

The following summarizes the technical achievements for the first six months of the first project year.

**Task 1. Pilot-Scale Fuel Production at PARC**  
(G. Wilson (PARC))

**Subtask 1.1 LCO and RCO procurement**

Light cycle oil (LCO) was procured from United Refining Company in Warren, PA. Refined chemical oil (RCO) was procured from Koppers, Inc., Harmarville, PA. These materials were blended to provide a feedstock RCO/LCO blend that was upgraded by deep hydrotreatment and fractionated in subsequent tasks. Simulated distillation (D2887) of LCO and RCO samples is shown in **Table 1**.

**Table 1 United LCO and Koppers RCO Simulated Distillations**

SAMPLE	LCO PR 1244	RCO 1:1 PR 1238	RCO :LCC PR 1251
Instrument	5880	5880	5880
IBP	350	335	341
5%	451	390	396
10%	485	429	431
20%	516	433	436
30%	533	435	440
40%	553	437	486
50%	570	438	534
60%	593	451	551
70%	618	500	577
80%	651	545	625
90%	684	598	667
95%	705	650	704
FBP	771	894	813
% at 356F (180C)	0.15	1.91	1.36
% at 518F (270C)	31.2	74.0	45.5
% at 572F (300C)	50.9	85.1	68.1

### Subtask 1.2 Catalyst Preparation

Catalyst, necessary for the deep hydrotreating of total liquid product (TLP), was obtained in this task. In previous work [1, 24], PARC has identified a Criterion Syncat-3 cobalt-molybdenum or Syncat 37, nickel-molybdenum catalysts as effective in converting the coal-based blend to a deeply hydrotreated total liquid product. This product has been found to be rich in hydroaromatic components and as a result the jet fuel is thermally very stable. These catalysts must be activated by presulfiding after drying in a flow of

hydrogen. The SYNCAT catalyst is received by PARC pre-impregnated with a sulfur compound, however, PARC employs a treatment with kerosene containing 0.25 wt% dimethyldisulfide to ensure proper sulfiding prior to use.

### **Subtask 1.3 Hydrotreatment of Blended Product**

Production of deeply hydrotreated total liquid product (TLP) to provide material for other tasks in this project by large-scale production of TLP is necessary. In this subtask, the blended RCO/LCO was catalytically hydrotreated at a rate necessary to produce a target LHSV of 0.85 at 710°F using high purity hydrogen. The non-jet-fuel components co-produced with the jet fuel was isolated by fractional distillation for further characterization and testing at Penn State University.

Since the best conditions for hydrotreatment and the optimum ratio of RCO/LCO is still being assessed, this subtask is being studied on a smaller scale than will eventually be used to produce production quantities. Subtask 1.4 describes work at smaller scale to isolate gasoline, diesel and fuel oil range products for evaluation.

### **Subtask 1.4 Fractionation into Refinery Product Slate**

The total liquid product produced in Task 1.3 was distilled to provide fractions corresponding to gasoline, diesel, and fuel oil range refinery product streams. These materials will be used in many of the remaining tasks of the proposal. Distillation of the composite total liquid product is directed at evaluation of all non-jet fuel range material. The total liquid product was distilled in PARC's 150-gallon still using "narrow cut" techniques. This is the same still used in PARC's distillation of jet fuel range product as

a part of our AFOSR contract. Standard D2887 simulated distillation analysis were performed on lower boiling fractions to insure that the boiling range of the fractions correspond to conventional refinery stream specifications. These materials were transferred to Penn State University for further evaluation.

### **Parametric Study for Coal-Tar Processing Approach**

This work is focusing on a parametric study to define optimum hydrotreating conditions, and how varying operating conditions can affect the performance features of each of the fractions that will need to be integrated into an existing refinery.

PARC Technical Services studies involved the procurement of starting materials and the hydrotreating and distillation of refinery products from the hydrotreated total liquid products. RCO and LCO were blended in ratios of 1:1, 2:1 and 3:1 by weight. These materials were then hydrotreated under a variety of hydrotreating conditions aimed at providing a range of low, intermediate and high levels of naphthalene conversion. The extent of hydrotreating severity was followed by measuring the degree of naphthalene conversion and the extent of desulfurization.

