

SYMPOSIUM ON GEOCHEMISTRY AND CHEMISTRY OF OIL SHALE
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PYROLYSIS OF SHALE OIL VACUUM DISTILLATE FRACTIONS

By

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INTRODUCTION

The freezing point of U. S. Navy jet fuel (JP-5) has been related to the amounts of large n-alkanes present in the fuel (1,2). This behavior applies to jet fuels derived from alternate fossil fuel resources, such as shale oil, coal, and tar sands, as well as those derived from petroleum. In general, jet fuels from shale oil have the highest and those from coal the lowest n-alkane content. The origin of these n-alkanes in the amounts observed, especially in shale-derived fuels, is not readily explained on the basis of literature information. Studies of the processes, particularly the ones involving thermal stress, used to produce these fuels are needed to define how the n-alkanes form from larger molecules. The information developed will significantly contribute to the selection of processes and refining techniques for future fuel production from shale oil.

Carbon-13 nmr studies indicate that oil shale rock contains many long unbranched straight chain hydrocarbon groups (3). The shale oil derived from the rock also gives indication of considerable straight chain material with large peaks at 14, 23, 30 and 32 ppm in the C-13 nmr spectrum.

Previous pyrolysis studies stressed fractions of shale crude oil residua, measured the yields of JP-5, and determined the content of potential n-alkanes in the JP-5 distillation range (4).

In this work, a shale crude oil vacuum distillate (Paraho) was separated into three chemical fractions. The fractions were then subjected to nmr analysis to estimate the potential for n-alkane production and to pyrolysis studies to determine an experimental n-alkane yield.

EXPERIMENTAL

Separation

Paraho shale oil was distilled at atmospheric pressure to an end point of 300°C. A second cut was obtained by continuing the distillation at reduced pressure, 40 mm Hg. This vacuum distillate, with an end point of 300°C, was used in the studies described in this paper.

The vacuum distillate was separated on silica gel into saturate, aromatic, and polar fractions by the procedure described earlier (4). The vacuum distillate comprised 33% of the crude shale oil and contained 1.82% (W/W) of nitrogen. The three chemical classes represented 36% saturates, 22% aromatics, and 42% polars of the vacuum distillate and contained < 0.01, 0.23 and 3.0% nitrogen, respectively. The mass recovery from the silica gel separation was 94%, but the nitrogen recovery was only 67%. The vacuum distillate contained 7.8% n-alkanes and 1.3% 1-olefins (21.5% and 3.5% of saturate fraction), respectively.

Carbon-13 nmr Analysis

Samples of the three compound classes were submitted to analysis by C-13 nmr. The C-13 spectrum affords a distinct separation of the aromatic and aliphatic absorption regions plus a good resolution of many peaks due to specific molecular structure. Thus, a good amount of useful information can be obtained even for a complex mixture such as a fuel fraction. With respect to the present study, the aliphatic region of the spectrum is of particular importance. A spectrum for the aliphatic region of the polar fraction is shown in Figure 1. The distinctive peaks at 14, 23, 32, and 30 ppm demonstrate the presence of significant amounts of long unbranched groups in this fuel fraction. Quantitation of the spectral information using the methanol internal standard gives the data listed in Table I. As expected, the content of long unbranched alkyl groups is greatest for the saturate fraction. Further, the straight chain alkyl groups in the saturate fraction are longer on the average than those in the aromatic and polar fractions. We conclude that there is a definite potential for making n-alkanes and 1-olefins in the jet fuel distillation range by cracking compounds found in the shale oil vacuum distillate.

TABLE I
CARBON-13 NMR EXAMINATION OF SHALE OIL
VACUUM DISTILLATE FRACTIONS

Fraction	Wt. % Carbon in Aliphatic Region	Wt. % Unbranched Alkyl Groups ^(a)	Average Carbon Chain Length ^(b)
Saturate	100	58	19
Aromatic	48	15	13
Polar	55	36	13

- (a) Sum of areas of absorption peaks at 14, 23, 30 and 32 ppm.
(b) For unbranched alkyl groups: based on ratio of 30 ppm peak area to average of 14, 23 and 32 peak areas.

