

A STATISTICAL METHOD OF DESIGNING A CATALYST TO UPGRADE SOLVENT REFINED COAL

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INTRODUCTION

Coal liquids from SRC-II process contain much higher sulfur and nitrogen than the products derived from petroleum and need to be upgraded to offer the potential of substituting for crude oil. A number of investigators have reported on the use of either commercially available or proprietary catalysts for this upgrading. Berg(1) investigated more than fifty different hydrotreating catalysts with SRC-II. Sullivan(2) treated SRC-II with some of Chevron's hydrotreating catalysts. Heck(3) reported the use of Mobil Oil catalysts on SRC-II. Riedl(4) showed the effectiveness of fluid cracking catalysts in upgrading SRC-II.

The objective of this research was to upgrade the solvent refined coal from Pittsburg & Midway Coal Mining Company's SRC-II process into clean distillate fuels suitable for transportation grade fuels. One way to accomplish this would be to make it acceptable as a feedstock for a conventional petroleum refinery. The analysis of SRC-II products, Vacuum Flash Feed(VFF) and Light Ends Column Feed(LECF), are given in Table I. The major handicap possessed by these SRC-II products as a refinery feedstock are their nitrogen content, 1.17 wt% for VFF and 0.88 wt% for LECF. They should be reduced to as low as possible in any event at least to less than 0.3 wt%. Examples of hydrocracking processes that can tolerate this level of nitrogen are Standard Oil's Ultracracking and Union Oil's Unicracking(5). Their sulfur contents, 0.72 wt% and 1.21 wt%, also should be lowered to meet the EPA's standard which is currently 0.5 wt%.

In this research SRC-II VFF and LECF have been converted into low nitrogen and low sulfur contents oils by the catalytic hydrotreatment carried out in a trickle bed reactor. The effect of catalytic compositions were systematically investigated through the factorial experimental design which included four metals, Co, Mo, Ni, and W, as variables and two levels for each metal. The most promising catalyst was further tested by a long run through periodic regeneration and the catalyst deactivation was moderated by starting at a higher space velocity and a lower temperature.

EXPERIMENTAL

Catalysts were made by impregnating a commercial catalyst carrier with metal salts using the incipient wetness technique. Only one catalyst carrier, Nalco-6008C-1/32", obtained from Nalco Company, was used. It is composed of 98% Al_2O_3 and 2% SiO_2 and possesses a surface area of 215 m^2 /gram, an average pore diameter of 156.5 Å, a medium pore diameter of 161 Å, and a pore volume of 0.84 ml/gram. Four metals were loaded on the support in the order of Co, Mo, Ni, and W by using the water solution of $Co(NO_3)_2 \cdot 6H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, and $5(NH_4)_2O \cdot 12WO_3 \cdot 7H_2O$, respectively. The catalysts were pretreated by calcining at 450°C and the catalyst compositions were reported as the weight percents of metal oxides which were the percent weight increase after impregnation of the blank catalyst carrier.

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The evaluation of the catalysts was carried out in a down-flow trickle bed reactor shown in Figure 1. The freshly prepared catalysts were sulfided with 10% H₂S in a hydrogen mixture for 12 hours at 325°C. The reactor was made by a 2.54 cm (one-inch) ID and 1.1 meter (40-inch) long Schedule 80 Inconel pipe. A one meter (36-inch) Stainless Steel tubing was inserted centrally in the reactor and served as the thermowell. The reactor was placed into a 36 cm (3 feet) long aluminum block and heated by three sets of Nichrome wire heating coils on the aluminum block. The reactor was extended 10 cm (4-inch) outside the top of aluminum block to provide the sufficient preheating. Starting from the top, the reactor was packed with 175 ml of 0.635 cm (1/4-inch) Denstone inert support, followed by 25 ml of 0.32 cm (1/8-inch) Denstone inert support to serve as the preheating section. The sixty milliliters of catalyst mixed with 60 ml of 0.32 cm inert support was loaded into catalyst section. The remaining space at the bottom of the reactor was filled with 0.32 cm Denstone inert support. Operating conditions were kept relatively mild because it was the aim of this program to develop a process which would be economically as well as technically attractive. The usual conditions are 425°C, 6,893 K-Pascals (1,000 psig), liquid hourly space velocity of 1.0 v/v/hr, hydrogen feed rate of 1.79 cubic meters/liter (10,000 scf/bbl) of oil, and liquid feed temperature of 85°C.