These materials were shipped to Penn State for evaluation as part of the various tasks depending on the boiling range of the product. A summary of the yield structure for fractional distillation cuts from the hydrotreated blends is shown in **Table 2**.

**Table 2 - Summary of Composition of HDT Blends of 1:1, 2:1 and 3:1 RCO/LCO  
1:1 FEED**

	X864 (P67-64-1)			X865 (P67-64-2)			X866 (P67-64-3)			X867 (P67-64-5)			X868 (P67-65-1)		
	Charge Sulfur (ppm): 1750			Charge Sulfur (ppm): 2000			Charge Sulfur (ppm): 929			Charge Sulfur (ppm): 780			Charge Sulfur (ppm): 41		
	Nitrogen (ppm): 1200			Nitrogen (ppm): 1800			Nitrogen (ppm): 403			Nitrogen (ppm): 130			Nitrogen (ppm): 11.6		
	cut1 OP-180C	cut2 180-270C	btms 270C+	cut1 OP-180C	cut2 180-270C	btms 270C+	cut1 OP-180C	cut2 180-270C	btms 270C+	cut1 OP-180C	cut2 180-270C	btms 270C+	cut1 OP-180C	cut2 180-270C	btms 270C+
wt %	6.9	56.5	31.8	4.7	57.6	36.7	5.5	58.9	35.3	4.6	63.2	31.9	5.6	64.7	29.2
vol %	7.8	56.9	30.6	5.4	58.3	35.3	6.3	65.9	33.8	5.2	63.8	30.6	6.2	65.7	28
Nitrogen (ppm)	227	967	915	277	1500	937	22	205	984	3	16	428	1	1	55
Sulfur(ppm)	28	190	3700	78	68	3400	4	23	2800	12	61	1400	4	1	155
Sim.Dist (D227)	OP-356F	356-518F	518-572F	OP-356F	356-518F	518-572F	OP-356F	356-518F	518-572F	OP-356F	356-518F	518-572F	OP-356F	356-518F	518-572F
IBP (%off)	180	357	503	176	335	485	176	308	484	176	277	467	178	288	468
5	213	410	532	185	374	517	184	355	519	184	346	521	185	365	516
10	228	419	544	216	417	534	215	389	538	215	371	540	216	375	531
20	266	423	562	240	423	552	235	391	558	234	390	561	250	383	551
30	375	426	573	274	427	569	273	393	577	269	392	578	274	415	570
40	395	431	588	278	434	581	277	394	589	276	393	591	286	426	582
50	313	438	601	288	440	598	290	395	606	287	395	607	312	430	598
60	327	461	618	311	460	615	312	401	622	310	406	620	330	435	610
70	341	483	636	323	481	633	328	433	640	328	438	637	345	459	626
80	343	501	659	342	502	658	344	458	663	344	459	658	357	489	649
90	354	520	687	374	521	685	374	476	690	356	478	687	360	517	681
95	382	536	711	353	536	708	357	491	713	360	494	711	368	530	711
EP	390	566	896	392	565	837	391	521	833	474	460	846	460	562	863
Key GC Comps															
cyclohexane	3.00	0.05	0.00	4.06	0.29	0.00	4.67	0.03	0.00	5.73	0.04	0.00	6.47	0.00	0.00
ETBenzene	6.56	0.12	0.00	6.00	0.02	0.00	5.90	0.00	0.00	5.84	0.04	0.00	3.67	0.04	0.00
xylene	14.54	0.03	0.00	20.80	0.17	0.00	18.12	0.62	0.00	17.03	0.45	0.00	11.80	0.67	0.00
tetralin	4.89	36.86	0.00	1.62	31.25	0.00	1.33	40.85	0.00	1.48	39.16	0.00	1.77	34.68	0.00
naphthalene	0.25	11.63	0.00	0.14	16.75	0.00	0.00	5.73	0.00	0.00	1.76	0.00	0.00	2.41	0.00
subst. naph.	0.00	9.66	66.92	0.00	11.11	66.66	0.00	9.24	67.30	0.00	10.72	67.02	0.00	6.03	61.74
Unidentified	70.76	41.65	33.08	67.38	40.41	33.34	69.98	43.53	32.70	69.92	47.83	32.98	76.29	56.17	38.26

