

UPGRADING JULIA CREEK SHALE OIL - SYNCRUDE OR FULLY REFINED PRODUCTS?

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ABSTRACT

Two upgrading strategies for refining Julia Creek shale oil have been evaluated, ie production of a syncrude, versus fully refined transport fuels. Results indicated that both options were viable for this Australian shale oil, and influencing factors are more likely to be market related than technical. During this study, suitable conditions were identified for the production of specification quality gasoline, jet and diesel fuels.

INTRODUCTION

The Cretaceous Julia Creek oil shale deposit is located in Queensland, Australia, approximately 600 km inland from the eastern seaboard as shown in Figure 1. It is an important Australian energy resource, with in-situ resources estimated at 20 billion barrels of oil and proven reserves of 2 billion barrels, comparable to Australia's petroleum reserves in Bass Strait. The oil shale seam is 7-14 metres thick (overburden to ore, 2:1), and dips slowly westward at less than one degree. With few geological anomalies, this deposit is suitable for open-cut mining.

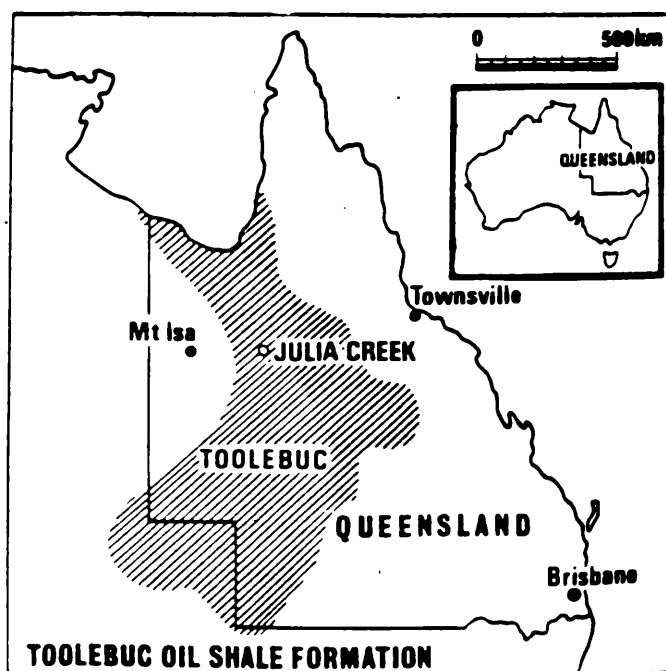


Figure 1. Julia Creek Deposit

Current addresses - 1. Caltex Oil (Australia) Pty Limited, GPO Box 3916, Sydney, Australia. 2001.

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The shale is of marine origin, having been deposited as an anaerobic sediment in a restricted epicontinental sea (1). Algae were the predominant source of organic matter. The shale is highly calcitic; its calcium carbonate content is up to 50 per cent of the mineral matter. Typical analyses for the oil shale are given in Table 1. Fresh Julia Creek shale typically yields 70 litres of oil per tonne.

A typical whole oil assay is given in Table 2. The oil is highly aromatic (atomic hydrogen:carbon (H/C) 1.39) and contains high levels of sulfur (4.86 weight %), nitrogen (1.1 wt%), arsenic (26 ppm) and vanadium (184 ppm). These deleterious characteristics necessitated upgrading at higher severity than is conventional at existing refineries.

TABLE 1

TYPICAL ANALYSIS OF JULIA CREEK OIL SHALE

PROXIMATE ANALYSES ¹	WEIGHT PER CENT
Total Carbon	19.06
Organic Carbon	14.38
Hydrogen	1.88
Sulfur	2.54
Forms of Sulfur - Pyritic	0.71
Sulfate	0.18
Organic	1.65
Carbonates (CO ₂)	16.5
MINERALS	WEIGHT PER CENT
Quartz	33.0
Calcite	54.0
Illite/Montmorillonite	4.0
Kaolinite	4.0
Pyrite	4.0
Gypsum	1.0

TABLE 2

TYPICAL JULIA CREEK WHOLE SHALE OIL ASSAY DATA

Specific gravity (15/15°C)	0.9834
Pour Point (°C)	-36
Viscosity @ 37.8°C (cSt)	9.67
Carbon Residue (wt%)	7.2
Water and Sediment (vol%)	9.00
Carbon (wt%)	81.4
Hydrogen (wt%)	9.4
Nitrogen (wt%)	1.1
Sulfur (wt%)	4.9
Oxygen (wt%)	3.2
H/C	1.39
Arsenic (ppm)	26
Vanadium (ppm)	184
H _a by NMR	12.4
Olefinic H by NMR	3.21

1. Analyses given on dry basis. Total moisture of sample was 5.9 wt%.

Two processing routes have been proposed for this oil - either the production of a syncrude, as shown in Figure 2, or processing to yield fully refined products as outlined in Figure 3. In this paper we present details of the pilot plant studies used to evaluate these refining options.

