

Supplementary information

Use of a cross-linked polystyrene/titanium tetrachloride tightly bound coordination complex as catalyst for the production of petroleum resins

Ali Rahmatpour^{1*}, Parvaneh Soleimani¹, Soroush Karamian², Razieh Dadvand²

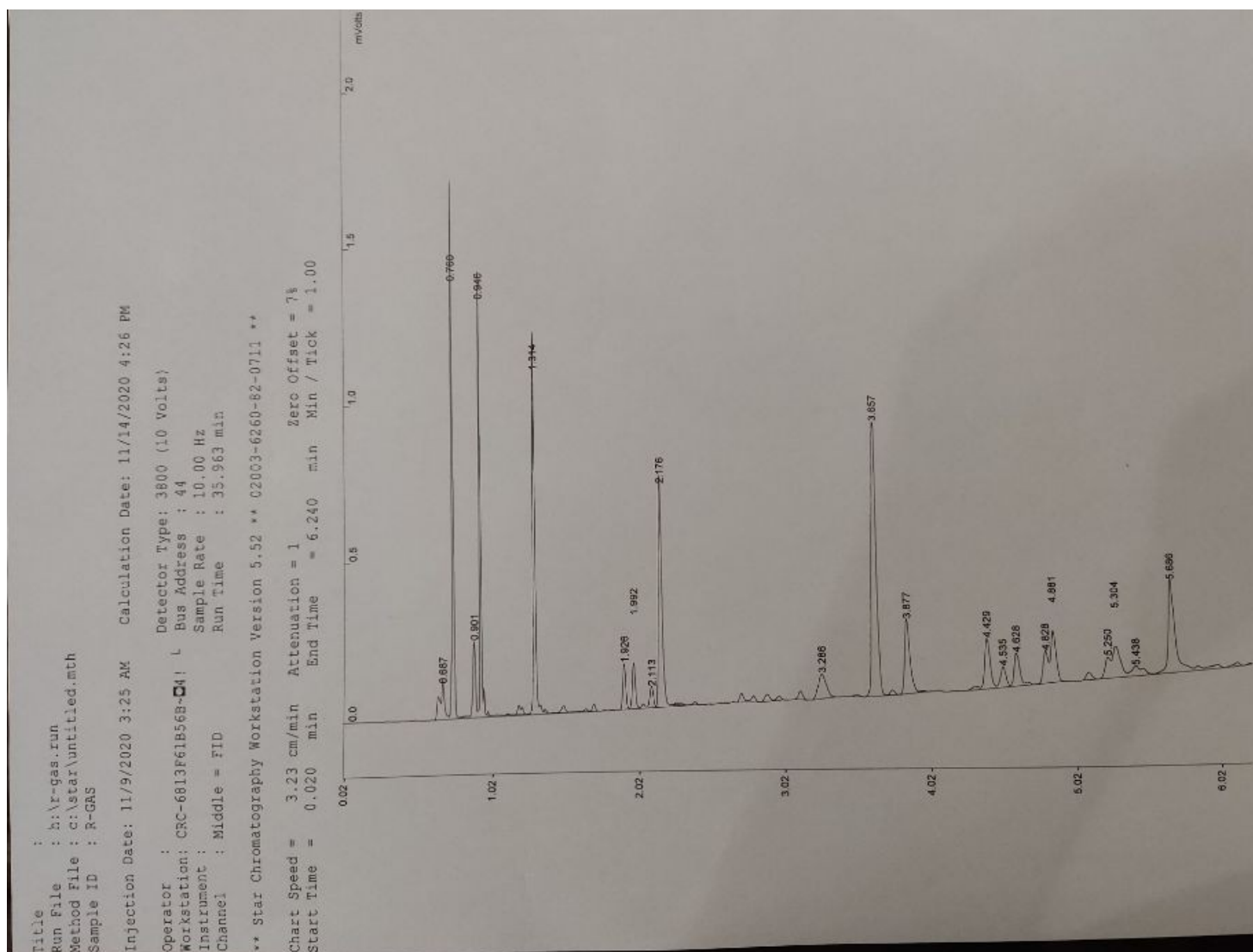


Fig. 1S Gas chromatogram of raw pygas feedstock

Title :
 Run File : R:\r-gas-run
 Method File : c:\atlas\untitled1.mth
 Sample ID : B-GAS

Injection Date: 11/9/2020 3:25 PM Calculation Date: 11/14/2020 4:26 PM

Operator :
 Workstation: CBC-0613P618968-04/ *
 Instrument :
 Channel : Middle - FID
 Detector Type: 3800 (10 Volts)
 Bus Address : 44
 Sample Rate : 10.00 Hz
 Run Time : 35.953 min

** Star Chromatography Workstation Version 5.32 ** 02003-0250-02-0711 **

Run Mode : Analytic
 Peak Measurement: Peak Area
 Calculation Type: Percent

Peak No.	Peak Name	Result (%)	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		1.5021	0.487	0.000	174	VV	1.2	
2		10.3249	0.760	0.000	1287	VV	0.6	
3		2.7085	0.901	0.000	317	VV	1.2	
4		6.5269	0.946	0.000	465	VV	0.6	
5		10.6221	1.314	0.000	1242	VV	0.9	
6		1.7318	1.926	0.000	302	PV	1.4	
7		1.8443	1.992	0.000	314	VV	1.6	
8		0.8474	2.113	0.000	311	VV	2.0	
9		10.4982	2.178	0.000	1244	VV	1.0	
10		2.5343	3.286	0.000	294	BB	3.8	
11		17.2369	3.857	0.000	2025	PP	2.1	
12		5.1104	3.877	0.000	597	PB	2.2	
13		3.4857	4.429	0.000	407	VV	2.4	
14		1.4464	4.535	0.000	169	VV	2.6	
15		2.2900	4.628	0.000	266	VV	2.6	
16		2.0511	4.828	0.000	240	PV	2.8	
17		3.4787	4.881	0.000	407	VV	2.8	
18		1.3967	5.250	0.000	143	VV	2.9	
19		3.1552	5.304	0.000	369	VV	4.8	
20		0.8835	5.432	0.000	113	VV	5.0	
21		8.0048	5.685	0.000	936	VV	2.7	
Totals:		100.0001		0.000	11590			

Total Unidentified Counts : 11488 counts

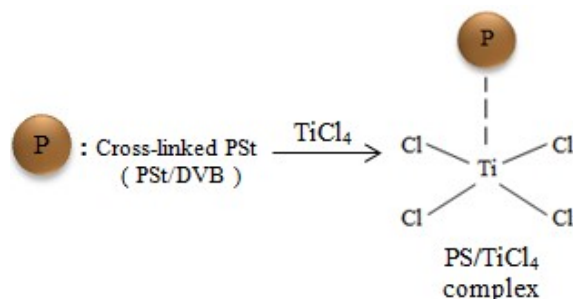
Detected Peaks: 22 Rejected Peaks: 31 Identified Peaks: 0

