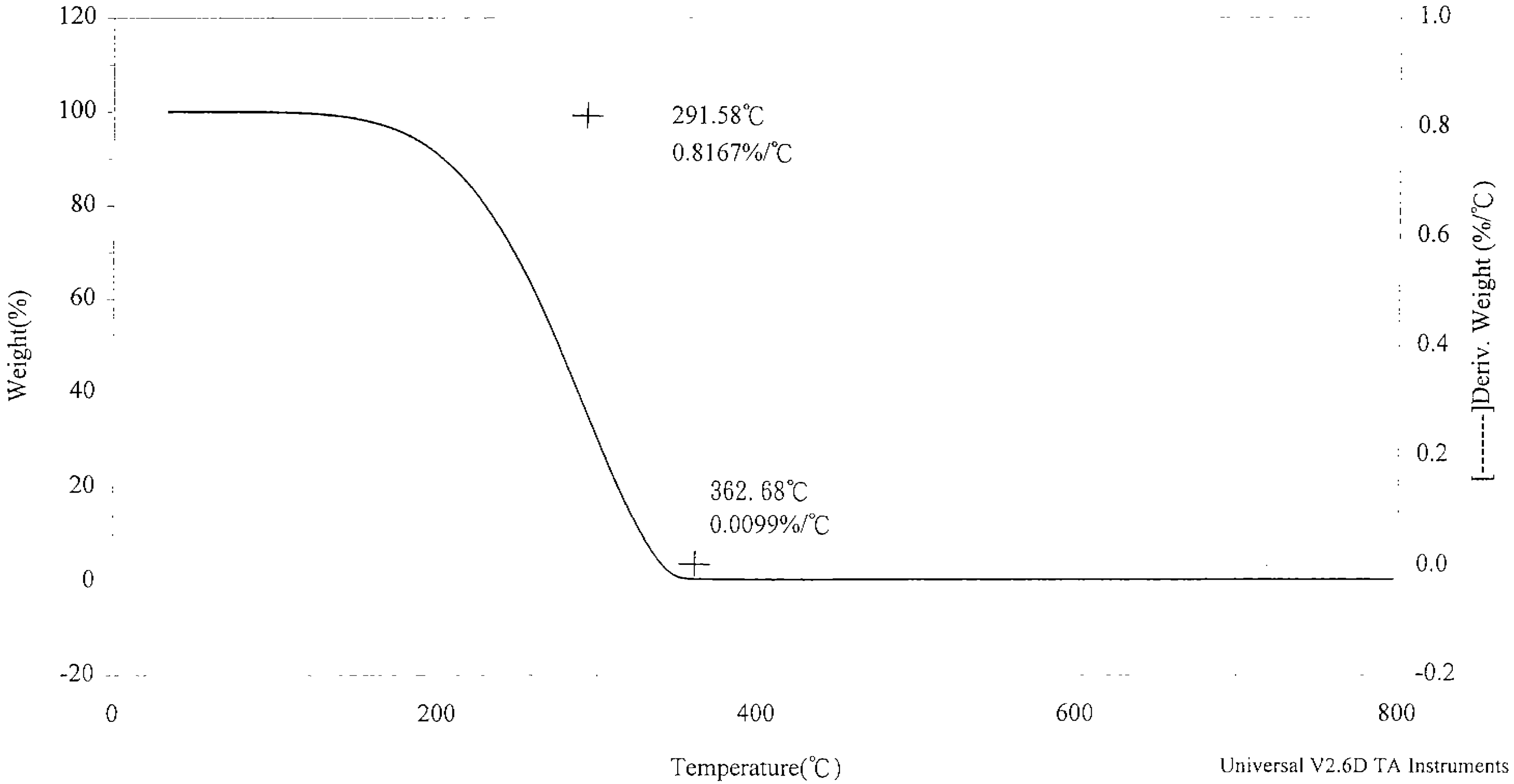
Fig. 8

TGA

Sample: HVGO
Size: 10.1550 mg

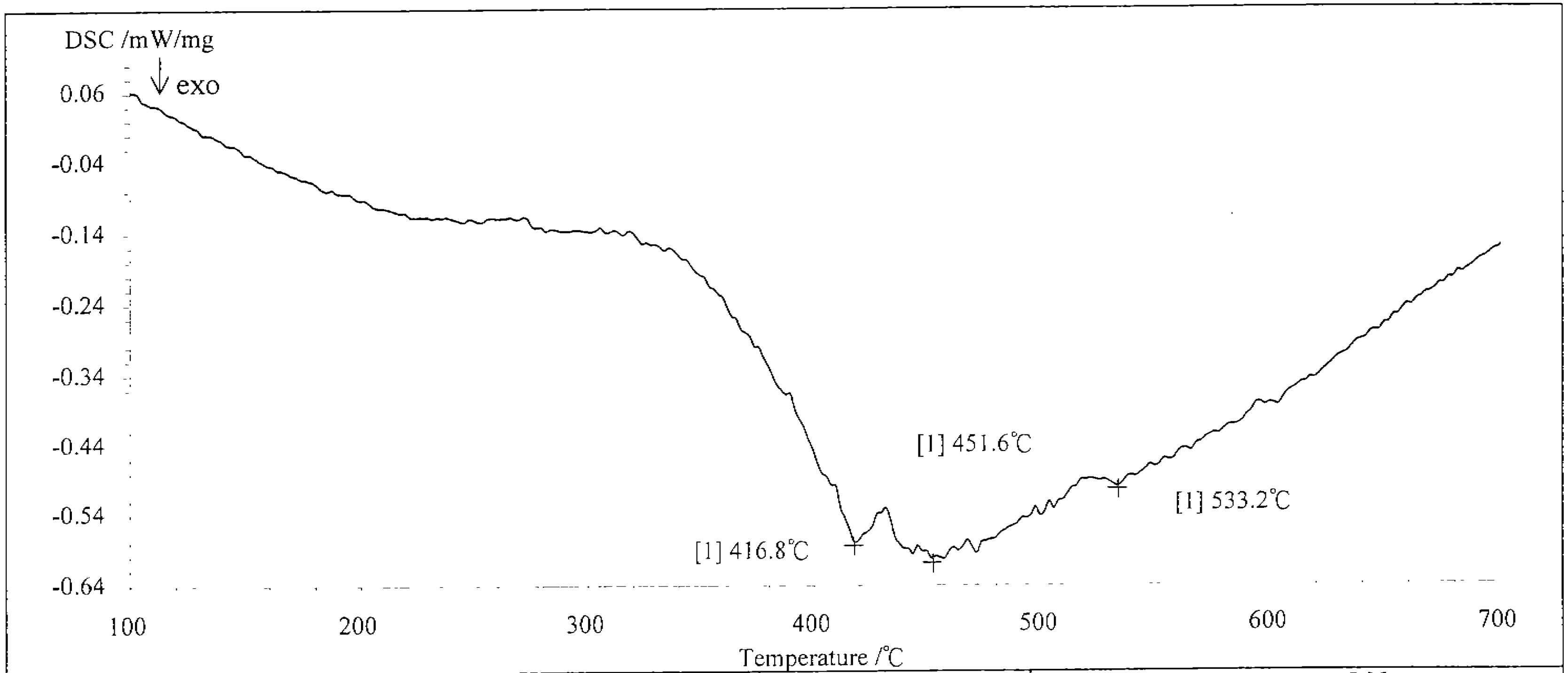
Comment: 10C/MIN N2 60CC/MIN

File:891229.02
Operator:KAO
Raun Date:29-Dec-00 03:58



NETZSCH-Ger tebau GmbH Thermal Analysis

Fig. 9



INSTRUMENT:	DSC 404	SAMPLE:	HVGO	7.000 mg	MODE/TYPE OF MEAS.:	DSC/samp.