**2:1 FEED**

	X871 (P67-66-1)			X872 (P67-66-3)			X873 (P67-66-4)			X874 (P67-66-5)		
	Charge Sulfur (ppm): 144			Charge Sulfur (ppm): 1400			Charge Sulfur (ppm): 225			Charge Sulfur (ppm): 79		
	Nitrogen (ppm): 119			Nitrogen (ppm): 1300			Nitrogen (ppm): 163			Nitrogen (ppm): 10.5		
	cut1 OP-180C	cut2 180-270C	btms 270C+	cut1 OP-180C	cut2 180-270C	btms 270C+	cut1 OP-180C	cut2 180-270C	btms 270C+	cut1 OP-180C	cut2 180-270C	btms 270C+
wt %	7.2	64.8	27.1	5.7	60.5	31.7	6.7	63.8	27.3	9.9	59.7	21.6
vol %	8.1	65.2	25.8	6.5	61.1	30.2	7.7	64.3	25.8	11.1	59.7	20.7
Nitrogen (ppm)	1	3.6	295	319	1000	2000?	8.5	18.6	518	68	9	94.7
Sulfur(ppm)	1	3.4	423	4.7	38.6	939?	1	101	444	5.5	3.4	94.1
Sim.Dist (D227)	OP-356F	356-518F	518-572F	OP-356F	356-518F	518-572F	OP-356F	356-518F	518-572F	OP-356F	356-518F	518-572F
IBP (%off)	177	312	490	177	352	480	177	282	491	167	338	493
5	186	355	523	215	400	525	184	346	528	183	356	525
10	217	373	540	232	440	540	201	359	542	187	362	539
20	259	390	560	273	445	558	228	389	553	219	390	558
30	375	393	578	277	449	571	257	392	578	268	392	571
40	279	394	591	288	457	588	274	393	592	277	383	584
50	305	395	607	312	464	602	278	394	609	307	395	599
60	317	397	623	327	468	623	303	397	627	320	397	611
70	338	418	639	343	493	636	317	403	643	340	424	627
80	345	444	662	345	527	662	342	439	668	347	449	650
90	356	470	695	347	547	693	355	466	706	358	472	685
95	359	486	723	356	567	720	358	482	748	362	487	713
EP	392	518	910	459	697	862	397	515	959	427	518	860
Key GC Comps												
cyclohexane	4.71	0.00	0.00	1.90	0.00	0.00	7.65	0.06	0.00	9.60	0.00	0.00
ETBenzene	4.88	0.00	0.00	5.54	0.00	0.00	6.84	0.03	0.00	4.12	0.00	0.00
xylene	17.62	0.10	0.00	20.62	0.00	0.00	17.63	0.36	0.00	11.96	0.00	0.00
tetralin	0.93	45.30	0.00	1.58	33.66	0.09	1.07	40.94	0.00	2.35	40.81	0.00
naphthalene	0.00	5.13	0.00	0.12	29.06	0.09	0.07	10.28	0.00	0.14	4.91	0.00
subst. naph.	0.00	7.74	66.68	0.00	9.99	67.92	0.00	8.43	67.70	0.00	3.46	65.29
Unidentified	71.86	41.73	33.32	70.24	27.29	31.90	66.74	39.90	32.30	71.83	50.82	34.71