Precision: $\pm 10\%$

Pyrolysis

The vacuum distillate fractions have been stressed at conditions corresponding to the petroleum refining process known as delayed coking (5). These conditions are 450°C and about 90 psi pressure. Each thermal stress was conducted in a 1/4 inch o. d. 316 s. s. tube fitted with a stainless steel valve via a Swagelok connection. The tube, with a weighed amount of sample (approximately 0.1 g), was attached to a vacuum system, cooled to -78°C, and pumped to remove air. The tube was then thawed and the cooling/pumping process repeated. The tubes were heated by inserting them into 9/32-inch holes in a six-inch diameter aluminum block fitted with a temperature controller.

Complete details of sample workup and analysis can be found in Literature Cited (4). One gas chromatographic (GC) technique determined the JP-5 yield from the pyrolysis by summing the total FID area for carbon numbers 9 through 16. A second GC analysis determined the individual n-alkanes and 1-alkenes with a fused silica capillary column.

The saturate fraction of the vacuum distillate contained about 25% n-alkanes plus p-alkenes (Table II). In keeping with the distillation characteristics of this fraction, the bulk (82%) of these compounds contained 17 or more carbons. However, this saturate material did contain significant amounts of the C14, C15 and C16 n-alkanes and 1-alkenes, compounds which fall within the JP-5 distillation range.

TABLE II
n-ALKANES AND 1-ALKENES IN UNSTRESSED SATURATE FRACTION

Carbon Number	Percent Concentration		
	n-Alkane	1-Alkene	n-Alkane + 1-Alkene
11	0.172	--	0.172
12	0.161	0.036	0.197
13	0.282	0.076	0.358
14	0.647	0.187	0.834
15	0.936	0.379	1.315
16	1.244	0.377	1.621
17	1.895	0.533	2.428
18	1.665	0.521	2.186
19	2.076	0.388	2.464
20	1.698	0.412	2.110
21	1.872	0.189	2.061
22	1.516	0.192	1.708
23	1.589	0.119	1.708
24	1.168	0.046	1.214
25	1.306	0.049	1.355
26	0.859	0.021	0.880
27	0.939	0.029	0.968
28	0.75	--	0.75
29	0.75	--	0.75
Totals (11-29)	21.53	3.55	25.08
Totals (9-16)	3.44	1.06	4.50
JP-5 range			

Pyrolysis of the saturate fraction for 30 minutes at 450°C gave the n-alkane and 1-alkene product distribution shown in Figure 2. Comparison between Figure 2 and Table II indicates a net loss in concentration for the n-alkanes C₁₆ and larger, and a net gain for those with 14 or less carbons. The 1-alkenes exhibit a similar relationship with carbon number. For this pyrolysis time, the yield of small olefins equals or exceeds the yield of small n-alkanes.

The effect of stress time on yield for the saturate fraction is illustrated in Figure 3. The n-alkane plus 1-alkene sum for each carbon number is plotted. The combined alkane/alkene yields for carbon numbers above 16 decrease with increasing stress time and are almost depleted at 180 minutes. The yields for carbon numbers below 13 increase with stress time through 120 minutes but exhibit a drastic reversal at 180 minutes. Thus, the larger n-alkanes and 1-alkenes are undergoing single-step Fabuss-Smith-Satterfield pyrolysis (6) to smaller hydrocarbons. The smaller alkanes and alkenes are initially products but, at the longer stress times, these compounds fragment also. The 1-alkenes are less stable than the n-alkanes; consequently, the latter predominate at the longer stress times.

Yields for the polar fraction pyrolyses are depicted in Figure 4. The combined n-alkane/1-alkene yields for carbon numbers less than 15 were reasonably good for a 15-minute pyrolysis but secondary fragmentation sharply reduced the yields for longer stress periods. The olefins were more reactive in the polar environment than the saturate environment and were generally minor products at all stress times. The low yield of alkanes and alkenes for carbon numbers above 14 corroborates the average chain length of 13 found by carbon-13 nmr analysis.

Limited experiments with the aromatic fraction from the vacuum distillate indicated this material resembled the polar fraction much more than the saturate in pyrolysis behavior. This would be consistent with the carbon-13 nmr results.