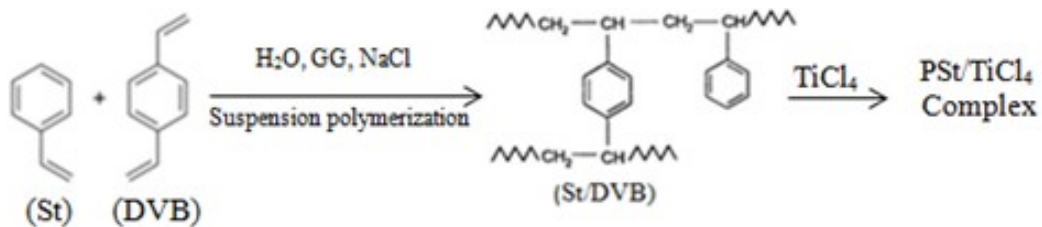
Multiplier: 1 Divisor: 1 Unidentified Peak Factor: 0

Baseline Offset: 0 microVolts

Noise (used): 3 microVolts - monitored before this run

Manual injection





Scheme S1 Synthetic route of polymeric catalyst

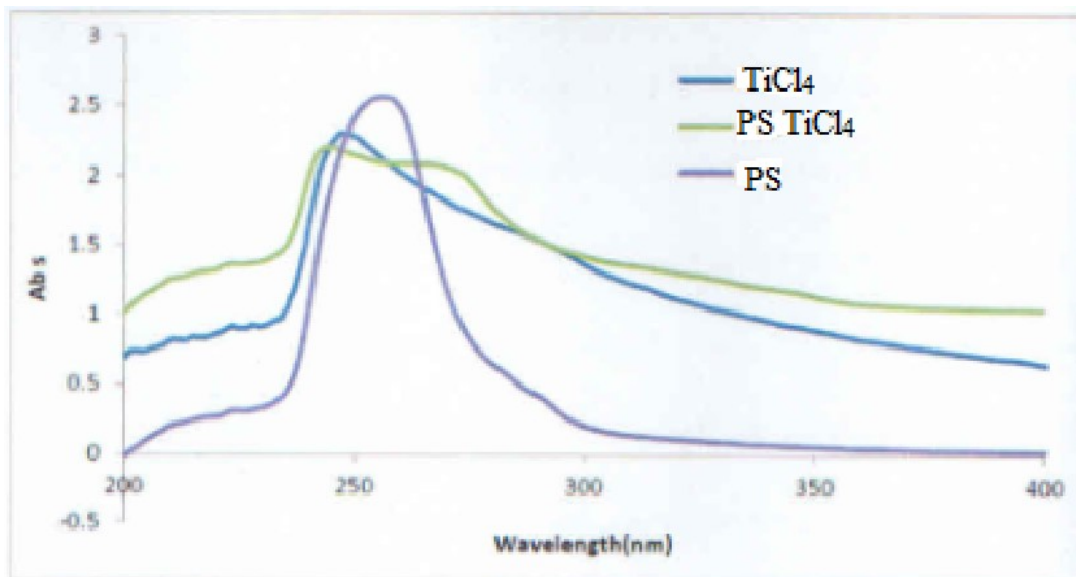


Figure S2 UV spectra of PS, PS/TiCl₄ in CS₂

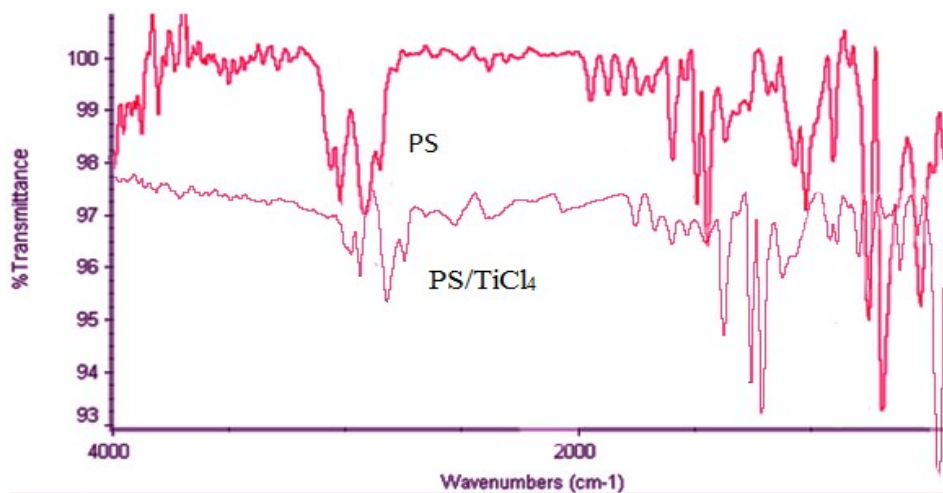


Figure S3 FT-IR spectra of PS carrier and PS-TiCl₄ complex samples

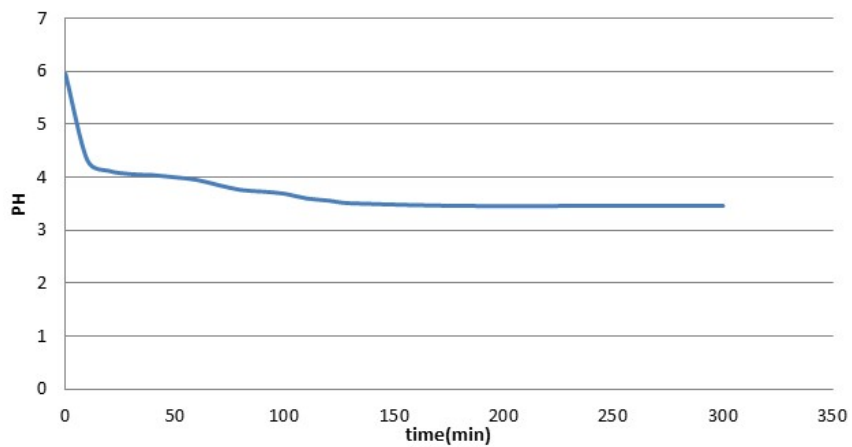
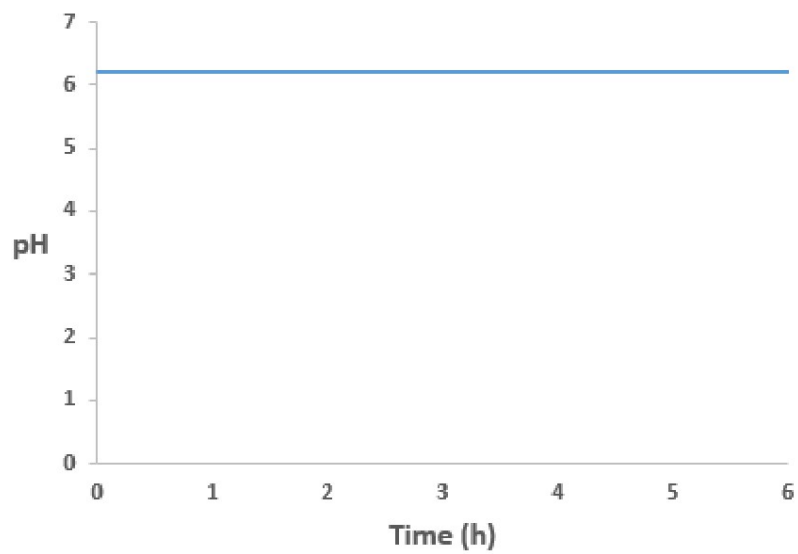