EXPERIMENTAL

Shale oil used in this study was produced in a 0.5 tonne per day continuous retort at 480-500°C under a nitrogen purge at atmospheric pressure.

Hydrotreating trials were carried out in two separate units. The low pressure naphtha experiments were performed using a 12 mm i.d. downflow reactor (catalyst volume 50-60 cm³). High pressure trials were carried

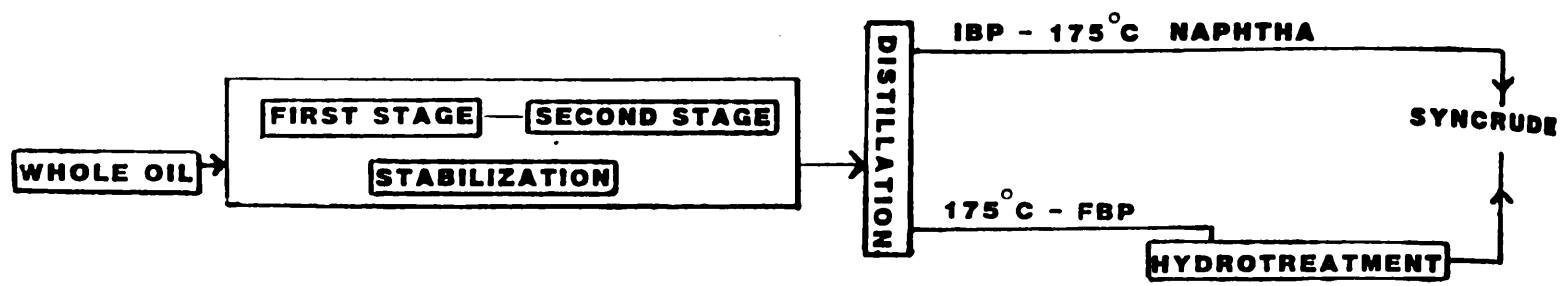


Figure 2. Processing scheme for syncrude production

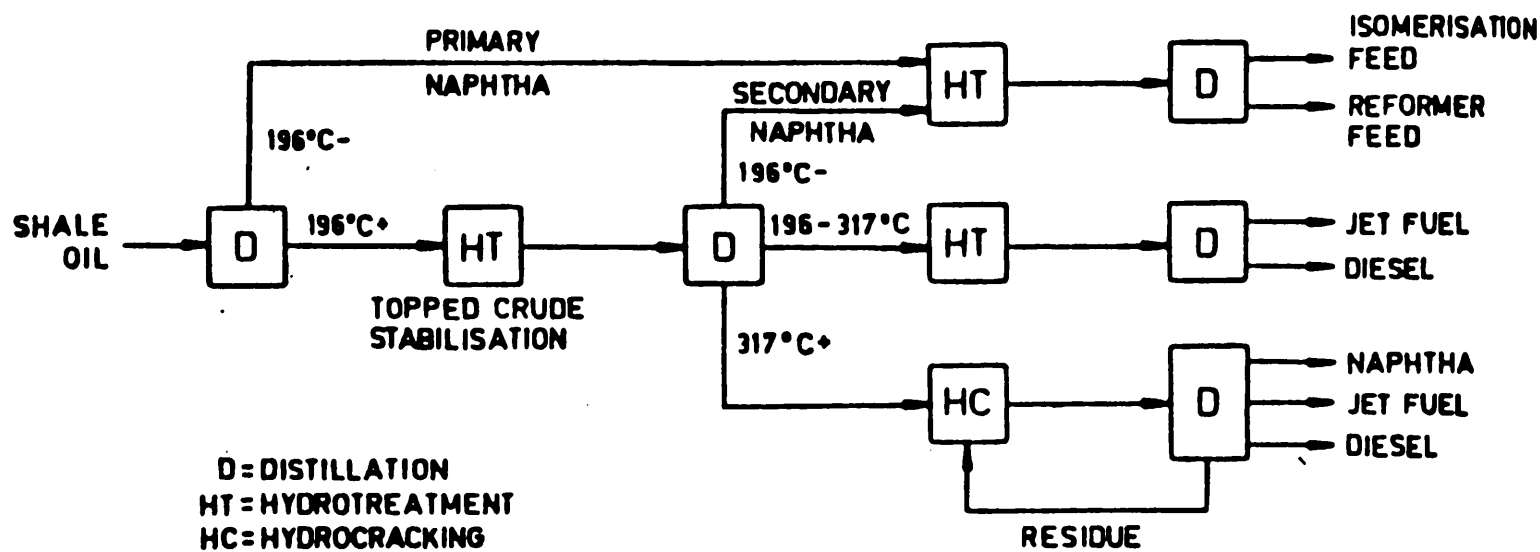


Figure 3. Refining scheme for production of fully refined products

out in a 1.2 litre/hour (max.) trickle bed reactor. Catalyst volume was varied from 350-1000 cm³ to meet LHSV requirements. Conventional petroleum catalysts (1.6 mm) were used without dilution.

Sulfur and nitrogen were analysed by Raney nickel reduction and chemiluminescence respectively. Nuclear magnetic resonance was carried out on a Jeol GX 400 instrument.

RESULTS AND DISCUSSION

1). Production of Fully Refined Products

Naphtha to gasoline. The refining scheme used in the production of marketable transport fuels (1983-85), is shown in Figure 3. To conserve hydrogen and avoid saturation of the high octane value aromatics in the naphtha, the IBP-196°C fraction was distilled from the raw oil for separate processing under milder conditions.

Analyses of both primary and secondary naphthas are given in Table 3. The very high sulfur content of the primary naphtha (almost exclusively thiophenes) accounted for more than half of the predicted hydrogen consumption during hydrotreatment. Preliminary trials indicated that

reforming of the hydrotreated naphtha would be required to produce specification gasoline, therefore, it was necessary during hydrotreatment to reduce heteroatom levels to less than 1 ppm to meet the tolerances of bimetallic reforming catalysts.

A series of hydrotreating trials on primary and secondary naphtha was carried out to determine the most suitable conditions to achieve maximum heteroatom removal with minimum saturation of aromatics. The optimum conditions and analysis of the products are shown in Table 4. The primary aim of heteroatom removal was achieved and aromatics saturation (4.5%) was minimized.

