

SYNFUEL STABILITY:
DEGRADATION MECHANISMS AND ACTUAL FINDINGS

by

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Introduction

While substantial quantities of only a few experimental synfuels have been generated, those which are available have demonstrated the degradation problems that were predicted from work with petroleum. The high heteroatom and unsaturate content of syncrudes derived from shale and coal will necessitate closer attention to processing parameters required to produce a commercially viable product. This paper presents basic and applied data which should aid in the tradeoff decisions between further costly processing and product stability.

Degradation Mechanisms

Considerable work has been published on degradation mechanisms for compounds found in petroleum (1-4). Much of the previously reported research involved pure compounds in pure hydrocarbon solvents. The work reported here was performed with additive-free #2 diesel fuel or JP-8, both of which are middle distillate fuels in increasing demand.

Relative results for a variety of nitrogen compounds are displayed in Figure 1 according to sediment formation during accelerated storage stability tests. Alkyl substitution on the α -carbon has an obvious deleterious affect, with the most severe occurring with five-membered ring compounds.

While the reactivities of single compounds are of interest, a more realistic test would include several compounds in order to study interactive effects. As an example, Table 1 presents results from a binary mixture in diesel fuel in which an obvious interaction has occurred after 56 days at 110°F. If trioctylamine had been tested only by itself in #2 diesel fuel, it would have been labeled innocuous. However, in combination with dimethylpyrrole there is evidence for a synergistic effect. Additional studies currently underway also include sulfur and oxygen compounds.

The effects of storage temperature on sediment formation were studied using 2,5-dimethylpyrrole as the model compound. Arrhenius plots for both #2 diesel and JP-8 are shown in Figures 2 and 3. The fairly linear plots permit estimation of apparent reaction activation energies of 10.7 kcal/mole in #2 diesel and 14.4 kcal/mole in JP-8. These are rather low and suggest some catalytic effects are involved.

Synfuel Test Results

When reviewing the test results from actual synfuel samples, one must consider the source and history of the samples. For example, Table 2 shows typical properties for the same shale oil jet fuel before and after additional hydrotreating. Much of this difference in stability can be traced directly to heteroatom contents. Table 3 compares the elemental composition of two synfuels and of the gum produced after aging. The tendency for nitrogen, oxygen, and sulfur compounds to preferentially participate in the degradation reactions is obvious.

In some applications, thermal degradation can be more of a concern than storage stability. Table 4 presents data on several middle distillate synfuels as compared to a petroleum-based fuel. The tube deposits from the Jet Fuel Thermal Oxidation Test (ASTM D3241) are significantly higher for the synfuels, but the pressure build-up is normal except for one case. This indicates either rapid reactions at the hot surface or slow agglomeration. In either case, the deposit level demands further study.

Conclusion

All information published to date implies that the production of stable synfuels is possible but will require refining processes altered from those now required for petroleum. Stability research is currently focussing on both basic and applied considerations, and the results are encouraging. By continuing these efforts, it is hoped that stability will not be the limiting factor in providing adequate future fuel supplies.

REFERENCES

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Table 1. Interaction Between 2,5-Dimethylpyrrole (A, 150 ppm) and Trioctylamine (B, 1350 ppm) in #2 Diesel¹

		Presence of Compound A	
		No	Yes
Presence of Compound B	Yes	0.5	61.8
	No	0.5	131.8

56 Days at 110°F

¹ Sediment given as mg/100 ml fuel.

Table 2. Upgrading Effect on Composition and Stability of Jet Fuel From Shale Oil

<u>Properties</u>	<u>Original</u>	<u>Upgraded</u>
Sulfur, total, wt-pct	0.015	0.005
Carbon, wt-pct	86.2	85.43
Hydrogen, wt-pct	13.32	14.42
Oxygen, wt-pct	0.28	0.05
Nitrogen, ppm	1500	3.2
Total gum after 32 weeks at 110° F, mg/100 ml	6.4	1.8

Table 3. Elemental Analyses of Gums and Fuels

Gum Composition	(wt-pct)		Soluble Gum	
	Middle Distillate, SRC II			Kerosene, Tar Sands
	Soluble Gum	Insoluble Gum		Soluble Gum
C	75.60	73.10	83.52	
H	6.65	6.57	8.41	
N	5.46	6.12	Trace	
O	10.99	14.12	7.34	
S	0.67	<0.01	<0.01	
<u>Original Fuel</u>				
C	86.28		87.05	
H	9.05		12.42	
N	0.98		0.0004	
O	3.36		0.30	
S	0.32		0	

Table 4. JFTOT Evaluations by ASTM Test Method D3241 Conducted for 2.5 Hours at 260°C Control Temperature

Description	JFTOT Ratings					
	Visual	Spun Tube	Spot Deposit	ΔP , mm Hg/Time, Minutes		
Paraho shale oil, JP-5	4	24.5	34.5	1/30	1/90	1.5/150
Tar sands, JP-5	4	15	17	0/30	0.5/90	0.5/150
COED coal liquid, JP-5	4	12	24	2/30	76/90	197/150
Paraho shale oil, Jet A(#4)	3	15	18	1/30	1/90	1/150
Paraho shale oil, Jet A(#23)	4	17	19	0.5/30	0.5/90	0.5/150
Paraho shale oil, Jet A(#10)	4	30	35	1/30	1/90	1/150
Petroleum based, JP-5	1	4	6	1/30	1/90	2/150
Paraho shale oil, DFM	3	11.5	19	0/30	0/90	0/150