**3:1 FEED**

	X875 (P67-67-1)			X876 (P67-67-2)			X877 (P67-67-4)		
	Charge Sulfur (ppm): 206			Charge Sulfur (ppm): 196			Charge Sulfur (ppm): 629		
	Nitrogen (ppm): 50			Nitrogen (ppm): 474			Nitrogen (ppm): 140		
	cut1 OP-180C	cut2 180-270C	btms 270C+	cut1 OP-180C	cut2 180-270C	btms 270C+	cut1 OP-180C	cut2 180-270C	btms 270C+
wt %	10.2	68.2	19.8	8.6	61.5	25.9	6.1	64.4	29.2
vol %	11.6	67.7	18.8	9.8	61.8	24.5	7	65	27.9
Nitrogen (ppm)	6.4	18.2	276	54.5	162	1500	0	64	2000
Sulfur(ppm)	15.4	18.5	81.4	112.1	9	631	906	1100	2100
Sim.Dist (D227)	OP-356F	356-518F	518-572F						
IBP (%off)	167	320	477	172	334	487	176	320	491
5	183	357	528	183	367	529	183	361	530
10	187	386	542	196	389	542	215	389	543
20	219	390	560	234	391	562	235	391	562
30	267	392	573	374	393	579	274	394	580
40	276	393	582	278	394	591	277	396	590
50	293	394	599	306	395	609	285	400	608
60	315	396	610	318	399	629	311	401	628
70	335	408	627	341	402	644	327	402	644
80	345	440	648	346	433	668	344	432	665
90	356	464	683	358	463	706	346	462	698
95	359	480	716	389	480	732	349	479	722
EP	390	517	880	459	516	936	399	516	854
Key GC Comps									
cyclohexane	9.60	0.00	0.00	6.01	0.00	0.00	3.96	0.03	0.00
ETBenzene	4.31	0.00	0.00	0.04	0.00	0.00	7.54	0.00	0.00
xylene	14.35	0.00	0.00	16.63	0.33	0.00	22.18	0.06	0.00
tetralin	1.05	46.38	0.00	6.52	46.17	0.06	1.40	31.53	0.00
naphthalene	0.00	6.08	0.00	0.62	16.01	0.04	0.17	31.95	0.00
subst. naph.	0.00	5.23	65.75	0.00	8.10	66.72	0.00	9.57	66.47
Unidentified	45.60	36.37	34.01	47.30	24.13	32.95	41.25	22.17	33.14

**Table 2. Summary of Composition of HDT Blends of 1:1, 2:1 and 3:1 RCO/LCO**

The evaluation of the jet fuels, as part of our AFOSR program, will provide guidance for selecting scale-up conditions and evaluating the most relevant non-jet fuel fractions as a part of this program.

### **Decant Oil Hydrotreating for Co-Coking Approach**

Decant oil (Heavy FCC Cycle Oil) was hydrotreated at several different levels of severity to produce feeds for Penn State's co-coking component of the Refinery Integration Study. The Decant Oil was provided by United Refining, Warren Pennsylvania and contained a high level of sulfur (3.5 wt%) and is a heavy oil with a high gravity (1.1203 gm/ml, API -5.2)

PARC's adiabatic hydrotreatment pilot unit, P67 was used for the hydrotreating. The catalysts charges were:

Reactor 1 2148 ml, 2474 gm, Criterion NiMo Syncat-37

Reactor 2 2656 ml, 3060 gm, Criterion NiMo Syncat-37

Total 4804 ml, 5534 gm

Seven hydrotreated products were produced with a range of sulfur removal from 37.9 to 99.0 wt%.

### **Pilot unit description**

In the configuration used for this study, P67 consists of two reactors operated in series. Three standard quench zones were included in the set up of Reactor 1 which contained catalytically inert quartz glass beads. Reactor 2 is not equipped with quench but heat loss does occur in the transfer line between the two reactors.

Hydrogen was recycled after amine scrubbing to remove H<sub>2</sub>S and the purity was maintained at 95 to 98%. Minimum bleed off was used within the constraint of maintaining recycle H<sub>2</sub> purity. Make-up hydrogen is thereby minimized to supplying the hydrogen consumed in the operation plus losses due to the on-line gas chromatograph demand.

The total liquid product was taken as fractionator bottoms after partial stripping of H<sub>2</sub>S and ammonia in the fractionation tower. In some cases this operation resulted in small amounts of fractionation tower overhead. In such cases the furnace oil tower overhead was combined with the fractionation tower bottoms. The tower system was operated at atmospheric pressure.

### **Hydrotreating operation**

A sulfiding procedure was provided by the catalyst vendor and was modified to fit PARC's unit. The SYNCAT-37 catalyst was received pre-impregnated with a sulfur compound. A commercial diesel containing 0.25wt% sulfur as dimethyl disulfide in addition too the naturally occurring sulfur in the base diesel (about 300 ppm) was used as

the catalyst activation feedstock. The sulfur in the feedstock would ensure that the catalyst had an adequate supply of sulfur during the sulfiding procedure. Catalyst bed temperatures were brought up to Rx1 530°F and Rx 2 545°F prior to switching to run feed.