Figure S4 The time-dependence of the pH of acetone-water solution (60%) containing (up) pristine PS, (down) polymeric catalyst (PS/TiCl₄)

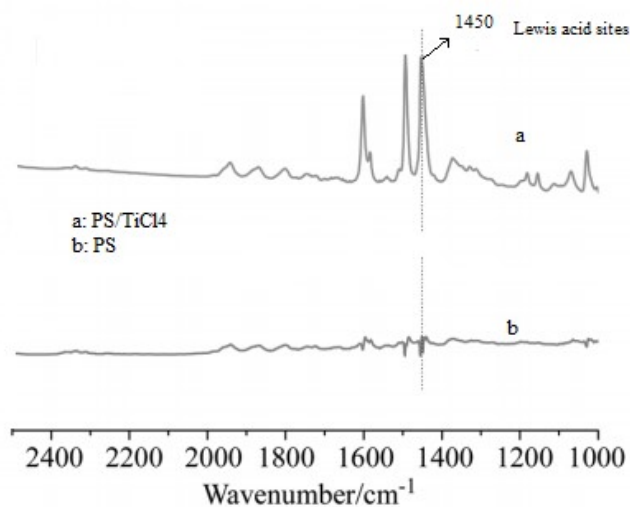


Figure S5 Pyridine-adsorbed FT-IR spectra of PS and PS/TiCl₄ samples

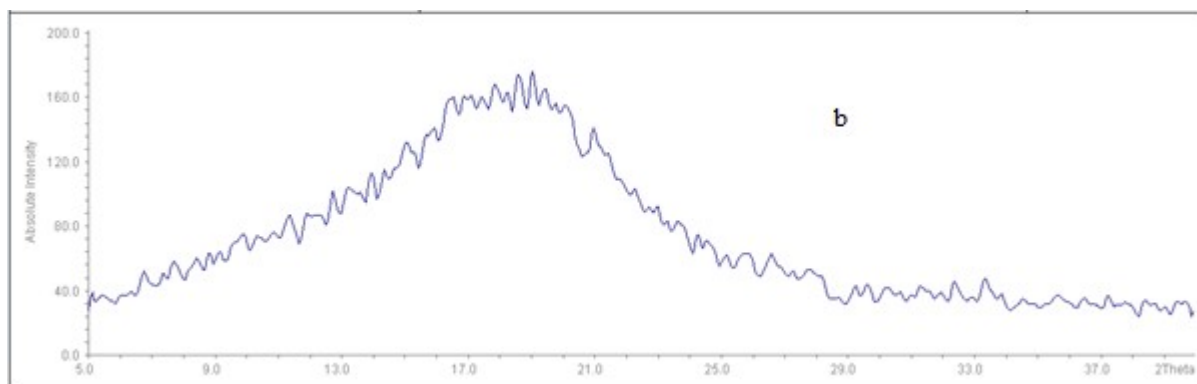
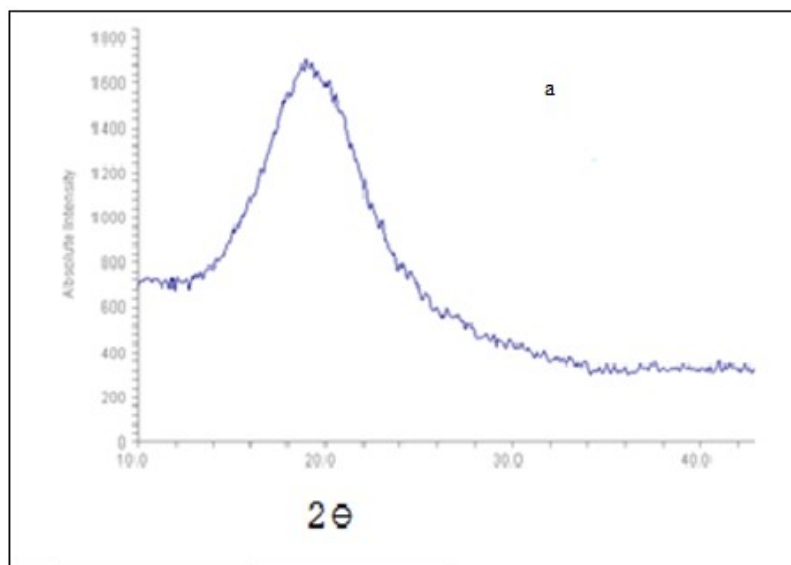