Octane ratings of the hydrotreated naphthas were well below the required 91-93 for Australian unleaded gasoline. It was not possible at that stage of the project to carry out the reforming work, however, it was calculated that reforming and isomerization of the appropriate fractions would yield specification fuel. A comparison of the N+2A indices (naphthenes plus twice aromatics contents) for the naphthas, and reformer feed derived from Australian Gippsland crude (N+2A =70), indicated the potential for high quality Julia Creek gasoline. Production of quality gasoline blendstock, by reforming and isomerization of hydrotreated Julia Creek naphtha was recently reported (2).

Topped crude to jet and diesel fuels. The hydrotreating scheme for distillate production involved initial stabilization of the topped crude (196°C-FBP) followed by secondary hydrotreating of the distillate fraction and hydrocracking of the residue (Figure 3). The aim of the first hydrotreatment was to produce stable oils, by saturating the olefins and removing the bulk of the heteroatoms. The conditions used, together with analyses of the products are given in Table 5. The aromaticity of the oil was reduced considerably but the H/C value (1.63) of the product was still below that typical of distillate fuels (1.8-1.9).

The stabilized oil was distilled and the 196-317°C fraction subjected to further hydrotreatment to increase the hydrogen content and eliminate the remaining heteroatoms. Optimum conditions found using a

TABLE 3
PROPERTIES OF PRIMARY AND SECONDARY NAPHTHAS

	Primary	Secondary
Carbon, wt%	81.7	85.3
Hydrogen, wt%	11.4	14.6
Sulfur, ppm	62000	190
Nitrogen (total), ppm	3000	250
(neutral), ppm	1200	4
Oxygen, ppm	6100	210
Arsenic, ppm	1	-
Atomic H/C	1.66	2.04
C _a	42.2	16.0
H _a	9.3	5.0
Olefinic H	9.6	0.03
Specific gravity (15°C)	0.818	0.765
Aromatics, wt%	17	17
Heteroaromatics, wt%	26	0.3
Thiophenes +	62000	-
Pyridines	1800	10
Anilines	15	230
Pyrroles	680	-
Isonitriles	140	-
Ketones	4500	-
Phenols	1600	210
Predicted H ₂ consumption,		
L/L	275	3

+ All heteroatomic compound classes expressed as ppm heteroatom

Cyanamid Trilobe HDN-30 Ni-Mo catalyst were 380-390°, 12.5 MPa, LHSV 0.8h⁻¹ and H₂ consumption 190 L kg⁻¹. The product jet and diesel fractions met all ATF-1A and ADO specifications, and were the first shale-derived syn-fuels produced in Australia to do so. Their test performances are shown in Table 6 and 7.