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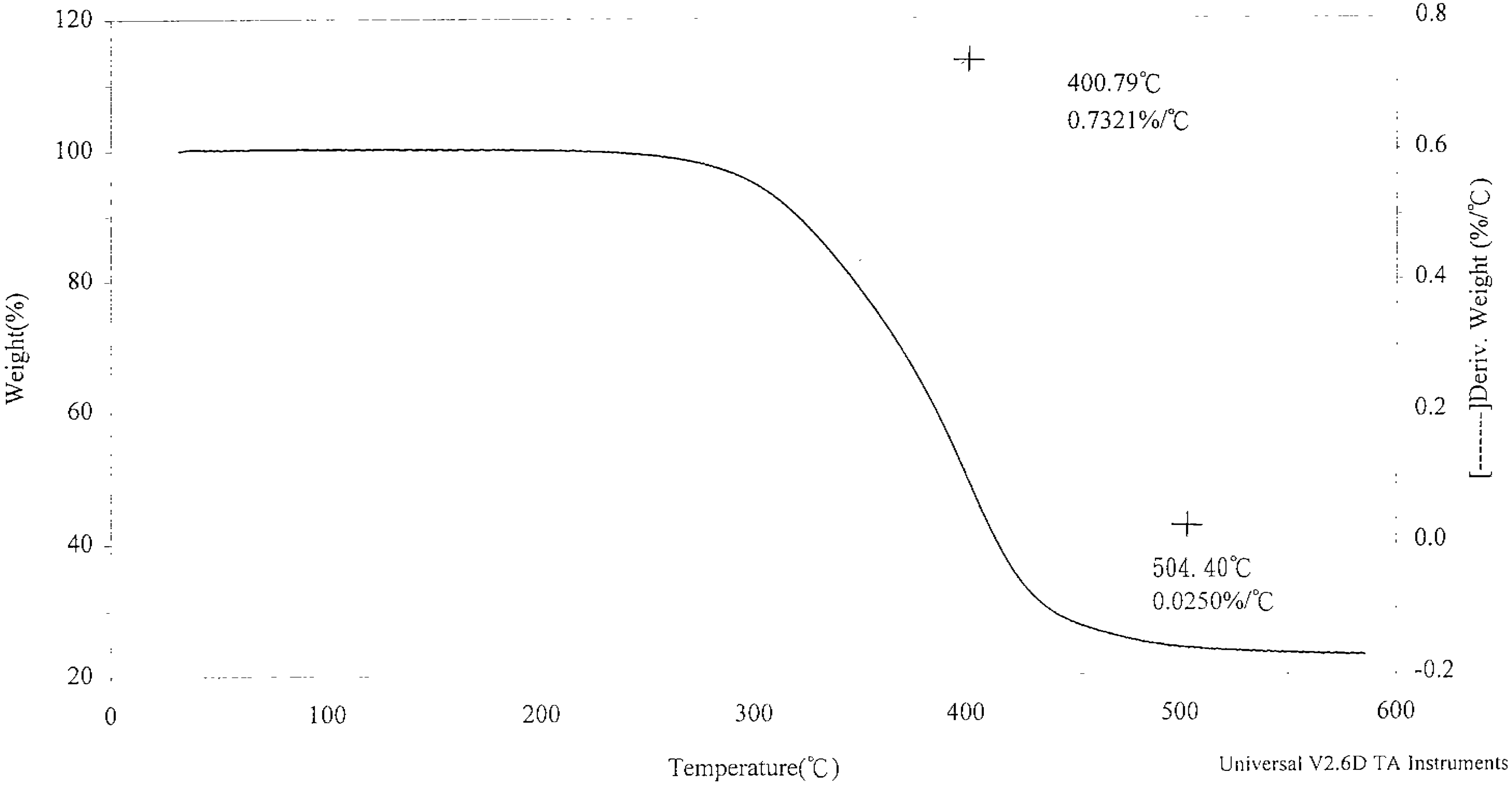
IDENTITY:	HVGO	CORR./TEMP.CAL:	---/FULRANGE.TDA		CRUC:	DSC/TG pan A1203
DATE/TIME:	02.01.01 14:25	SENS-FILE:	FULRANGE.EDA		ATMOS.:	N2/none/75/0
LABORATORY:	Ca	RANGE:	20℃/10.0(K/min0/800℃		CORR/M.RANGE:	000/500
OPERATOR:	Wiener Penn	SAMOLE CAR./TC:	DSC(/TG) HIGH RG 2/S			