Fig. S6 XRD patterns of (a) PS/DVB; (b) PS/TiCl₄ complex samples

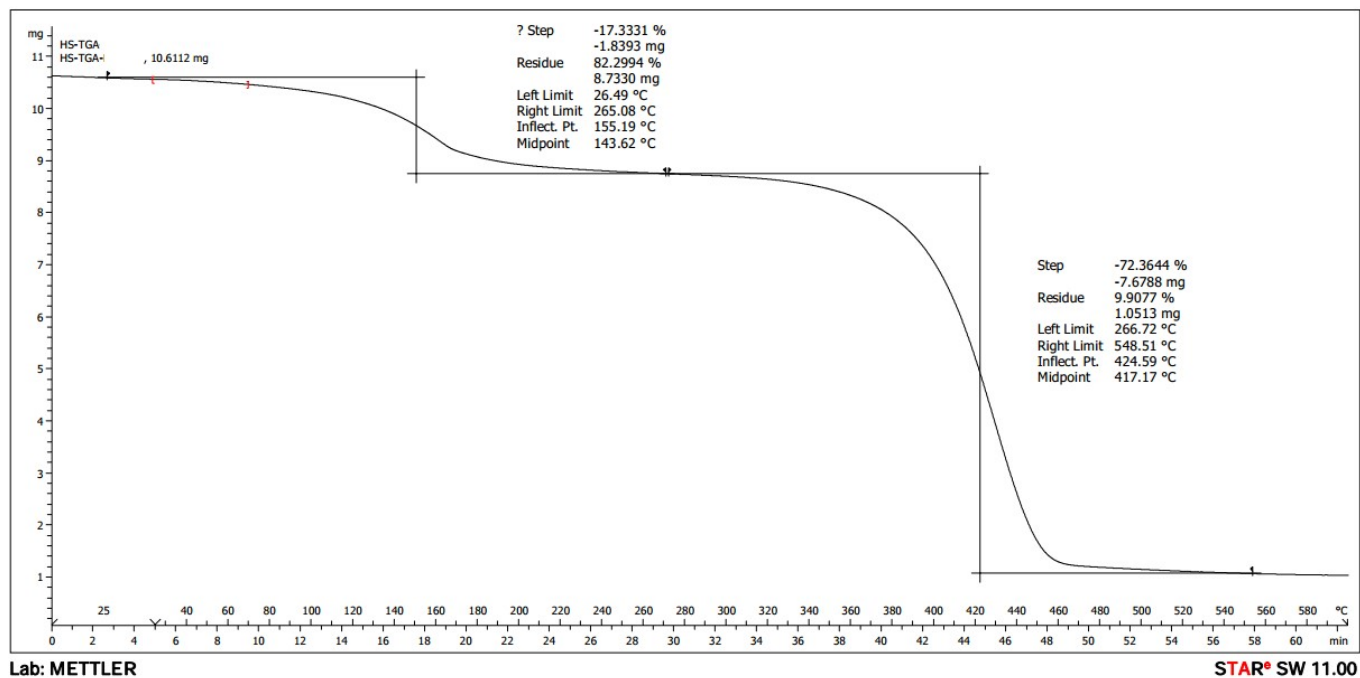
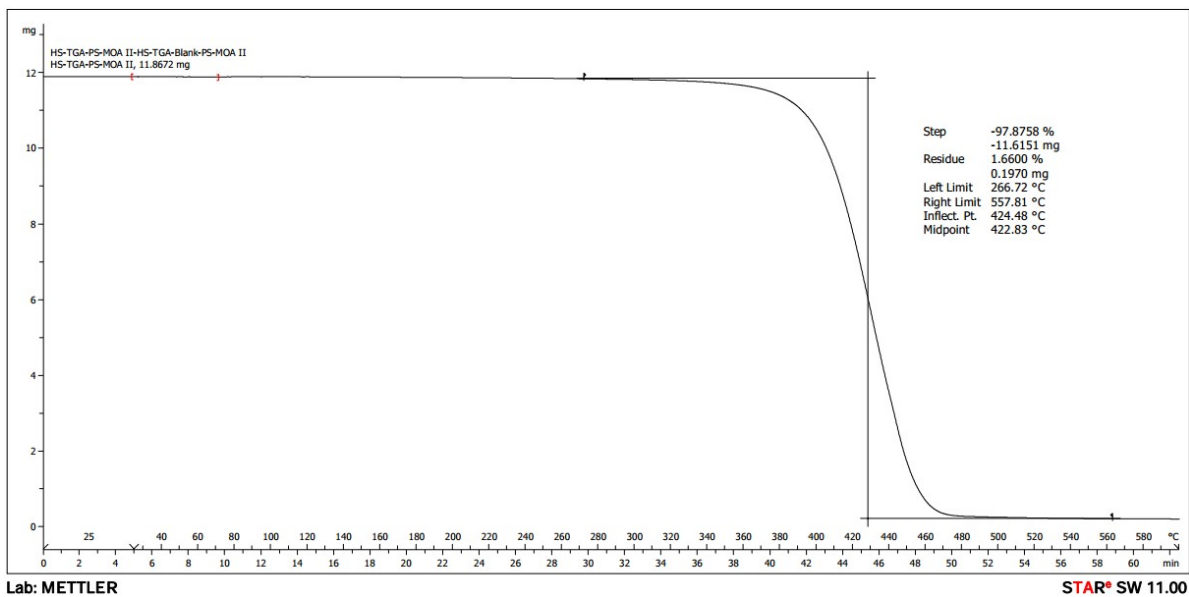


Figure S7 TGA thermograph of DVB-crosslinked PS (up) and PS/TiCl₄ complex catalyst (down)

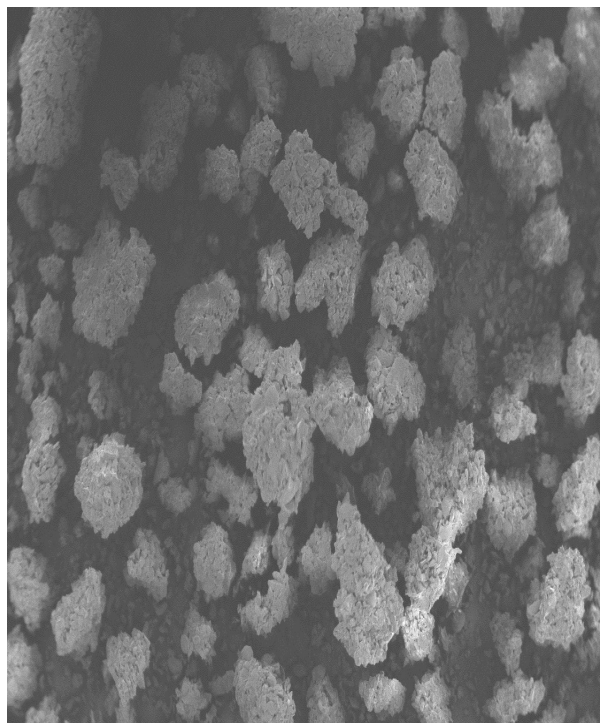
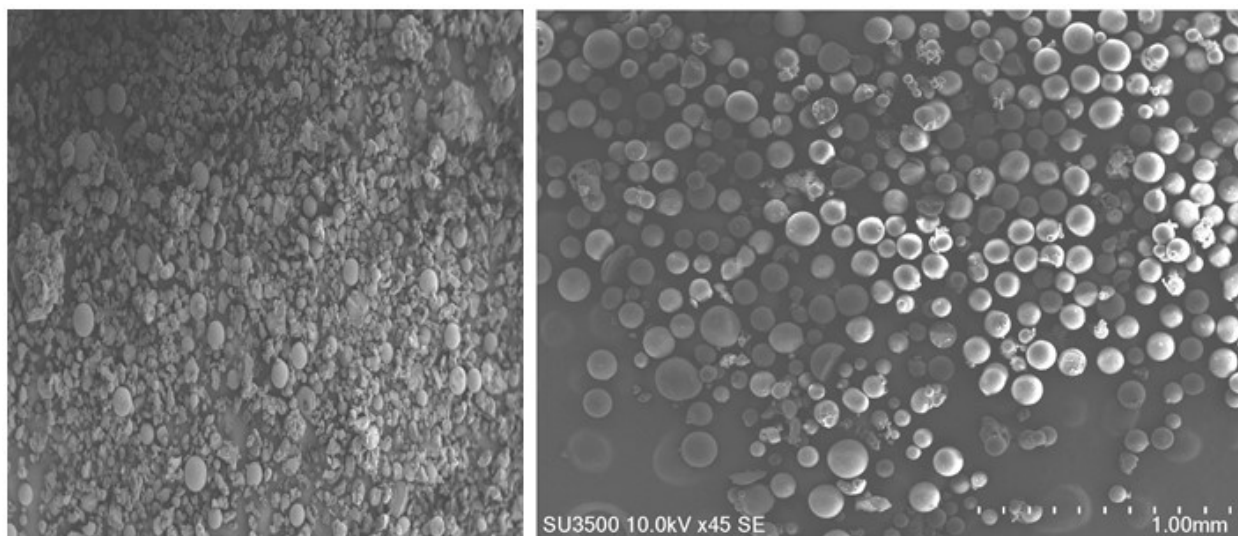