Although the aromatics content of the Julia Creek jet fuel was lower than that of typical petroleum-derived samples, its density was close to the upper limit. This was shown to be due to the much higher naphthene content of the synthetic fuel. A naphthenic jet fuel could be beneficial as high density offers the advantages of higher energy value per litre, increased flying range and reduced vapour emissions.

The excellent jet fuel thermal oxidative test (JTOT) result was at least partly due to a very low nitrogen level of 3 ppm. Reynolds (3) found that for shale-derived jet fuels, JTOT stability increased with decreasing nitrogen content. A level of 20 ppm was sufficiently low for US military jet fuel made from Paraho shale oil to pass thermal stability tests (4). The low freezing point, at -58.5°C, meets the most stringent specification required for USAF jet aircraft.

Engine tests indicated that Julia Creek diesel would be an excellent fuel, since its cetane number was almost five units higher than that of typical commercial samples. The synthetic diesel easily passed the distillation requirement at 335°C, and had a very low pour point, thus there is potential for increasing yields by extending the boiling range.

Similar high quality jet and diesel fuels were produced from hydrocracking of the stabilized residue (317°C+).

2). Production of Syncrude

Stabilization of whole oil. The refining scheme used for syncrude production is shown in Figure 2. A two stage stabilization process was selected based on the findings of Sikonia and Houde (5). A Ni-Mo catalyst (Cyanamid HDN-30) was used for the first step, and after investigating the effects of process conditions, 55 kg of oil was

TABLE 4
HYDROTREATING PRIMARY AND SECONDARY NAPHTHAS

	Primary	Secondary
<u>Conditions</u>		
Temperature (av), °C	330	345
(max.), °C	350	355
Pressure, MPa	3	3
LHSV, h ⁻¹	1	2
H ₂ :Oil, L/L	550	550
H ₂ consumption, L/L	250	6
<u>Product Properties</u>		
Carbon, wt%	85.8	85.4
Hydrogen, wt%	14.0	14.2
Sulfur, ppm	0.2	0.2
Nitrogen, ppm	0.5	0.9
Atomic H/C	1.94	1.98
C _a	16.7	15.2
H _a	5.4	4.7
Olefinic H	<0.002	<0.002
Specific gravity (15°C)	0.741	0.760
Research Octane Number	49.3	56.0
Aromatics, wt%	17	16
P/N/A, wt%	55/28/17	44/41/15
N+2A	62	71
<u>Distillation, wt%</u>		
IBP-90°C	19	15
90-175°C	70	76
175-196°C	11	9

TABLE 5

HYDROTREATING TOPPED CRUDE

	FEED	PRODUCT
<u>Conditions</u>		
Average Temperature, °C		385
Pressure, MPa		12.7
LHSV, h ⁻¹		0.7
H ₂ consumption, L kg ⁻¹		320
<u>Properties</u>		
Carbon, wt%	81.0	87.6
Hydrogen, wt%	9.1	12.0
Nitrogen, wt%	2.0	0.3
Oxygen, wt%	2.0	0.4
Sulfur, wt%	5.9	0.3
Vanadium, ppm	61	1
Nickel, ppm	4	<1
Iron, ppm	49	1
Arsenic, ppm	39	0.2
Atomic H/C	1.34	1.63
C _a	50.3	27.7
H _a	16.2	9.8
Specific gravity (15°C)	1.037	0.877
Viscosity (40°C) mm ² s ⁻¹	104.1	1.03
Simulated distillation, wt%		
<196°C	6	23
>317°C	56	33

processed at 270°C, 12 MPa, LHSV 3 h⁻¹ and a H₂ rate 530 L/L. The primary aims of diene saturation and arsenic removal were readily achieved under these conditions. However, vanadium reduction was less than 40% throughout most of the trial.

The aim of the second stage was to increase hydrogen content, reduce heteroatom contents and complete demetallation of the oil. Conditions chosen were 400°C, 12 MPa, 0.7 h⁻¹ and 1070 L/L hydrogen over Shell 444 Co-Mo catalyst, based on preliminary trials which suggested that at these conditions the correct balance between aromatics saturation in the naphtha versus maximum saturation in heavier fractions, and maximum heteroatom and metal removal across the boiling range, could be achieved.