Fig. 10

TGA

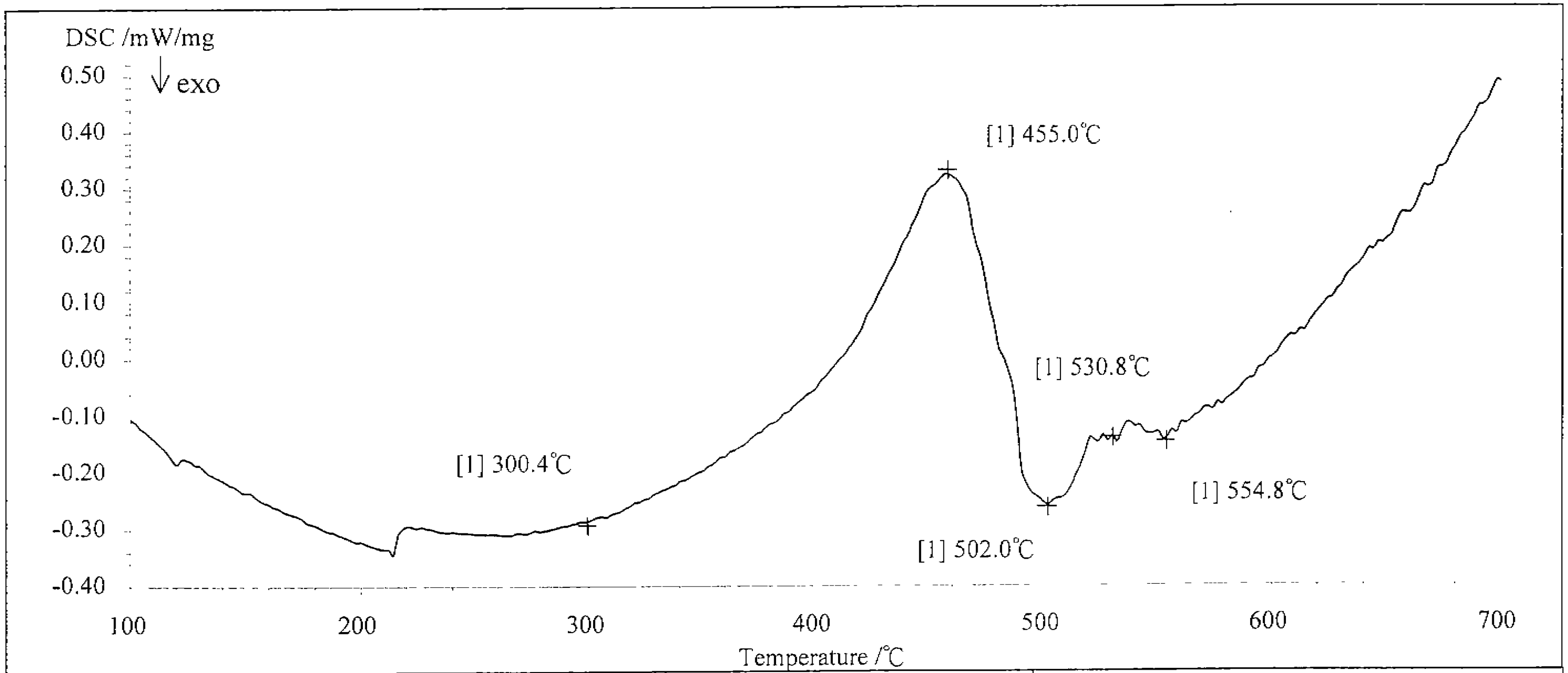
Sample: ASPHALT
Size: 3.5520 mg
Method: Hi-Res TGA Method
Comment: 50C/MIN S=1 R=4 N2 60CC/MIN