Figure S8. SEM images of (up) PS carrier, (down) PS/TiCl₄ samples

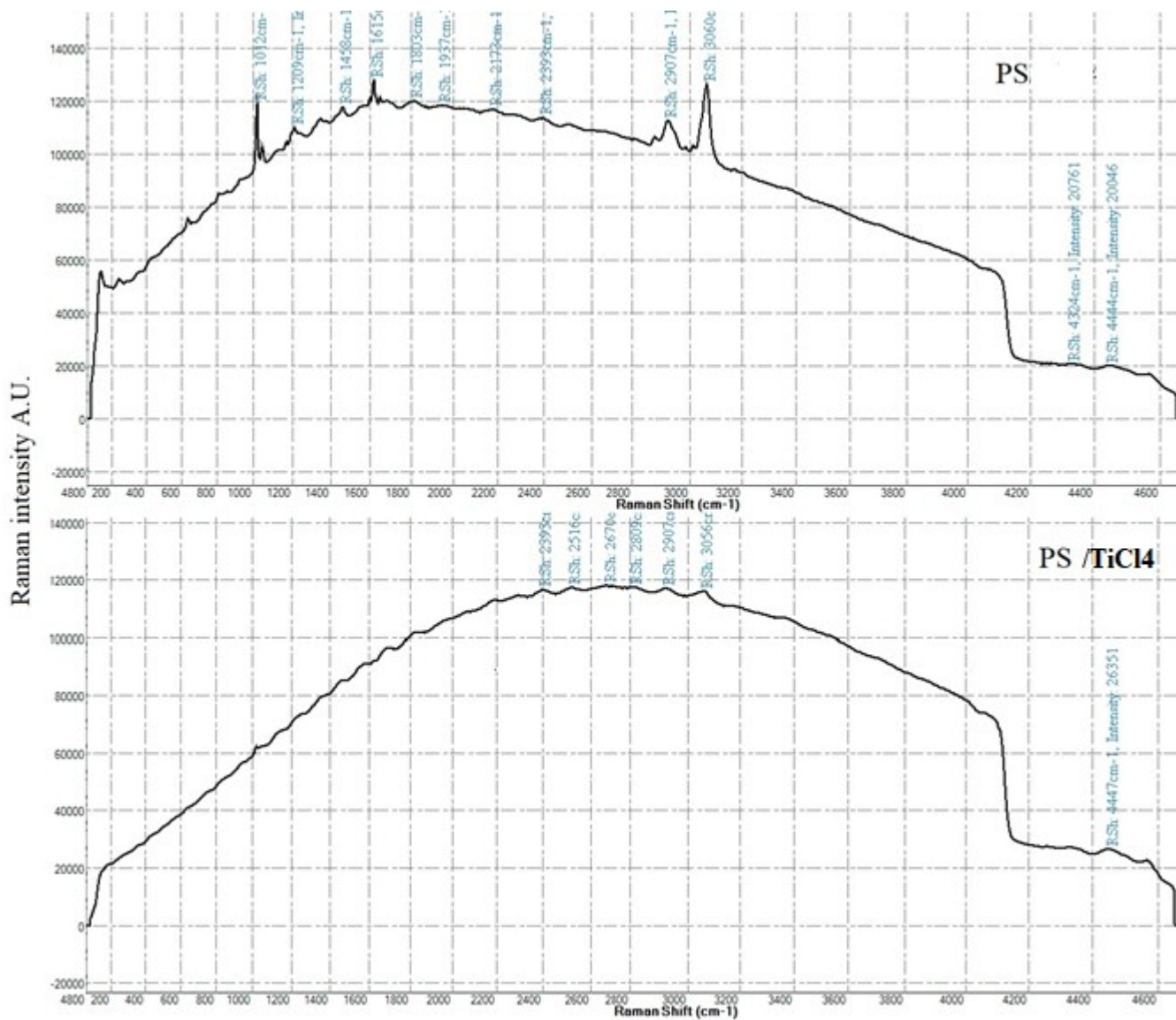


Fig. S9 Raman spectra of PS and PS/TiCl₄ samples

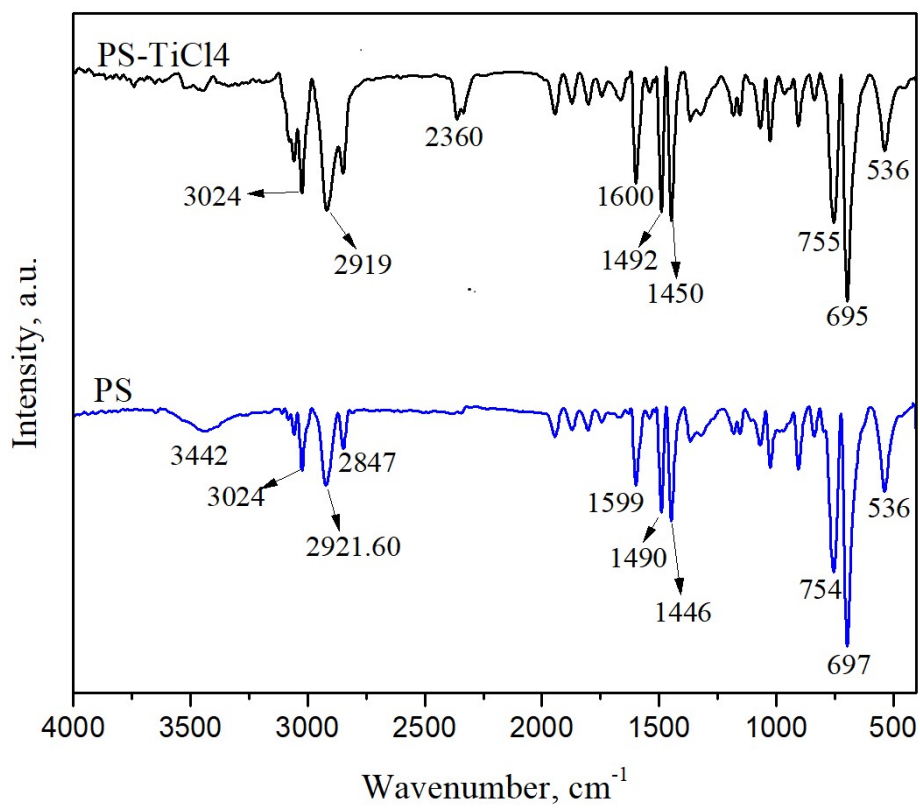
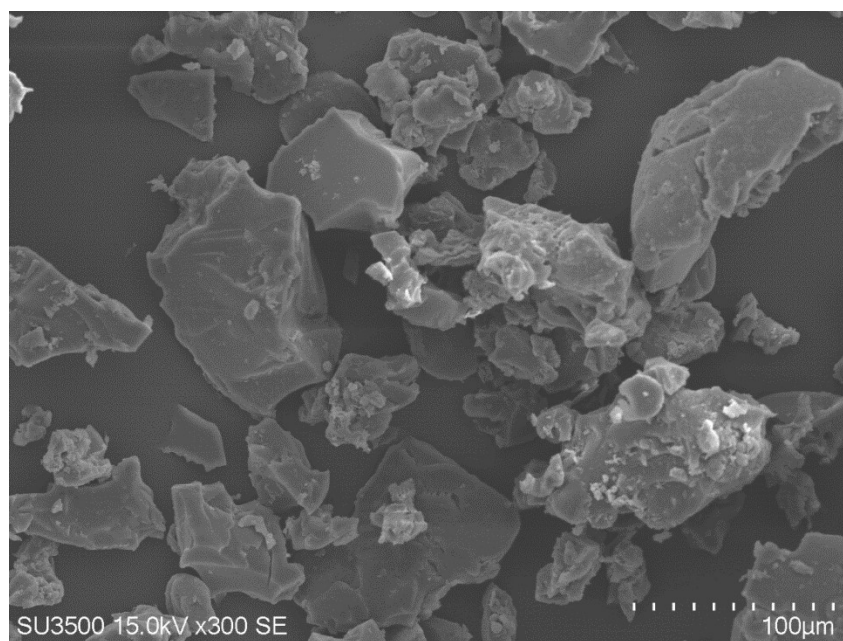


Fig. S10 FT IR spectra of re-prepared PS and PS/TiCl₄ samples