### **Operation on run feed -run P67-69-1 through 7**

The run feed was set at 5500gm/hr. (about 1 LHSV) and the inlet hydrogen rate at 75 scf/hr. (2,400 scf/bbl). Inlet gas purity was initially targeted at 98 % hydrogen minimum. Unit pressure was maintained at 600 psig for runs 1 through 5 and was increased to 1200 psig for runs 6 and 7.

The decant oil was processed for 10 days (Feb 3 through 13, 2004). Feed was processed at nominally seven different conditions representing seven levels of severity. To achieve this reactor temperature and feed rate were varied in the first four runs. The results for the first four runs confirmed our expectation that the decant oil difficult to desulfurize. Since the first drum of product (Run 1) had not achieved the target level of desulfurization it was decided to re-pass it at a reduced feed rate. The desulfurization level achieved was still only 82%. It was therefore decided, in the interest of time, to increase the reactor pressure to 1200 psig rather than reduce the feed rate further to achieve a target of about 95% desulfurization. Runs 5 and 6 achieved desulfurization levels of 88 and 99%, respectively. A decrease in reactor temperature was made in Run 7 to attempt to produce a product with a lower Desulfurization level than the 88% of Run 5. However, the product maintained 99 % Desulfurization in the limited time remaining.

The summary of the daily operating conditions for each run is given in **Table 3** together with the sulfur and nitrogen levels in the feed and the product. This information is further condensed in **Table 4** with the addition of the net weights and volumes of the seven samples shipped to Penn State. The API and specific gravities of the seven products are given in **Table 5**.

Catalyst		CRITERION SYNCAT-37 (PC-723)																						
CHARGE	<i>ml</i>	<i>gm</i>	Heats On		1100		2/3																	
Rx1	2148	2474	Start Diesel in		1100		2/4																	
Rx2	2656	3060	Start Run Feed:		2400		2/4		PR1542															
Total	4804	5534																						
Runs 1-5 NOMINAL RUN PRESSURE 600 PSIG																								
Runs 6-7 NOMINAL RUN PRESSURE 1200 PSIG																								
Pressure Test 1500 psig																								
Run No	Time	Date	FEED gm/hr 8hr Av	REACTOR 1				REACTOR 2				WABT COMB 8HR AVG	LHSV 8HR AVG	Inlet gas SCFB	Quench SCFB	Makeup SCFB	%H2 INLET	HYDROGEN CONSUMP SCFB	WT. BAL % (8 HR)	PRODUCT ANALYSES				
				IN	OUT	MAX	WABT 8HR AVG	IN	OUT	MAX	WABT 8HR AVG									S, wt% (1)	N, PPM (1)	Spec Grav gm/ml	%DES	%DEN
	0000	2/5	Started Run Feed																					
																		Feed Drum 1	3.54	1300	1.1203	-5.2 API		
																		Feed Drum 3	3.44	1374				
																		Feed Drum 4						
P67-69-1	1430 grab	2/5	5490	529	594	594	556	545	615	615	581	568	1.02	2440	0	2611	98.2	975	100.9		1300	1.0760	100.0	0.0
	0800 grab	2/6	5490	530	596	596	557	545	614	614	582	570	1.02	2511	0	1786	98.2	685	99.0		1200	1.0760	100.0	7.7
P67-69-1	08-20	2/5-6	Product Drum No 1																					
P67-69-2	1600	2/6	Increasing temp																					
	04 grab	2/7	5274	560	666	666	603	577	637	637	610	606	0.98	2598	0	2148	97.7	908	99.0	1.67	1100	1.0679	52.8	
P67-69-2	20-08	2/6-7	Product Drum No 2																					
	0400	2/8	3875	567	687	687	622	590	651	651	629	626	0.72	3517	0	3428	97.9	1159	99.7	nr	nr	1.0575		
	04 grab	2/9	4144	568	685	685	621	590	647	647	626	624	0.77	3388	0	4879	98.7	1081	99.2	1.16	968	1.0568	67.2	
P67-69-3	08-04	2/7-9	Product Drum No 3																					
P67-69-4	0400	2/9	STARTED RAISING TEMPERATURES																					
	15 grab	2/9	4090	607	716	716	668	632	678	678	663	666	0.76	3500	0	5577	97.5	1185	99.3	0.58	917	1.0568	83.6	29.5
	08 grab	2/10	3821	608	712	712	669	662	692	692	680	675	0.71	3283	0	2626	95.7	1080	100	0.56	935	1.0583	84.2	28.1
P67-69-4	04-16	2/9-10	Product Drum No 4																					
																			1.22	1000		65.5	23.1	
P67-69-5	1600	2/10	STARTED 2ND PASS OF Drum No 1																					
	08 grab	2/11	2691	607	652	652	634	660	675	675	667	650	0.50	4602	0	1455	95.6	657	99.7	0.49	625	1.0451	86.2	51.9
	900	2/11	STARTED RAISING TEMPERATURES																					
P67-69-5	16-12	2/10-11	Product Drum No 5																					
P67-69-6	1345	2/11	STARTED RAISING PRESSURE TO 1200 PSIG																					
	08 grab	2/12	2745	686	786	786	753	716	757	757	744	749	0.51	4020	0	4775	95.2	1268	97.5	0.0087	78	1.0246	99.8	94.0
	08 grab	2/13	2745	688	794	794	754	722	759	759	746	750	0.51	2858	0	4333	95.2	1288	97.1	0.0130	132	1.0239	99.6	89.8
	12-08	2/11-13	Product Drum No 6																					
																			0.0591	185				
	09	2/13	STARTED TO REDUCE TEMPARTURE																					
	1600	2/13	2745	655	771	771	735	694	740	740	733	734	0.51	3095	0	4587	97.2	1300	96.5					
	08-12	2/13																	0.0141	137		99.6	89.5	
	12-16	2/13																	0.0254	141		99.3	89.2	
	16-18	2/13																	0.0368	108		99.0	91.7	
	08-1800	2/13	Product Cans for Drum No 7																					
																			0.0348	147	1.0224	99.0	88.7	