A summary of the JP-5 yield data for all fractions stressed for various times at 450°C is presented in Table II. The saturate fraction affords the highest yield of JP-5 but the polar fraction also gives good yields. The maximum yields for these two fractions came at 60-minutes stress but the overall effect of time on yield was moderate. The results for the aromatic fraction were inconclusive because of limited amount of starting material. The general pattern of JP-5 yield for the vacuum distillate fractions was similar to that found for shale oil residual fractions (4).

TABLE III
PRODUCT YIELD^(a)

Pyrolysis Time (min.)	JP-5 Yield (Percent)		
	Saturate	Aromatic	Polar
15	24.0	--	17.8
30	25.6	11.8	17.9
60	27.0	25.8	21.7
120	24.8	--	20.4
180	15.7	--	20.2

(a) Pyrolysis Temperature - 450°C

The potential n-alkane yields in the JP-5 cut are listed in Table IV. These values were obtained by summing the capillary GC yields of n-alkanes and 1-alkenes for carbon numbers 9 through 16. This total was divided by the corresponding JP-5 yield in Table III to give the potential n-alkane yield.

TABLE IV
POTENTIAL n-ALKANE YIELD FROM VACUUM DISTILLATE FRACTIONS

Pyrolysis Time (min.)	Potential n-Alkane Yield ^(a)		
	Saturate	Aromatic	Polar
15	31.0	--	12.7
30	31.0	4.2	11.4
60	33.0	15.5	10.3
120	24.8	--	11.5
180	18.5	--	9.4

(a) Pyrolysis Temperature - 450°C; yield in percent is sum of n-alkanes + 1-alkenes for C₉ to C₁₆ hydrocarbons divided by JP-5 yield from Table III.