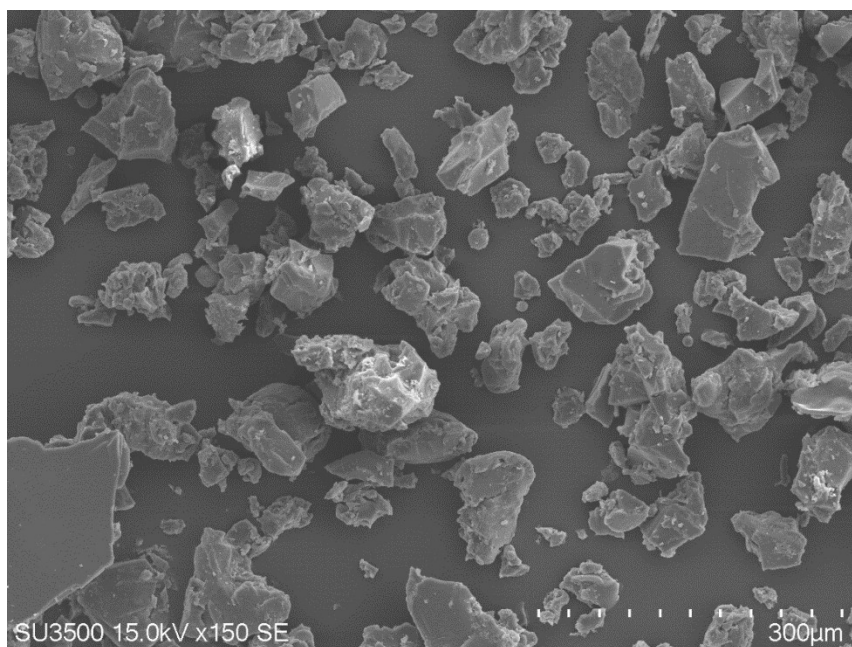


Fig. 11S SEM images of PS/TiCl₄ catalyst used after four polymerizations at different magnifications

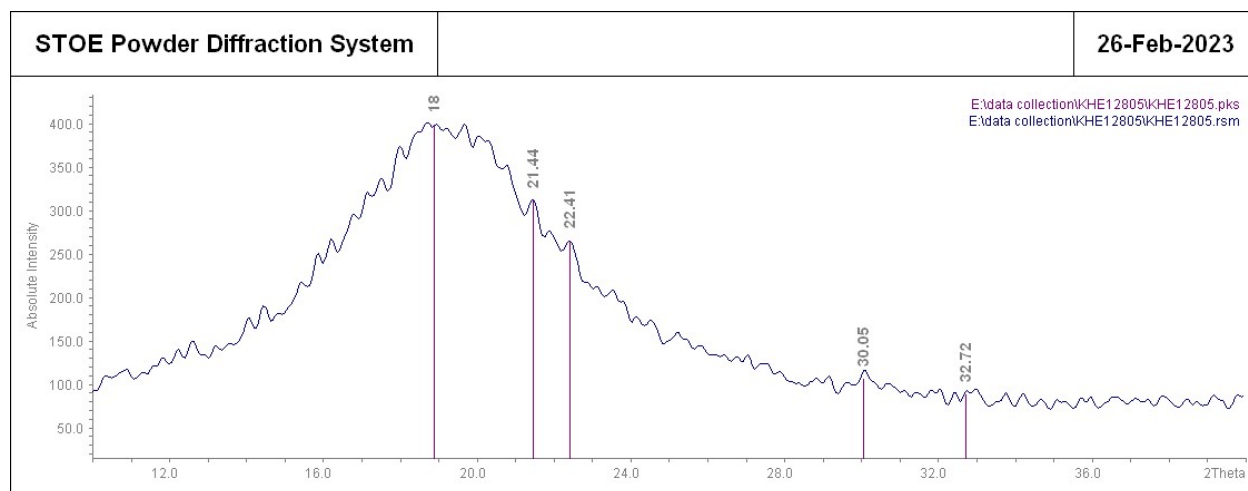


Fig. 12S XRD diffraction pattern of PS/TiCl₄ recovered after four polymerizations