File:891229.11
Operator:KAO
Raun Date:8-Jan-01 23:14



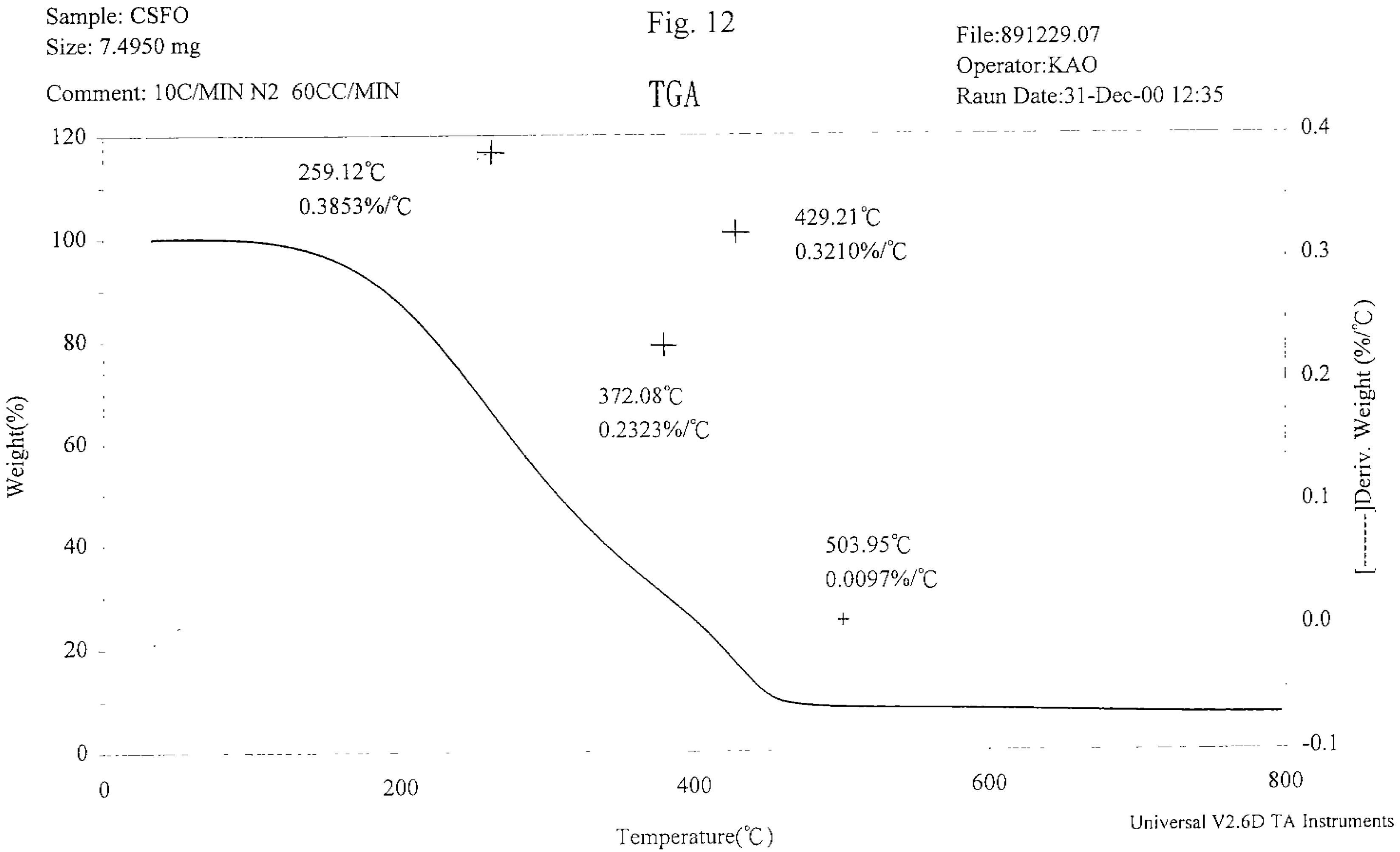
NETZSCH-Ger tebau GmbH Thermal Analysis

Fig. 11



INSTRUMENT:	DSC 404	SAMPLE:	P-OIL	9.200 mg	MODE/TYPE OF MEAS.:	DSC/samp.
FILE:	891230-9	REFERENCE:	none	0.000 mg	SEGM:	1/ 1
IDENTITY:	P-OIL	CORR./TEMP.CAL:	---/FULRANGE.TDA		CRUC:	DSC/TG pan A1203
DATE/TIME:	08.01.01 09:24	SENS-FILE:	FULRANGE.EDA		ATMOS.:	N2/none/75/0
LABORATORY:	Ca	RANGE:	20℃/10.0(K/min0/800℃		CORR/M.RANGE:	000/500
OPERATOR:	Wiener Penn	SAMOLE CAR./TC:	DSC(/TG) HIGH RG 2/S			

Fig. 12


Sample: CSFO
Size: 7.4950 mg
Comment: 10C/MIN N2 60CC/MIN
TGA
File:891229.07
Operator:KAO
Raun Date:31-Dec-00 12:35