RESULTS AND DISCUSSION

The blank catalyst carrier was first tested for its capability of removing nitrogen and sulfur for each feedstock using the typical operating conditions. Runs 1 and 2 in Table II used VFF as the feedstock and Runs 5 and 6 in Table III used LECF. Their denitrogenation data are plotted as a function of running time in Figure 2. The regression lines showed that the denitrogenation of VFF gave a higher initial activity of catalyst but much higher deactivation rate than the LECF did. It was believed that the heavier carbonaceous materials of VFF have caused the shorter active life of the catalyst. The sulfur contents of VFF and LECF, 0.72% and 1.21%, were reduced to 0.55 wt% and 0.38 wt%, respectively, shown in Table IV and V. The oil product recovery of LECF in Runs 5 and 6, 77 wt%, was much higher than that of VFF in Runs 1 and 2 which was 45 wt%. The metal effects studies were based on the performance of these blank runs.

A sixteen experiment 2⁴ full two level metal-loading factorial design was developed to determine the metal effects for each feedstock. The catalysts designated from C-41 to C-56 in Table II comprising every combination of 2 and 4% CoO, 2 and 8% MoO₃, 1 and 4% NiO, and 2 and 8% WO₃ were tested in Run 7 to 22 using SRC-II VFF as feedstock and in Run 23 to 38 using SRC-II LECF. The operating conditions of these runs were the same as those of blank runs. The average denitrogenation data from Run 7 to 22 varied from 61.9% (0.46 wt% N of product) to 81.1% (0.22 wt% N of product) and was regressed on the weight percent of metal oxides by using the forward stepwise linear regression technique at a confidence level of 90%. The regressed equation became

$$\%DN = 31.8 + 11.29 \text{ CoO} + 2.36 \text{ MoO}_3 + 3.26 \text{ WO}_3 - 0.589(\text{CoO})(\text{MoO}_3) - 0.893(\text{CoO})(\text{WO}_3),$$

where metal oxides represent the weight percent of catalytic compositions. The intercept, 31.8, is the average %DN for blank runs. The

result showed that three metals, Co, Mo, and W, significantly increased the catalytic activity for denitrogenation and the interactive effects of Co-Mo and Co-W were negative. The effect of Ni was found to be insignificant. Figure 3 plots the denitrogenation data for Run 7 to 22 as a function of the running time. The effect of Co concentration is also shown in the plot.

The denitrogenation data from Run 23 to 38 using LECF as the feedstock is shown in Table III. The nitrogen content of LECF, 0.88 wt%, has been reduced to an average of 0.07 wt% N (91.8 %DN) in Run 33 and 0.28 wt% (67.6 %DN) in Run 36. The fitted equation for the average denitrogenation data became

$$\%DN = 40.1 + 6.47 \text{ CoO} + 5.23 \text{ MoO}_3 + 1.56 \text{ WO}_3 - 0.86(\text{CoO})(\text{MoO}_3)$$

with a confidence level of 90%. The intercept of the equation is the average %DN for blank runs. It was found that the adding of Co, Mo, and W significantly increased the catalyst activity for denitrogenation and the interactive effect of Co-Mo was negative. The adding of Ni was again ineffective.

The average desulfurization, ASTM D-86 distillation yield at 650°F, and oil product yield data for VFF shown in Table IV were regressed for the catalyst compositions using a confidence coefficient of 0.90. The average desulfurization for blank runs were 24.95% and the average desulfurization in Runs 7 to 22 varied from 14.9% (0.61 wt% S) to 71.4% (0.16 wt% S). The regression equation for desulfurization of VFF was

$$\%DS = 24.95 - 6.43 \text{ CoO} + 6.66 \text{ MoO}_3 + 4.8 \text{ WO}_3 - 0.556(\text{MoO}_3)(\text{WO}_3),$$

which showed the main effects of Mo and W to be positive and Co giving a negative effect. The interactive effect of Mo-W was found to be insignificant. Tungsten was found to effect the oil product yield negatively. The effect of metals on the ASTM-D86 distillation yield was found to be insignificant.