Start Saving Product 0300, 2/5

(1) 2nd sample after re-mixing drum

Table 3. Hydrotreating Operating Conditions Summary

Catalyst CRITERION SYNCAT-37 (PC-723)																
Run Feed: UNITED REFINING DECANT OIL																
NOMINAL RUN PRESSURE 600 PSIG																
NOMINAL RUN PRESSURE 1200 PSIG																
Drum No	Run No	Time	Date	Rx1	Rx2	Rx1+2	LHSV 8HR AV	Inlet gas Nominal SCFB	H2 Consup Nominal SCFB	PRODUCT ANALYSES					Net Wt.	
				WABT 8HR AVG	WABT 8HR AV	WABT 8HR AV				S, wt% (1)	N, PPM (1)	Spec Grav gm/ml	%HDS	%HDN	in drum lbs	gallons
		0000	2/5	Started Run Feed							3.54	1300	1.1203	-5.2 API		
										3.44	1374					
1	P67-69-1	08-20	2/5-6	556	582	568	1.02	2500	750	2.20	1300	1.0810	37.9	0.0	26.4	2.9
2	P67-69-2	20-08	2/6-7	603	610	606	0.98	2600	908	1.75	1200	1.0730	50.6	7.7	133.8	15.0
3	P67-69-3	08-04	2/7-9	622	626	624	0.75	3450	1100	1.22	1000	1.0591	65.5	23.1	377.2	42.7
4	P67-69-4	04-16	2/9-10	669	680	675	0.74	3400	1150	0.64	944	1.0575	81.9	27.4	304.2	34.5
	<b>P67-69-5</b>	<b>1600</b>	<b>2/10</b>	<b>STARTED 2ND PASS OF Drum No 1</b>												
5	P67-69-5	16-12	2/10-11	634	667	650	0.50	4600	657	0.42	678	1.0489	88.1	47.8	91.6	10.5
	P67-69-6	1345	2/11	<b>STARTED RAISING PRESSURE TO 1200 PSIG</b>												
6	P67-69-6	12-08	2/11-13	754	745	750	0.51	3000	1268	0.0411	179	1.0254	98.8	86.2	260.8	30.5
7	P67-69-7	08-1800	2/13	735	733	734	0.51	3100	1300	0.0591	185	(1)	99.0	88.7	49.9	5.9
										0.0348	147	1.0224				

(1) 2nd sample after re-mixing drum

Table 4. Product Drum Analyses