C-13 NMR-ALIPHATIC REGION
SHALE VACUUM DISTILLATE
POLAR FRACTION

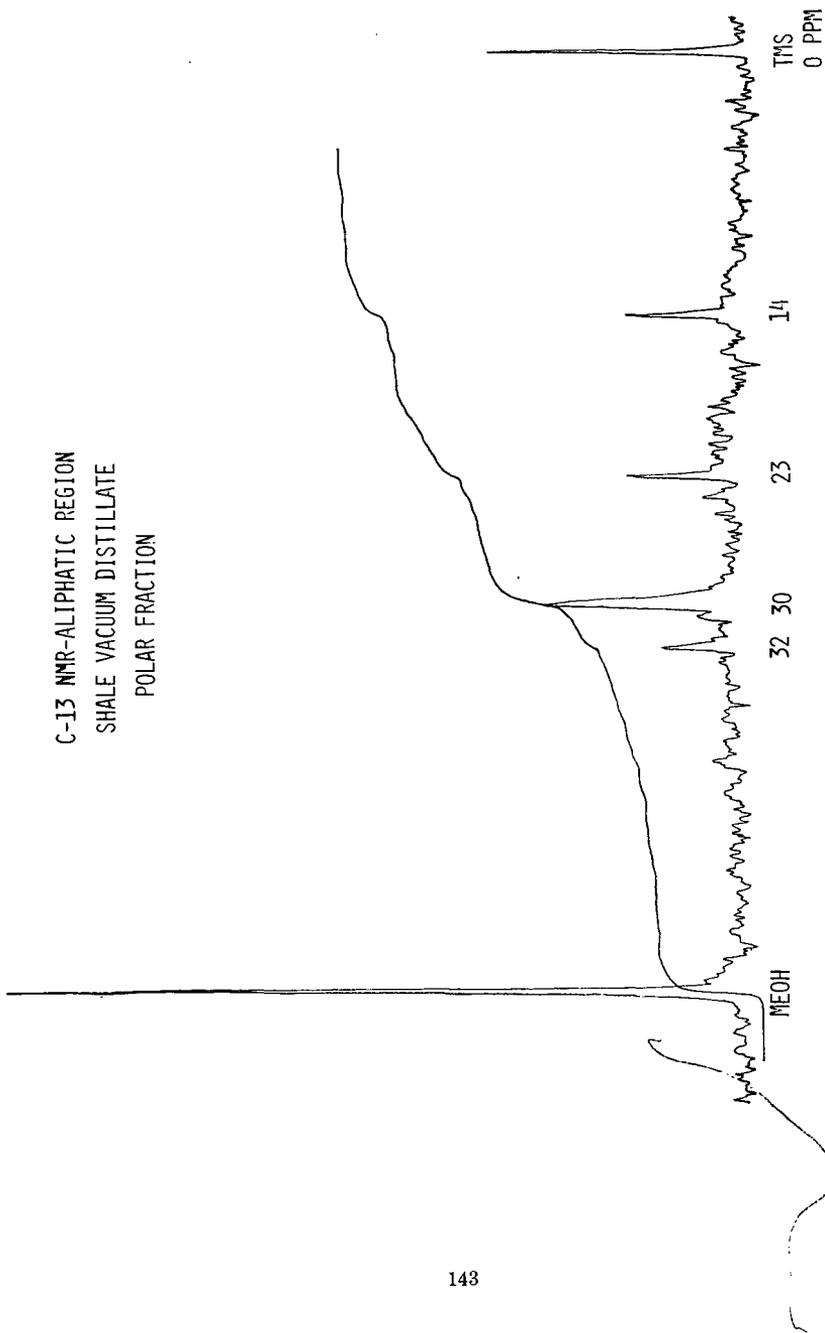


Figure 1. C-13 nmr spectrum of shale oil vacuum distillate polar fraction, aliphatic region, TMS reference, methanol internal standard, integration trace (upper curve).

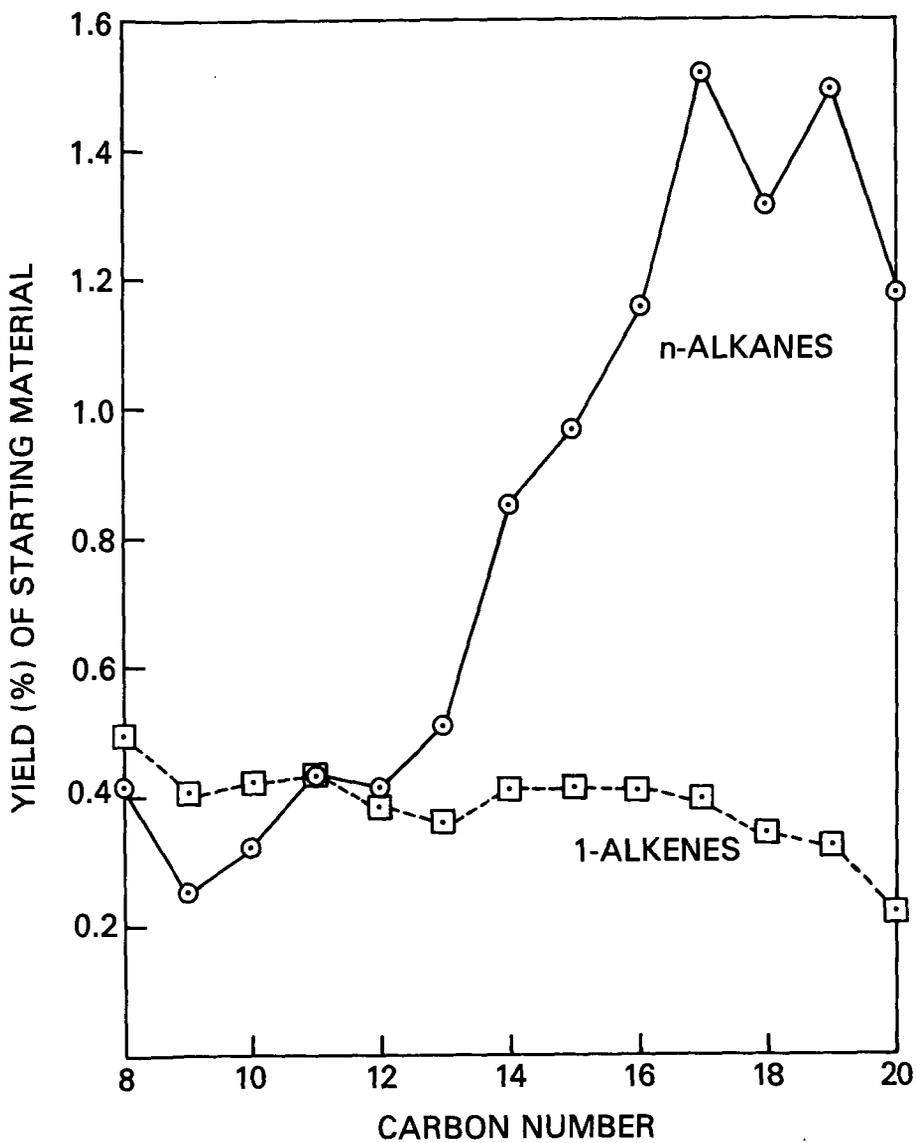


Figure 2. Pyrolysis of shale oil vacuum distillate saturate fraction at 450°C, for 30 minutes.