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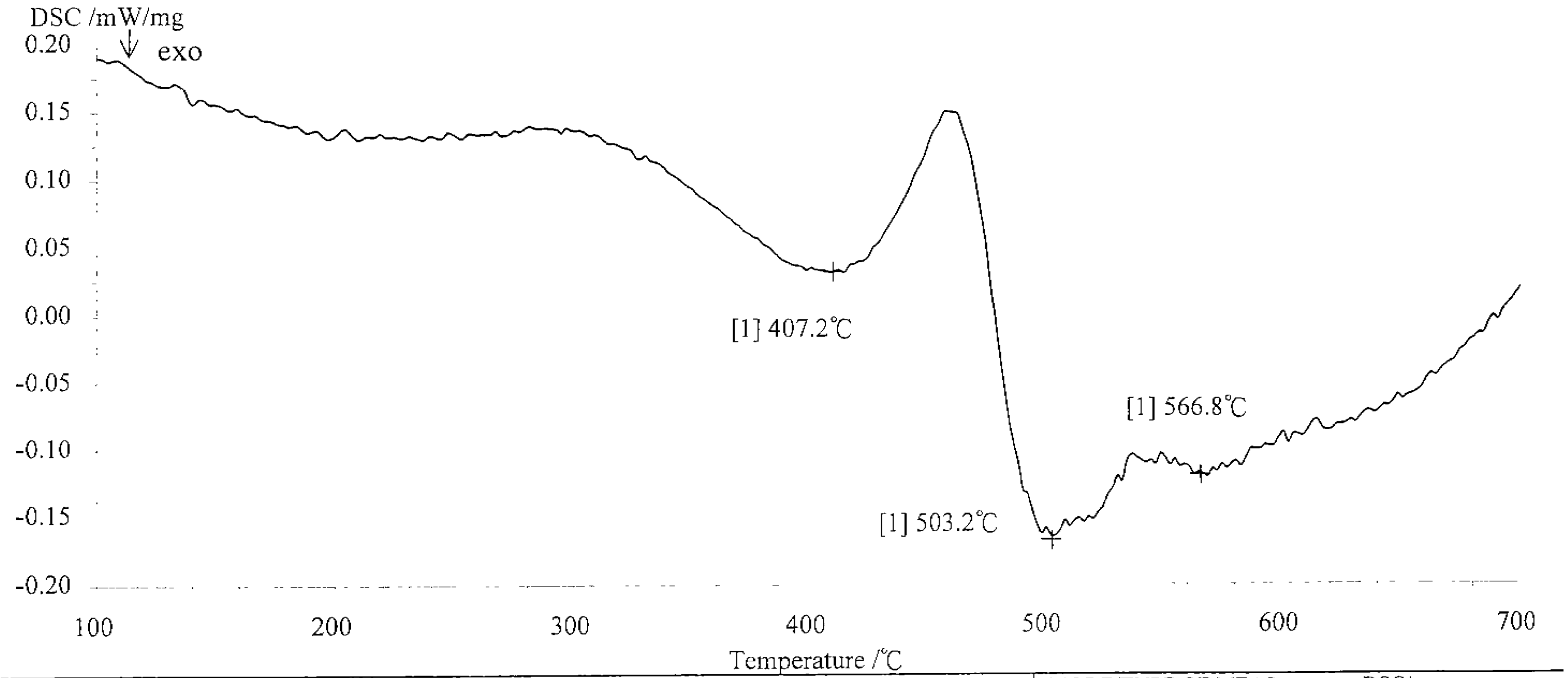
429.21℃
0.3210%/℃
372.08℃
0.2323%/℃
503.95℃
0.0097%/℃
Weight(%)
120
100
80
60
40
20
0
0
200
400
600
800
Temperature(℃)
0.4
0.3
0.2
0.1
0.0
-0.1
[-------]Deriv. Weight (%/℃)
Universal V2.6D TA Instruments

Fig. 13

NETZSCH-Ger tebau GmbH Thermal Analysis



INSTRUMENT:	DSC 404	SAMPLE:	CSFO	13.000 mg	MODE/TYPE OF MEAS.:	DSC/samp.
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IDENTITY:	CSFO	CORR./TEMP.CAL:	---/FULRANGE.TDA		CRUC:	DSC/TG pan A120
DATE/TIME:	05.01.01 10:13	SENS-FILE:	FULRANGE.EDA		ATMOS.:	N2/none/75/0
LABORATORY:	Ca	RANGE:	20℃/10.0(K/min0/800℃		CORR/M.RANGE:	000/500
OPERATOR:	Wiener Penn	SAMOLE CAR./TC:	DSC(/TG) HIGH RG 2/S			