The data of desulfurization and oil product yield for LECF is shown in Table V. These two variables were again regressed for the catalyst compositions at a confidence level of 90%. The regression equation for desulfurization was

$$\%DS = 68.5 + 4.175 \text{ CoO} + 2.38 \text{ MoO}_3 - 0.63(\text{CoO})(\text{MoO}_3)$$

The intercept, 68.5 %DS, was the averaged activity of blank runs. Co and Mo were found to increase the catalyst activity significantly for desulfurization of LECF. The interactive effect of Co-Mo was negative. The adding of Ni to the catalyst appeared to be ineffective. The effect of metals on oil product yield was found to be insignificant.

The above regression equations were used for analyzing the factorial design but were not appropriate to use for prediction because the experiments were not designed for this. There were some similarities of metal effects for both feedstocks. Table VI summarizes the metal effects. Three metals, Co, Mo, and WO₃ affected the catalyst activity for denitrogenation significantly, while Ni did not. The interactive effects of certain metals on both denitrogenation and desulfurization

were negative. The effect of Ni on desulfurization on both feedstocks was found to be insignificant. Observing of the experimental data shows that catalyst C-49 with a metal combination of 4% CoO, 8% MoO₃, 1% NiO, and 8% WO₃ gives a consistent catalyst activity for the denitrogenation. An attempt was made to moderate the catalyst deactivation by starting at a lower temperature and a higher space velocity. Run 39 and 40 in Figure 4 used the blank catalyst carrier as the catalyst and started at 425°C and space velocities of 5 and 20 v/v/hr, respectively, for the first five minutes. Then the temperature was increased to 475°C in two hours and the space velocities reduced to 1.0 hr⁻¹. Run 39 coked up after 6 hours due to the increased temperature and low initial space velocity. Run 40 proceeded for 8 hours without pressure build-up. The data of blank Runs 1 and 2 are also plotted in Figure 4 for comparison. The activities of Runs 39 and 40 were slightly lower at the beginning but much less deactivated than those of Runs 1 and 2 which were made at a constant temperature of 425°C and a space velocity of 1.0 hr⁻¹. Run 39 gave a better denitrogenation than Run 40 because of its lower initial space velocity. Run 41 and 42 in Figure 5 employed the same operating conditions as Run 39 and 40 except that it was started with an initial space velocity of 10 for the first five minutes. Run 41 used blank catalyst carrier as the catalyst and Run 42 used catalyst C-49. Run 41 and 42 were carried out for 10 and 8 hours, respectively without pressure build-up. Figure 5 shows that catalyst C-49 gives a better catalyst activity than its blank carrier and that the use of starting at higher space velocity decreased the catalyst deactivation rate. Run 42 reduced the nitrogen content of SRC-II VFF, 1.17 wt%, to 0.08 wt% after 30 minutes and to 0.42 wt% after 8 hours. The average nitrogen content of the liquid product for Run 42 was 0.3 wt% compared to 0.62 wt% for Run 41.

To pursue the feasibility of reusing a promising catalyst, a process which reactivates the spent catalyst via periodic air burn-off and resulfiding is required. Fresh catalyst C-49 was again tested for 8 hours using SRC-II LECF as feedstock. The operating conditions were typical: 6,983 K-Pascals(1,000psig), 425°C, a hydrogen flow rate of 1.79 cubic meters/liter(10,000 scf/bbl), a space velocity of 1.0 hr⁻¹ and a liquid feed temperature of 85°C. The results showed that the nitrogen content was reduced to 0.05 wt% after one hour and to 0.27 after 8 hours and the sulfur content was reduced to an average of 0.17 wt%. This spent catalyst was burned-off under atmospheric pressure at 550°C for the first 4 hours with 5% O₂ in nitrogen at a gas flow rate of 5 scf/hr and for another 4 hours with 40 % O₂ in the nitrogen at the gas flow rate of 1.5 scf/hr.

This catalyst was reactivated by sulfiding and further reused for periods of 8 hours between regeneration for 104 hours. Figure 6 plots the average nitrogen and sulfur contents of the liquid product as a function of time. The results show that the catalyst activity has been restored through the regeneration process and the average nitrogen and sulfur contents have been consistently reduced to less than 0.3 wt%. The liquid product recovered averaged 91 wt%.