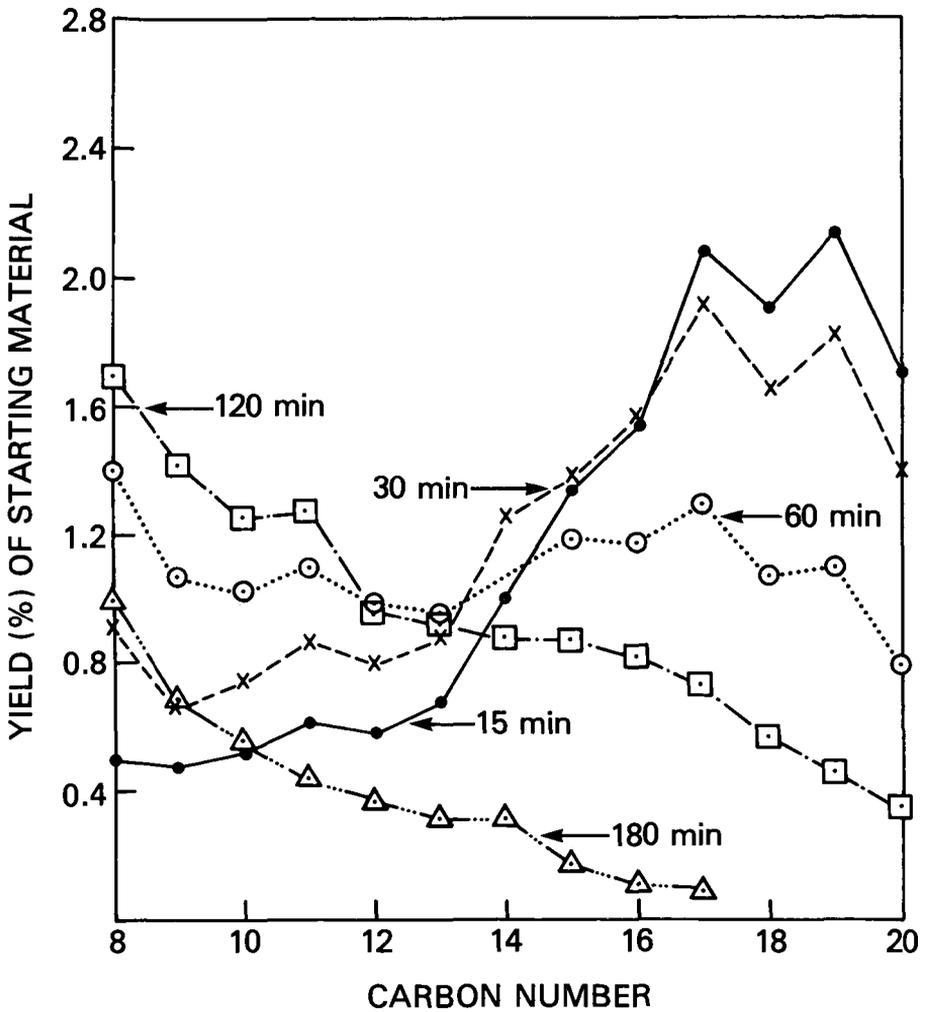


Figure 3. Pyrolysis of shale oil vacuum distillate saturate fraction at 450°C. The yield is the sum of n-alkane plus 1-alkene for the indicated chain length.