Sample: DJENO
Size: 6.4500 mg

Comment: 10C/MIN N2 60CC/MIN

Fig. 14

TGA

File:891229.03
Operator:KAO
Raun Date:29-Dec-00 05:27

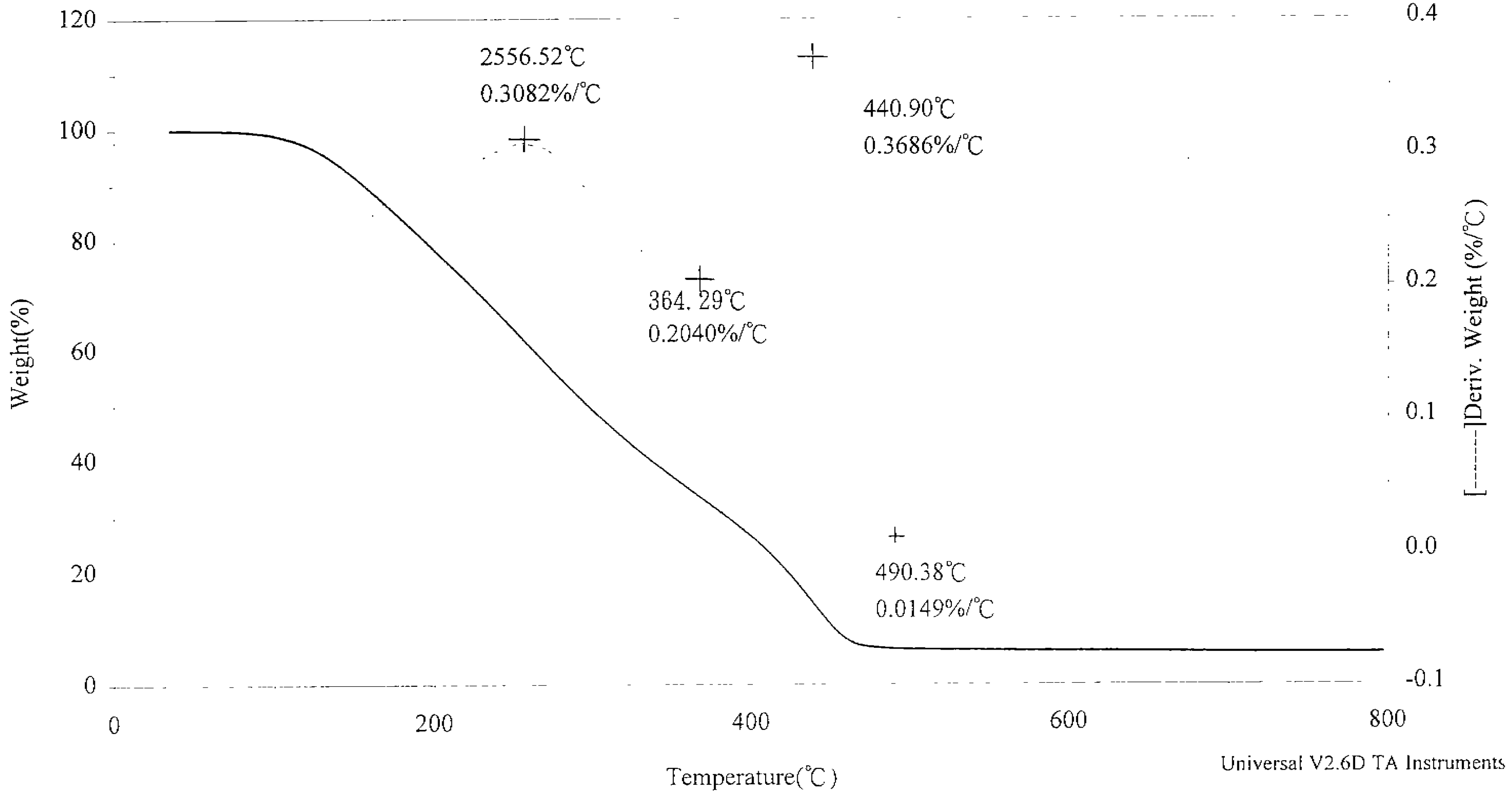

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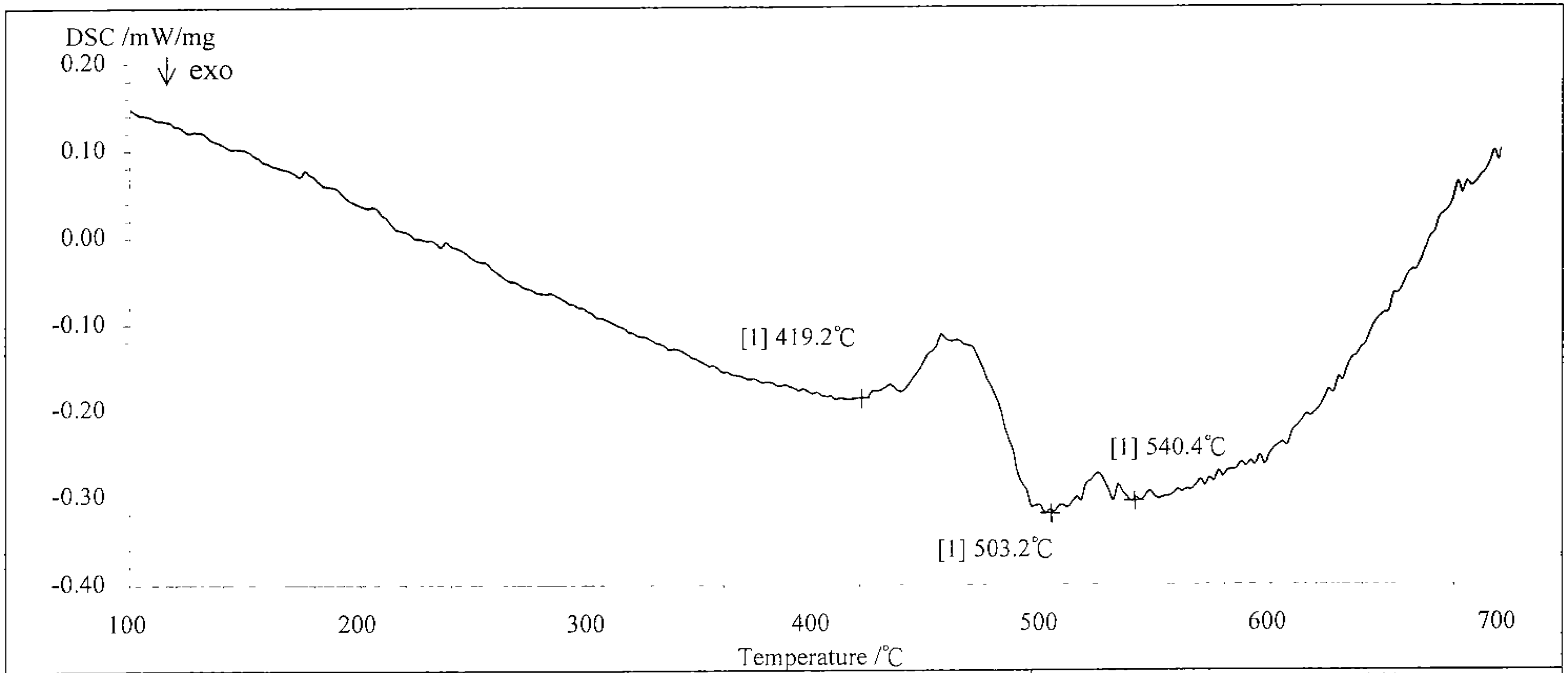
Fig. 15