CONCLUSION

The catalyst activity for the denitrogenation of SRC-II Vacuum Flash Feed and Light Ends Column Feed was significantly increased by the adding of Co, Mo, and W but decreased by the interactive effect of Co-Mo. The interaction between Co and W gave a negative effect on denitrogenation of VFF. The effect of Co and Mo on the desulfurization of LECF was positive. The effect of Mo and W on the desulfurization of VFF was also positive but Co was negative. The interaction between Mo and W gave a negative effect on the desulfurization of VFF, while between Co and Mo gave a negative effect on the desulfurization of LECF. It was found that the adding of Ni was ineffective. The catalyst deactivation was moderated by starting at a lower temperature and higher space velocity. A catalyst with a metal combination of 4% CoO, 8% MoO₃, 1% NiO, and 8% WO₃ has reduced the nitrogen and sulfur contents of SRC-II of LECF to as low as 0.3 wt% for 104 hours with an average liquid product recovery of 91 wt%.

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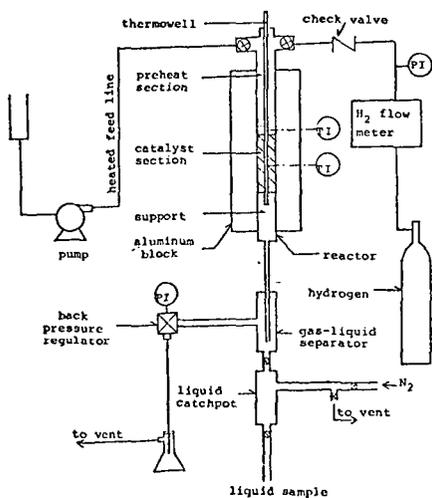


Figure 1. Trickle Bed Reactor

TABLE I
Properties of SRC-II Products

	Vacuum Flash Feed	Light Ends Column Feed
% Carbon	87.43	~4
% Hydrogen	7.15	~*
% Nitrogen	1.17	0.88
% Sulfur	0.72	1.21
% Oxygen	3.72	~*
% Ash	0.249	0.02
Sp. Gravity 60/60°F	1.08	0.903
ASTM D-86 Distillation, °F		
TRP	408	122
5%		217
10%	445	288
20%	485	381
30%	544	446
40%	598	488
50%	642	541
60%		577
70%		611
80%		660
90%		727
95%		795
End Point	684	956

Data not available

Table .II

Denitrogenation Data of Factorial Design for SRC-II VFF

Run	Catalyst	N ₂ ^o time, minutes				N ₂ on stream, min.	Catalyst Composition, wt% COO MoO ₃ NiO WO ₃						
		45	60	75	90								
1	carrier	64.4	39.7	35.9	27.4	26.6	18.8	-	35.5	0	0	0	0
2	carrier	40.2	27.8	23.6	27.4	21.5	23.5	-	28.0	0	0	0	0
7	C-41	92.0	89.3	85.5	77.8	72.6	61.5	50.0	75.5	2	8	1	8
8	C-42	85.5	82.8	69.2	61.5	48.7	44.0	35.9	62.5	2	8	1	2
9	C-43	97.0	95.2	91.0	80.3	65.4	56.4	51.7	76.8	2	8	4	8
10	C-44	98.6	82.2	80.8	68.8	51.3	42.7	43.6	68.3	2	8	4	2
11	C-45	93.8	79.2	72.5	62.9	56.4	45.3	30.3	65.7	2	2	1	8
12	C-46	93.8	79.2	72.5	62.9	56.4	45.3	30.3	65.7	2	2	1	2
13	C-47	95.5	89.7	81.6	66.7	58.5	52.3	35.9	66.8	2	2	4	2
14	C-48	93.2	80.0	70.5	64.1	57.7	54.3	48.7	67.0	2	2	4	2
15	C-49	98.6	93.8	88.9	80.3	66.7	60.7	56.8	77.9	4	8	1	8
16	C-50	97.3	91.7	84.6	78.6	69.7	60.3	57.3	77.1	4	8	1	2
17	C-51	97.4	92.1	88.2	70.9	62.0	55.6	57.3	73.8	4	8	4	8
18	C-52	89.7	87.2	82.0	72.2	68.4	66.7	50.8	73.8	4	8	4	2
19	C-53	95.1	88.9	79.1	70.1	57.7	52.6	57.3	71.5	4	2	1	8
20	C-54	97.3	89.1	81.4	73.5	71.8	70.1	63.2	81.1	4	2	1	2
21	C-55	94.9	81.4	78.5	59.1	51.6	49.8	38.3	75.6	4	2	4	2
22	C-56	94.9	81.4	78.5	59.1	51.6	49.8	38.3	75.6	4	2	4	2