Table 1S Swelling properties of the crosslinked-PS with different degrees of cross-linking^b in toluene

Degree of crosslinking (%)	4	6	8	10
EWC (%)	86 ^a	78	74	62

^a Less mechanical strength in successive polymerizations

^b Crosslinking agent up to 8% was used to ensure a balance between rigidity and swelling properties.

“Analysis of raw pygas in different time intervals”

Accredit	Analysis	Result	Unit Measurement	Specification	Analysis Method
Unit Category: OLEFIN					
Unit Tag: 650					
SCNo: S-651[Raw Gasoline (PyGas) bottom Debutanizer 10-T-651 to Storage]					
Sampling Time: 15/04/22 1394/02/02 08:04					
Sample ID: 348113					
Unchecked	R.V.P	53.8	KPa		ASTM D6378
Unchecked	Density at 15.6C	0.8440	gr/cm3		ASTM D4052
Unchecked	Total Sulfur	144	mg/Kg		ASTM D5453
Unchecked	Water Content	360	ppm		ASTM E203
Sampling Time: 15/04/25 1394/02/05 08:04					
Sample ID: 348542					
Unchecked	IBP	36.1	°C		ASTM D86
Unchecked	10%Recovery	58.8	C		ASTM D86
Unchecked	90%Recovery	186.5	C		ASTM D86
Unchecked	60%Recovery	97.5	C		ASTM D86
Unchecked	R.V.P	51.7	KPa		ASTM D6378
Unchecked	FBP	213.4	C		ASTM D86
Unchecked	5%Recovery	53.8	C		ASTM D86
Unchecked	80%Recovery	162.7	C		ASTM D86
Unchecked	95%Recovery	206.5	C		ASTM D86
Unchecked	20%Recovery	66.4	C		ASTM D86
Unchecked	30%Recovery	73.6	C		ASTM D86
Unchecked	40%Recovery	81.0	C		ASTM D86
Unchecked	50%Recovery	88.4	C		ASTM D86
Unchecked	70%Recovery	117.3	C		ASTM D86
Unchecked	Density at 15.6C	0.8457	gr/cm3		ASTM D4052
Unchecked	Water Content	400	ppm		ASTM E203
Unchecked	Total Sulfur	108	mg/Kg		ASTM D5453
Sampling Time: 15/04/29 1394/02/09 08:04					
Sample ID: 349154					
Unchecked	Density at 15.6C	0.8394	gr/cm3		ASTM D4052
Unchecked	Water Content	460	ppm		ASTM E203
Unchecked	Total Sulfur	120	mg/Kg		ASTM D5453

Unchecked	R.V.P	58.3	KPa		ASTM D6378
Sampling Time: 15/05/06 1394/02/16 08:05					
Sample ID: 349869					
Unchecked	Density at 15.6C	0.8274	gr/cm3		ASTM D4052
Unchecked	Water Content	550	ppm		ASTM E203
Unchecked	Total Sulfur	99	mg/Kg		ASTM D5453
Unchecked	R.V.P	54.1	KPa		ASTM D6378
Sampling Time: 15/05/09 1394/02/19 08:05					
Sample ID: 350369					
Unchecked	FBP	181.5	C		ASTM D86
Unchecked	IBP	36.2	C		ASTM D86
Unchecked	5%Recovery	49.4	C		ASTM D86
Unchecked	10%Recovery	53.5	C		ASTM D86
Unchecked	80%Recovery	107.3	C		ASTM D86
Unchecked	90%Recovery	162.6	C		ASTM D86
Unchecked	95%Recovery	181.3	C		ASTM D86
Unchecked	20%Recovery	59	C		ASTM D86
Unchecked	30%Recovery	64.5	C		ASTM D86
Unchecked	40%Recovery	70.9	C		ASTM D86
Unchecked	50%Recovery	77.7	C		ASTM D86
Unchecked	60%Recovery	84.2	C		ASTM D86
Unchecked	70%Recovery	91.2	C		ASTM D86
Unchecked	Density at 15.6C	0.8153	gr/cm3		ASTM D4052
Unchecked	Total Sulfur	66.2	mg/Kg		ASTM D5453
Unchecked	R.V.P	61	KPa		ASTM D6378
Unchecked	Water Content	560	ppm		ASTM E203
Sampling Time: 15/05/13 1394/02/23 08:05					
Sample ID: 351053					
Unchecked	Density at 15.6C	0.8368	gr/cm3		ASTM D4052
Unchecked	Water Content	440	ppm		ASTM E203
Unchecked	Total Sulfur	120.8	mg/Kg		ASTM D5453
Unchecked	R.V.P	57.4	KPa		ASTM D6378
Sampling Time: 15/05/16 1394/02/26 08:05					
Sample ID: 351518					
Unchecked	FBP	219.9	C		ASTM D86
Unchecked	IBP	37.2	C		ASTM D86
Unchecked	5%Recovery	53	C		ASTM D86

Unchecked	10%Recovery	57.8	C		ASTM D86
-----------	-------------	------	---	--	----------

Unchecked	80%Recovery	163.1	C		ASTM D86
Unchecked	90%Recovery	187.2	C		ASTM D86
Unchecked	95%Recovery	211.8	C		ASTM D86
Unchecked	20%Recovery	65.2	C		ASTM D86
Unchecked	30%Recovery	72.9	C		ASTM D86
Unchecked	40%Recovery	80.9	C		ASTM D86
Unchecked	50%Recovery	88.7	C		ASTM D86
Unchecked	60%Recovery	98.2	C		ASTM D86
Unchecked	70%Recovery	118.7	C		ASTM D86
Unchecked	Density at 15.6C	0.8439	gr/cm3		ASTM D4052
Unchecked	Water Content	330	ppm		ASTM E203
Unchecked	Total Sulfur	101.5	mg/Kg		ASTM D5453
Unchecked	R.V.P	52.1	KPa		ASTM D6378