INSTRUMENT:	DSC 404	SAMPLE:	DJENO	11.700 mg	MODE/TYPE OF MEAS.:	DSC/samp.
FILE:	891230-4	REFERENCE:	none	0.000 mg	SEGM:	1/ 1
IDENTITY:	DJENO	CORR./TEMP.CAL:	---/FULRANGE.TDA		CRUC:	DSC/TG pan A1203
DATE/TIME:	03.01.01 11:05	SENS-FILE:	FULRANGE.EDA		ATMOS.:	N2/none/75/0
LABORATORY:	Ca	RANGE:	20℃/10.0(K/min0/800℃		CORR/M.RANGE:	000/500
OPERATOR:	Wiener Penn	SAMOLE CAR./TC:	DSC(/TG) HIGH RG 2/S			

Sample: NKOSSA
Size: 5.3960 mg

Comment: 10C/MIN N2 60CC/MIN

Fig. 16

TGA

File:891229.06
Operator:KAO
Raun Date:31-Dec-00 11:05

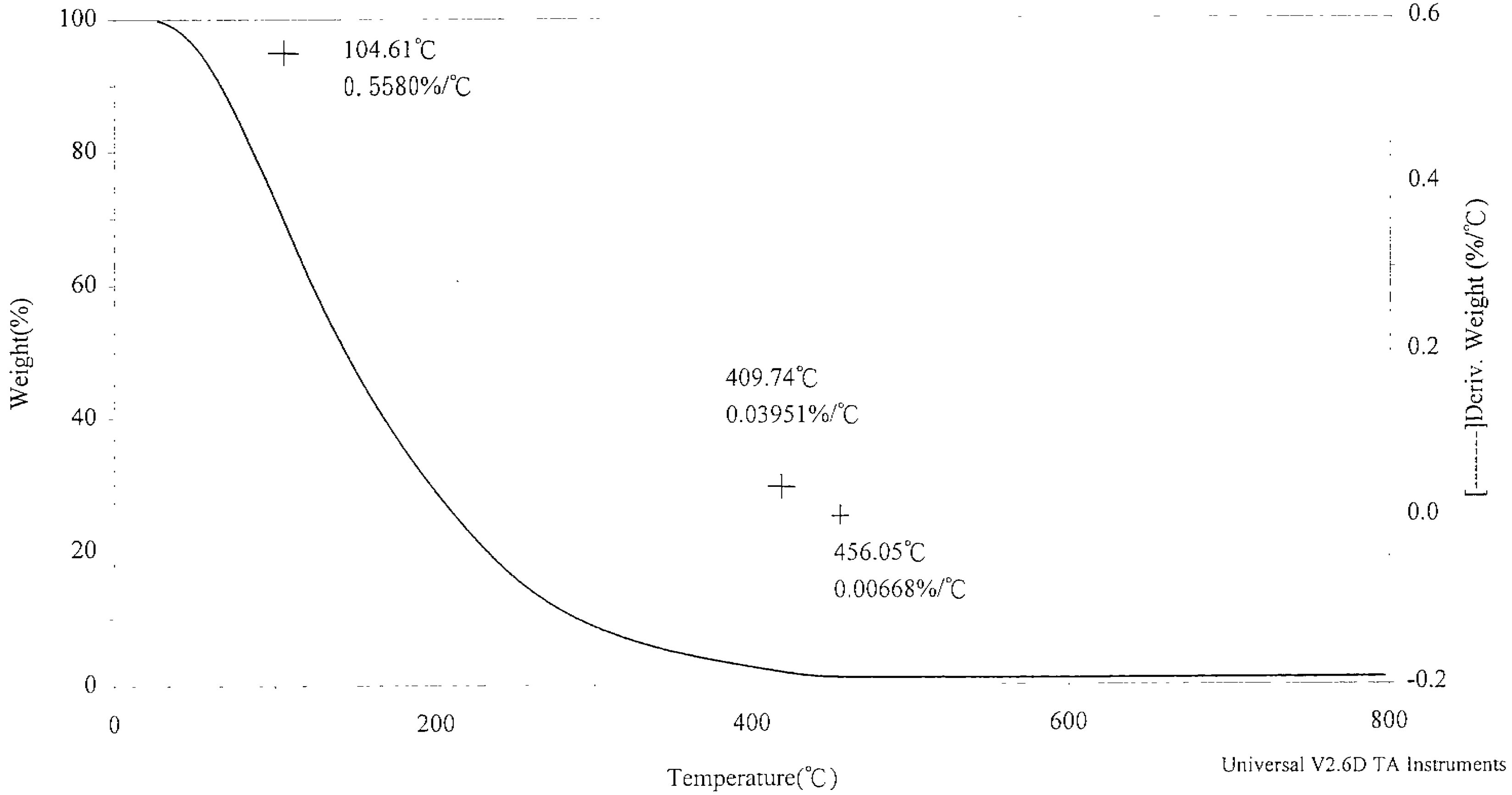
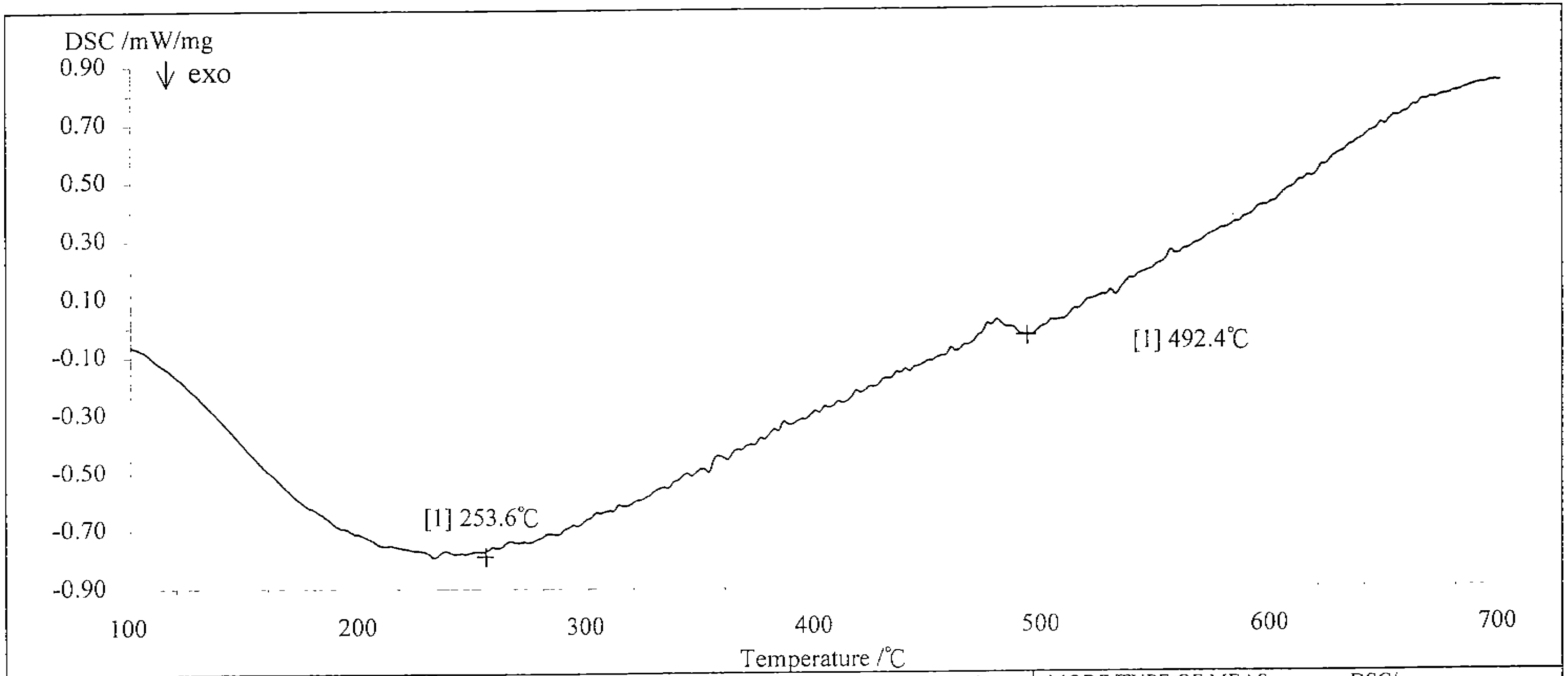


Fig. 17

NETZSCH-Ger tebau GmbH Thermal Analysis



INSTRUMENT:	DSC 404	SAMPLE:	NKOSSA	8.200 mg	MODE/TYPE OF MEAS.:	DSC/samp.
FILE:	891230-7	REFERENCE:	none	0.000 mg	SEGM:	1/1
IDENTITY:	NKOSSA	CORR./TEMP.CAL:	---/FULRANGE.TDA		CRUC:	DSC/TG pan A1203
DATE/TIME:	04.01.01 14:26	SENS-FILE:	FULRANGE.EDA		ATMOS.:	N2/none/75/0
LABORATORY:	Ca	RANGE:	20℃/10.0(K/min0/800℃		CORR/M.RANGE:	000/500
OPERATOR:	Wiener Penn	SAMOLE CAR./TC:	DSC(/TG) HIGH RG 2/S			

Fig 18 Reaction time vs Product composition of TOR's Reduced Crude (at 350^{0}C and under 1kg/cm^2 N2 initial pressure)