* Nitrogen content of SRC-II VFF is 1.17 wt%

Table III
Denitrogenation Data of Factorial Design for SRC-II LECP

Run	Catalyst	N ₂ ^o time on stream, min.				N ₂ on stream, min.	Catalyst Composition, wt% COO MoO ₃ NiO WO ₃			
		56	39	33	30					
5	carrier	56	39	33	30	39.2	0	0	0	0
6	carrier	56	40	39	28	40.6	0	0	0	0
23	C-41	98	98	86	80	90.3	2	8	1	2
24	C-42	98	89	73	67	81.5	2	8	1	2
25	C-43	86	93	80	77	81.3	2	8	4	8
26	C-44	98	53	84	84	89.8	2	8	4	2
27	C-45	98	98	81	77	88.9	2	2	1	8
28	C-46	93	93	80	75	85.2	2	2	1	2
29	C-47	93	93	80	75	85.2	2	2	1	2
30	C-48	92	89	59	58	74.4	2	2	4	2
31	C-49	98	93	88	83	90.3	4	8	1	8
32	C-50	98	98	85	80	90.0	4	8	1	2
33	C-51	98	98	88	84	91.8	4	8	4	8
34	C-52	98	94	77	72	85.2	4	8	4	2
35	C-53	98	62	68	68	74.1	4	2	1	8
36	C-54	98	90	50	52	67.6	4	2	1	2
37	C-55	97	75	57	56	71.2	4	2	4	2
38	C-56	97	75	57	56	71.0	4	2	4	2

Table V

Denitrogenation and Product Yield Data for SRC-II LECP

Run	Catalyst	IDS on stream, min.	Oil Product Yield, wt%	Catalyst Composition, wt% COO MoO ₃ NiO WO ₃						
					76	69	72.5	77		
5	carrier	76	69	72.5	77	0	0	0	0	0
6	carrier	65	64	64.5	77	0	0	0	0	0
23	C-41	82	87	84.7	89	2	8	1	8	8
24	C-42	90	86	88.2	100	2	8	1	2	2
25	C-43	90	94	97.0	96	2	8	4	8	8
26	C-44	79	77	76.1	98	2	8	4	2	2
27	C-45	83	86	83.9	88	2	2	1	8	8
28	C-46	83	82	82.4	86	2	2	1	2	2
29	C-47	83	82	82.4	86	2	2	1	2	2
30	C-48	89	88	88.8	100	2	2	4	2	2
31	C-49	77	83	80.0	91	4	8	1	8	8
32	C-50	86	87	86.6	87	4	8	1	2	2
33	C-51	80	73	76.2	94	4	8	4	8	8
34	C-52	90	92	91.1	88	4	8	4	8	2
35	C-53	86	76	81.0	80	4	2	1	8	8
36	C-54	78	81	87.1	84	4	2	1	2	2
37	C-55	91	80	85.5	100	4	2	4	2	2
38	C-56	91	80	85.5	100	4	2	4	2	2

o Sulfur content of SRC-II VFF is 0.72 wt%, distillation yield at 650°F for SRC-II VFF is 55 vol%.