Sampling Time: 15/05/20 1394/02/30 08:05

Sample ID: 352140

Unchecked	Density at 15.6C	0.8408	gr/cm3		ASTM D4052
Unchecked	Water Content	350	ppm		ASTM E203
Unchecked	Total Sulfur	73	mg/Kg		ASTM D5453
Unchecked	R.V.P	53.0	KPa		ASTM D6378

Sampling Time: 15/05/23 1394/03/02 08:05

Sample ID: 352570

Unchecked	FBP	186.9	C		ASTM D86
Unchecked	IBP	35.1	C		ASTM D86
Unchecked	5%Recovery	50.1	C		ASTM D86
Unchecked	10%Recovery	54.2	C		ASTM D86
Unchecked	80%Recovery	101.1	C		ASTM D86
Unchecked	90%Recovery	155.9	C		ASTM D86
Unchecked	95%Recovery	178.3	C		ASTM D86
Unchecked	20%Recovery	60.2	C		ASTM D86
Unchecked	30%Recovery	66.2	C		ASTM D86
Unchecked	40%Recovery	72.1	C		ASTM D86
Unchecked	50%Recovery	78	C		ASTM D86
Unchecked	60%Recovery	83.2	C		ASTM D86
Unchecked	70%Recovery	89	C		ASTM D86
Unchecked	Density at 15.6C	0.8222	gr/cm3		ASTM D4052
Unchecked	Water Content	310	ppm		ASTM E203
Unchecked	Total Sulfur	64	mg/Kg		ASTM D5453
Unchecked	R.V.P	61.4	KPa		ASTM D6378

Sampling Time: 15/05/27 1394/03/06 08:05					
Sample ID: 353209					
Unchecked	Density at 15.6C	0.8401	gr/cm3		ASTM D4052
Unchecked	Water Content	520	ppm		ASTM E203
Unchecked	R.V.P	53.1	KPa		ASTM D6378
Sampling Time: 15/05/30 1394/03/09 08:05					
Sample ID: 353770					
Unchecked	10%Recovery	58.4	C		ASTM D86
Unchecked	60%Recovery	97.3	C		ASTM D86
Unchecked	FBP	217.7	C		ASTM D86
Unchecked	IBP	38.1	C		ASTM D86
Unchecked	5%Recovery	53.8	C		ASTM D86
Unchecked	80%Recovery	161.8	C		ASTM D86
Unchecked	90%Recovery	186	C		ASTM D86
Unchecked	95%Recovery	206.8	C		ASTM D86
Unchecked	20%Recovery	65.3	C		ASTM D86
Unchecked	30%Recovery	72.6	C		ASTM D86
Unchecked	40%Recovery	80.3	C		ASTM D86
Unchecked	50%Recovery	88.1	C		ASTM D86
Unchecked	70%Recovery	116.2	C		ASTM D86
Unchecked	Density at 15.6C	0.8428	gr/cm3		ASTM D4052
Unchecked	Water Content	460	ppm		ASTM E203
Unchecked	Total Sulfur	58.5	mg/Kg		ASTM D5453
Unchecked	R.V.P	50.2	KPa		ASTM D6378
Sampling Time: 15/06/03 1394/03/13 08:06					
Sample ID: 354409					
Unchecked	Density at 15.6C	0.8442	gr/cm3		ASTM D4052
Unchecked	Water Content	330	ppm		ASTM E203
Unchecked	Total Sulfur	96	mg/Kg		ASTM D5453
Unchecked	R.V.P	50.4	KPa		ASTM D6378
Sampling Time: 15/06/06 1394/03/16 08:06					
Sample ID: 354891					
Unchecked	FBP	216.6	C		ASTM D86
Unchecked	IBP	37.3	C		ASTM D86
Unchecked	5%Recovery	53.5	C		ASTM D86
Unchecked	10%Recovery	58.4	C		ASTM D86
Unchecked	80%Recovery	166.5	C		ASTM D86
Unchecked	90%Recovery	187.9	C		ASTM D86

Unchecked	95%Recovery	208.3	C		ASTM D86
Unchecked	20%Recovery	65.8	C		ASTM D86
Unchecked	30%Recovery	73.7	C		ASTM D86
Unchecked	40%Recovery	81.8	C		ASTM D86
Unchecked	50%Recovery	89.9	C		ASTM D86
Unchecked	60%Recovery	100.3	C		ASTM D86
Unchecked	70%Recovery	123.4	C		ASTM D86
Unchecked	Density at 15.6C	0.8441	gr/cm3		ASTM D4052
Unchecked	Water Content	370	ppm		ASTM E203
Unchecked	Total Sulfur	94	mg/Kg		ASTM D5453
Unchecked	R.V.P	50.4	KPa		ASTM D6378

Sampling Time: 15/06/10 1394/03/20 08:06

Sample ID: 355714

Unchecked	Density at 15.6C	0.8416	gr/cm3		ASTM D4052
Unchecked	Water Content	480	ppm		ASTM E203
Unchecked	Total Sulfur	158	mg/Kg		ASTM D5453
Unchecked	R.V.P	51.8	KPa		ASTM D6378

Sampling Time: 15/06/13 1394/03/23 08:06

Sample ID: 356258

Unchecked	FBP	214.3	C		ASTM D86
Unchecked	IBP	36.5	C		ASTM D86
Unchecked	5%Recovery	49.3	C		ASTM D86
Unchecked	10%Recovery	54.0	C		ASTM D86
Unchecked	80%Recovery	165.7	C		ASTM D86
Unchecked	90%Recovery	189.7	C		ASTM D86
Unchecked	95%Recovery	210.3	C		ASTM D86
Unchecked	20%Recovery	61.6	C		ASTM D86
Unchecked	30%Recovery	69.5	C		ASTM D86
Unchecked	40%Recovery	78.5	C		ASTM D86
Unchecked	50%Recovery	87.2	C		ASTM D86
Unchecked	60%Recovery	97.0	C		ASTM D86
Unchecked	70%Recovery	118.1	C		ASTM D86
Unchecked	Density at 15.6C	0.8339	gr/cm3		ASTM D4052
Unchecked	Water Content	850	ppm		ASTM E203
Unchecked	Total Sulfur	84	mg/Kg		ASTM D5453
Unchecked	R.V.P	57.1	KPa		ASTM D6378
Unchecked	Recovery	97.0	%		ASTM D86
Unchecked	Residue	1.1	%		ASTM D86

Unchecked	Loss	1.9	%		ASTM D86
-----------	------	-----	---	--	----------