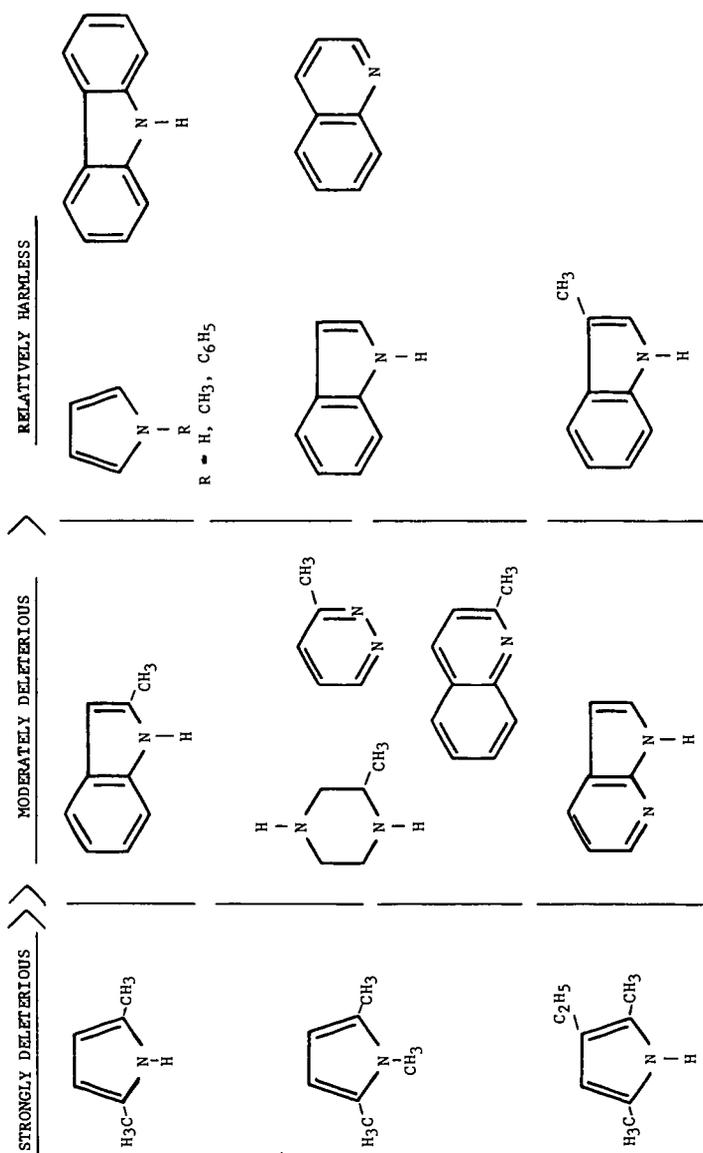


Figure 1. Structural Effects on Sediment Formation

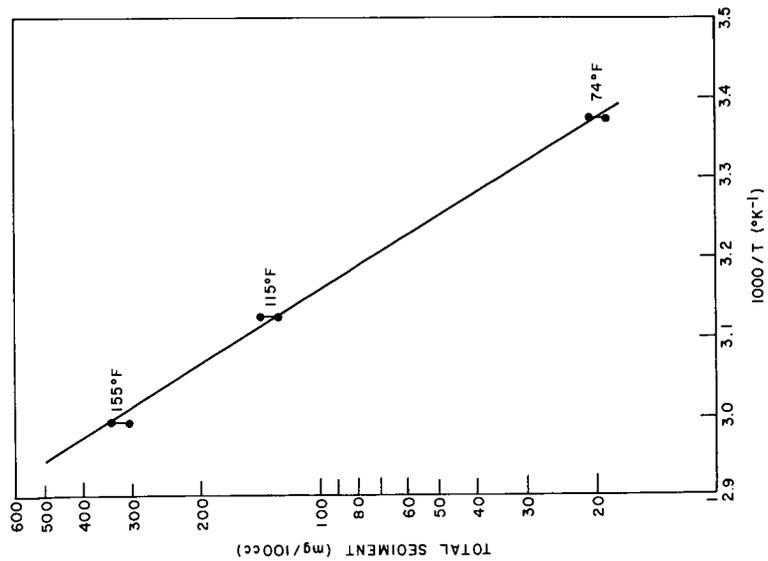


Figure 2. Arrhenius Plot of Dimethylpyrrole in #2 Diesel Fuel

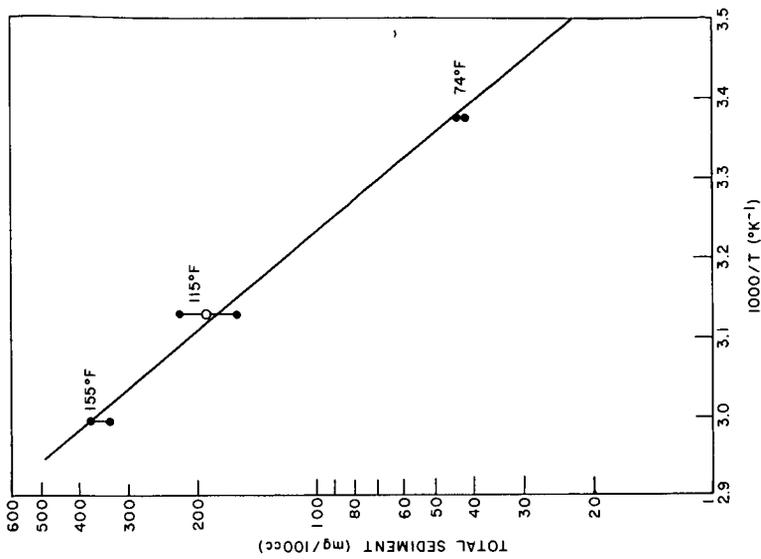


Figure 3. Arrhenius Plot of Dimethylpyrrole in JP-8