Table VI
Summary of Metal Effects

	DN		DS		Carbon* Laydown	Oil Product* Yield
	VFF	LECF	VFF	LECF		
Co	+	+	-	+	0	0
Mo	+	+	+	+	0	0
W	+	+	+	0	0	-
Ni	0	0	0	0	0	0
Interaction						
Co-Mo	-	-	0	-	0	0
Co-W	-	0	0	-	0	0
Mo-W	0	0	-	0	0	0

* Vacuum flash feed
+ Positive effect
- Negative effect
0 Ineffective

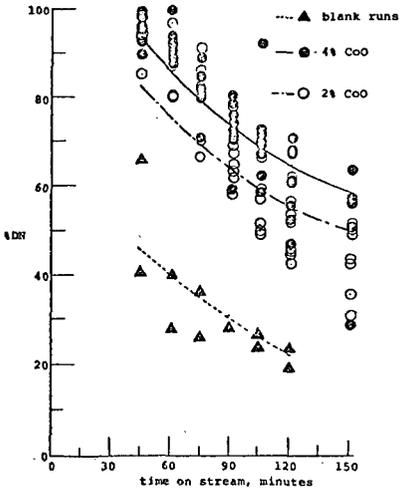


Figure 3. Denitrogenation of SRC-II VFF from Run 7 to Run 22.

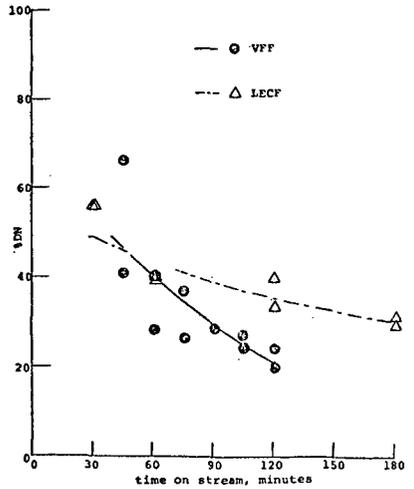


Figure 2. Feedstock Comparison of Denitrogenation with Catalyst Carrier.

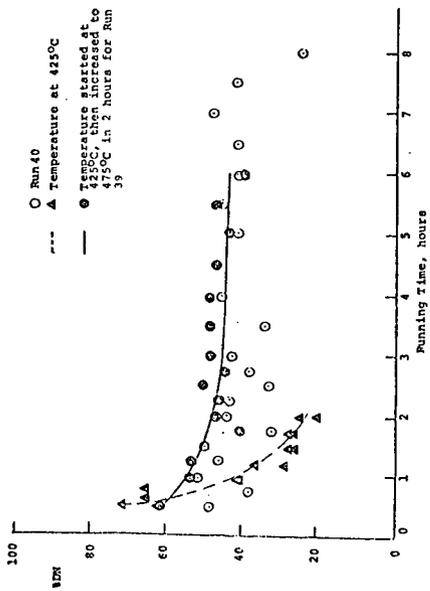


FIGURE 4. Effect of Temperature and Initial Space Velocity on Denitrogenation

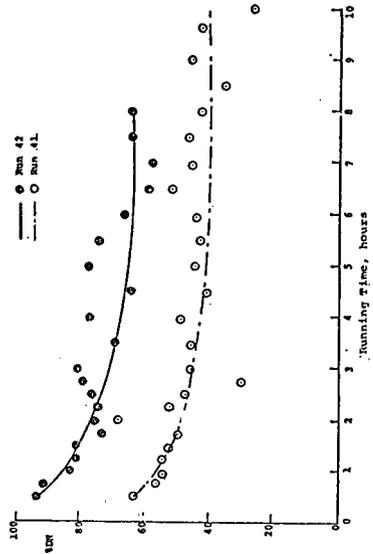


Figure 5. Comparison of Catalyst C-49 and Its Carrier for Denitrogenation at 475°C.

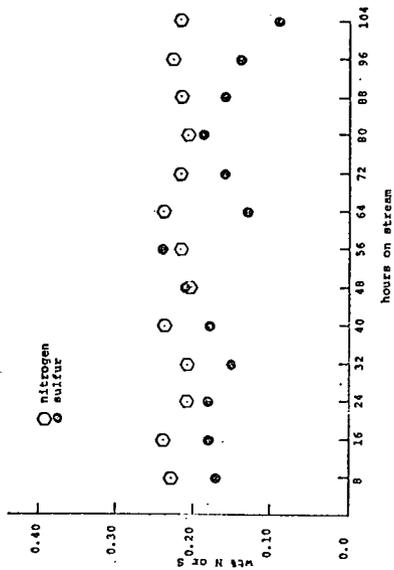


Figure 6. Average Nitrogen and Sulfur Contents from Run 77 to Run 89