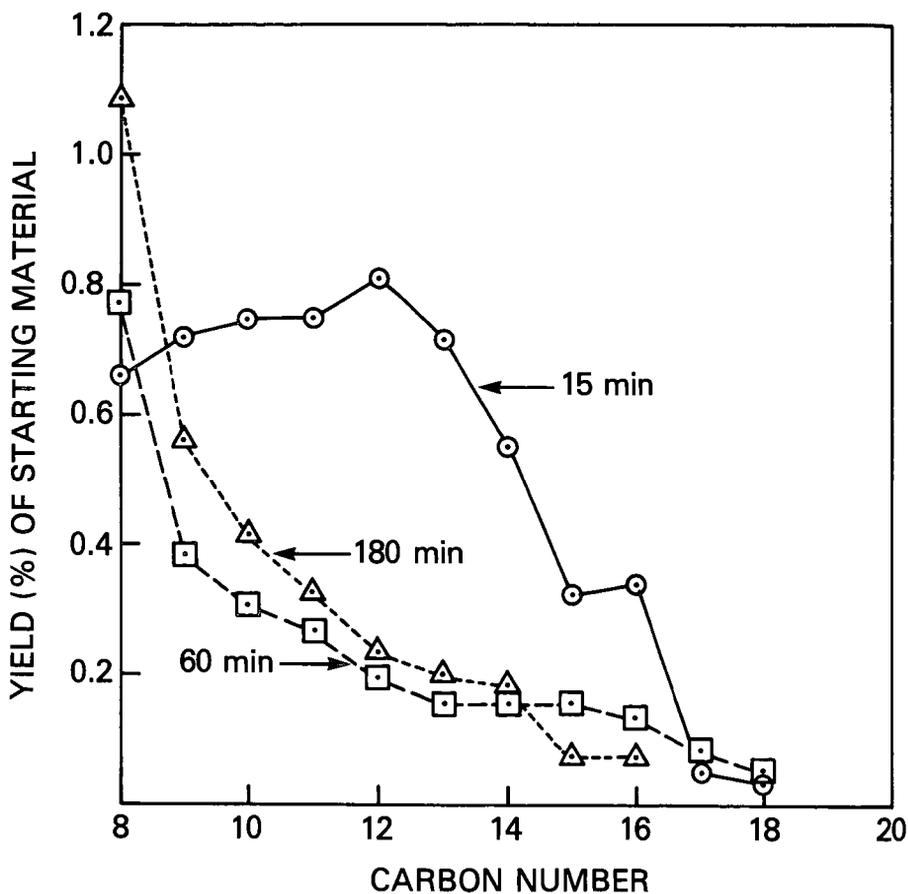


Figure 4. Pyrolysis of shale oil vacuum distillate polar fraction at 450°C. The yield is the sum of n-alkane plus 1-alkene for the indicated chain length.

The saturate fraction gave substantial yields of potential n-alkanes in the JP-5 range at all stress times. The highest yields were for shorter stress times, however, and the maximum of 33% was found at 60 minutes.

The potential n-alkane yield for the aromatic and polar fractions fell much below that of the saturates. This is consistent with the much lower wt. % unbranched alkyl group and average chain length data found by nmr.

DISCUSSION AND CONCLUSIONS

Over 50% of unbranched alkyl groups in the saturate fraction can be converted to potential n-alkanes in the JP-5 distillation range. This indicates that the average chain length of 19 is fragmenting during the pyrolysis to give substantial amounts of n-alkanes and l-alkenes with carbon numbers in the 9 to 16 range. Single step Fabuss-Smith-Satterfield breakdown would explain this behavior. The potential n-alkane yields in excess of 30% approach those of 37% found for JP-5 made from shale oil by a delayed coking operation (1). Thus, the saturate molecules in the vacuum distillate portion of Paraho shale oil seem to be significant contributors to JP-5 and n-alkane production in the delayed coking process.

The aromatic and polar fractions in the shale oil vacuum distillate contribute much less than the saturate fraction to n-alkane production. This is consistent with studies on model compounds (7). Substituted benzenes and pyridines preferentially fragment to give n-alkanes and l-alkenes with one and two fewer carbons than the length of the side chain. For the average side chain of 13 for the polar fraction, which contains large amounts of pyridines, the alkane/alkene fragment would be primarily 11 or 12 carbons. Figure 4 illustrates a sharp increase in yield near these carbon numbers at the longer stress times for the polar fraction.

Highest yields of JP-5 come at 60 minutes for the various fractions. Unfortunately, this time also gives the highest yield of potential n-alkanes for the saturate fraction. Thus, differentiation between a good yield of JP-5 and a low yield of n-alkanes cannot be made on the basis of pyrolysis time.

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