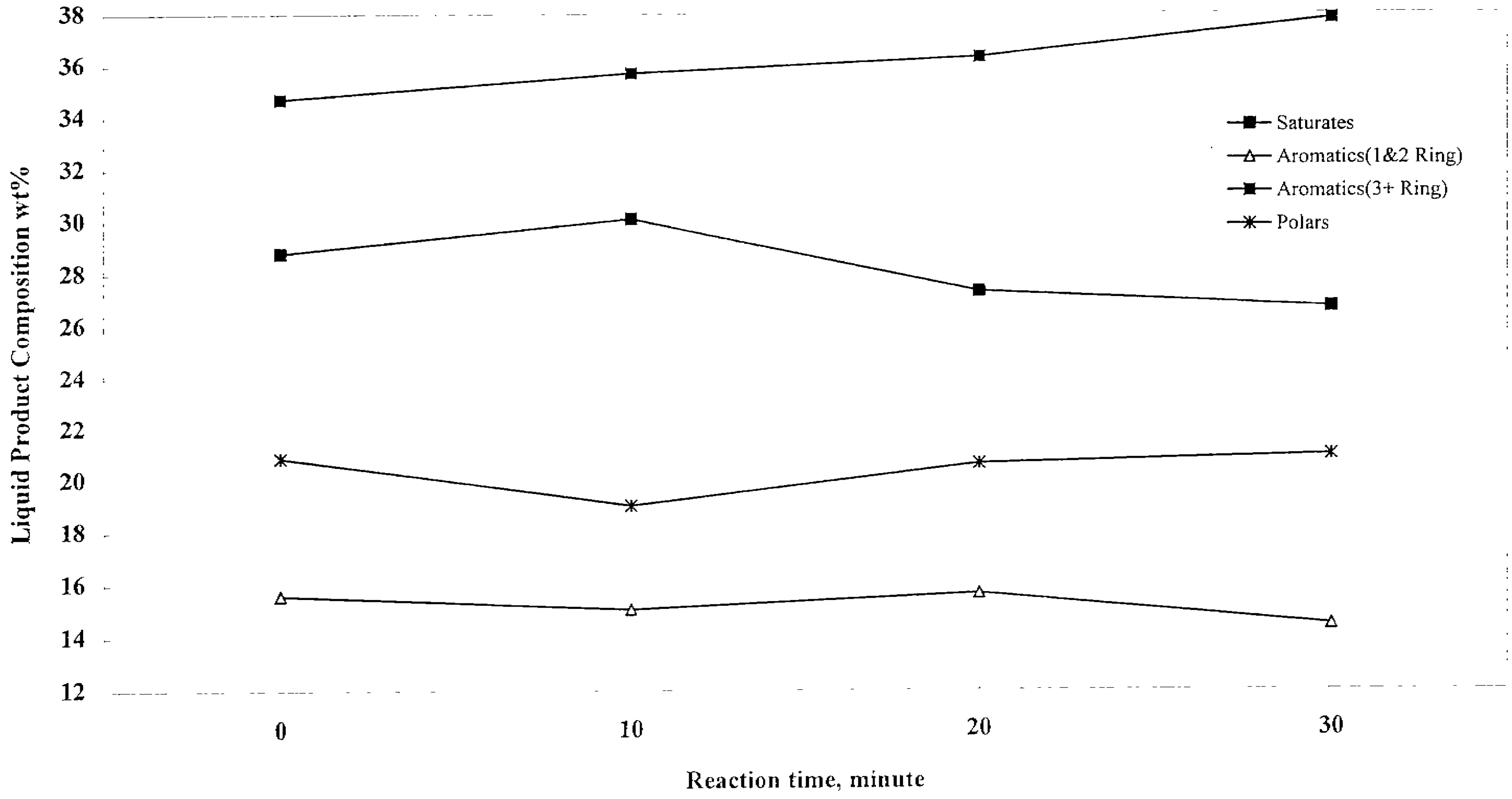


Table 1 The main physical properties of crude oil and its reduced crude in TOR

Name	API,60°F	S wt%	C.C.R. wt	wt% at TBP400℃
AH	27.5	2.92	7.9	41
KC	30.5	2.55	5.8	50.5
IL	33.1	1.53	3.50	56
OM	34.2	1.01		52
Djeno	28.0	0.29		40.5
Nkossa	49.1	0.025		67.2
AH-RC	14.8	3.30		22.4
IL-RC	15.3	3.17		25
Asphallt（AC-10）	5.9			0.5

Table 2.Thermal analysis of crude oil, reduced crude and asphalt

			Condensation temperature, ºC			Cracking temperature, ºC	
Name	APL60ºF	S wt%	DTA （EXO）	DSC （EXO）	DTG （Const wt	DSC （ENDO）	DTG （max wt loss
AH	27.9	2.85	346-383	371-383	363-380	483	429
KC	32.5	2.66	345-377.2	370-412	375		456
IL	33.8	1.35	341-375	340-375	370		454
OM	36.3	0.79	391	395	390		444
Y-Crude IL. 74vol%	32.8	1.88	339-369	378-405	378		456
TOR-RC （IL）	15.3	3.17	372-404	375-405	372		460
OR-Asphalt （IL）	5.9	4.62	378-410	350-405	387		
Djeno	28.0	0.29		419	364	419	440
Nkossa	49.1	0.025		475	409		492
TOR-RC （AH）	15.3	3.30		401	372	401	435
OR-Asphalt （AH）	5.9			335	350		400

Table 3. Temperature effect vs product aromatic type distribution of TOR's reduce crude（under 1kg/cm2 N2 initial pressure）

Run NO.	Feed	TOR-330	TOR-340	TOR-350	asphalt
Reaction time, minute	0	30	30	30	
Reaction temperature, °C		330	340	350	
Product yield, wt%					
liquid		98.6	98.5	98.4	
gas		1.2	1.3	1.4	
Liquid product composition, wt%					
saturates	28.8	30.1	27.3	26.7	9.3
aromatics（1 & 2 ring）	15.6	15.1	15.7	14.5	11.3
aromatics（3+ ring）	34.7	35.7	36.3	37.8	38.8
polars	20.9	19.1	20.7	21.0	40.6
Total recovery, wt%		99.8	99.8	99.8	

Table 4. Temperature effect vs cracked gases composition of TOR's reduce crude

（under 1 kg/cm2 N2 initial Pressure 30 minutes）

Run No.	TOR-330 (17/19)	TOR-340 (17/15)	TOR-350 (17/171)
Reaction temperature ℃	330	340	350
Gas field wt%	1.2	1.3	1.5
Gas composition mol%			
H2	0.14	0.29	0.46
C1	0.94	1.79	3.12
C2	0.96	1.21	1.61
C2=	0.50	0.45	0.21
C3	0.31	0.93	1.19
C3=	0.21	0.34	0.46
C4（n+iso）	0.19	0.46	0.79
C4=	0.11	0.28	0.67
C5（n+iso）	0.23	0.45	0.92
C0	0.20	0.29	0.30
C02	0.40	0.78	0.62
H2S	0.17	1.02	0.67
N2	93.0	87.0	84.3
C6+	2.65	4.69	4.62

Table 5 The Performance of Vacuum Unit at TOR

●Asphalt Grade	AC-10(85～100)	AC-20(50～70)
●Feed API 60^{0}F	14.8	14.7
●Feed rate, B/D (kl/hr)	22,000(150)	18,300(120)
●Conditions :		
Vacuum,mmHg		
TOP	10.7	8.24
Flash Zone	24.4	19.1
Temperature,^{0}c		
Furnace outlet	368	382
Flash zone	357.5	371.9
●Product,yield wt%		
LVGO	13.3	18.3
HVGO	39.7	39.2
SWO	2.6	5.7
Asphalt	44.9	36.8
●Asphalt quality		
Penetration,25℃,100g,5sec	98	50
Viscosity,60℃ poise	1115	1919