The product was sampled regularly to monitor catalyst activity - there was a general trend for decreased nitrogen removal and aromatics saturation during the trial (Table 8). It was postulated that the metals, principally vanadium, and some entrained dust in the feed, were deactivating the catalyst, but more extensive trials are required to establish full details of catalyst life under these conditions. The product was distilled to separate out naphtha, with a 175°C cut point. Hydrotreatment of the 70-175°C fraction (32 ppm N, 23 ppm S) at conditions typically used in Australian refineries, gave feed suitable

TABLE 6

PROPERTIES OF JULIA CREEK JET FUEL

	JET FUEL	ATF-1A SPECIFICATION
Specific gravity (15°C)	0.8267	0.775 min 0.830 max
Flash Point, °C	61.5	40 min, 65 max
Freezing Point, °C	-58.5	-50 max
Viscosity (-34.4°C), mm ² s ⁻¹	7.72	15 max
Corrosion-Copper strip, 2h @ 100°C	1A	1 max
Aniline gravity product	5320	5250 min
Smoke Point, mm	23	20 min
Naphthalenes, wt%	0	3 max
FIA-aromatics, vol%	8.7	20 max
-olefins, vol%	0	5 max
Sulfur, ppm	15	2000 max
Existent gum, mg/100 cm ³ JFTOT	5.0	7 max
Filter ΔP, mm Hg	0	25 max
Visual deposit rating, ASTM code No.	1	3 max
Spun deposit rating	8	Report
Spot deposit rating	9	Report

TABLE 7

PROPERTIES OF JULIA CREEK AUTOMOTIVE DIESEL

	DIESEL	ADO SPECIFICATION
Cetane Index	49.9	50 min
Cetane Number	59.5	
Flash Point, °C	105	66 min
Pour Point, °C	-30	-6.5 min
Viscosity (37.8°C), mm ² s ⁻¹	2.86	2.1 min 4.3 max
Sulfur, ppm	52	1500 max
Distillation, % recovered @ 335°C	99.5	90 min
Simulated distillation, wt%		
<196°C	0.5	
196-235°C	10.6	
235-317°C	87.6	
>317°C	1.3	

TABLE 8

SECOND STAGE HYDROTREATMENT

	#3	#5	#9	#14	#22	#26	#30	#38	#42	#45
Max Temp, °C	402	397	404	410	399	400	401	402	394	398
Pressure MPa	12.0	12.1	11.8	13.0	12.2	11.7	11.7	12.4	12.2	12.5
LHSV, h ⁻¹	0.72	0.76	0.69	0.79	0.70	0.67	0.66	0.73	0.72	0.61
Nitrogen, ppm	n.d.	n.d.	743	796	765	877	1147	1066	1502	n.d.
H _a	5.80	5.88	5.99	6.15	6.27	6.30	6.38	6.49	6.58	6.25

for bimetallic reforming, but additional sulfur was required to maintain the HDN activity of the Co-Mo hydrotreating catalyst. Full details of this work are given in reference (2).

Hydrotreatment of topped stabilized oil. The aim of this step was to upgrade the 175°C-FBP fraction such that the product could be reblended with the naphtha to produce a quality syncrude, acceptable to a conventional petroleum refinery. This oil was high in aromatics, particularly in the kerosene range. Reduction of sulfur and nitrogen was also required to meet acceptable feedstock levels at petroleum refineries. Results indicated that these aims were achieved. At 415°C, 12.3 MPa and 0.5 h⁻¹, nitrogen content was reduced from 1260 to 17 ppm, and C_a was lowered from 25.4 to 16.3 %. The products were distilled for closer examination of the fuel fractions.

The kerosenes were high in aromatics (26 vol % for sample produced @ 415°C, 0.5 h⁻¹), and therefore had low smoke points (18 mm max). Nitrogen levels were reduced from 400 ppm to 3ppm under the most severe conditions, which indicates that the kerosene fraction of a Julia Creek syncrude would not present refineries with any stability problems, but rather would be financially unattractive due to the cost of increasing hydrogen content sufficiently to meet the aromatics specification of 20 vol% maximum.

Based on the earlier experiments (Figure 3), it was expected that high quality jet fuel could also be produced by this alternate route, however the results indicate that further distillation is required after stabilization, ie hydrotreat a narrower cut, for example 175-350°. It was suggested that the residue successfully competed for available hydrogen, and perhaps active catalyst sites, resulting in lower quality kerosene than expected.

The diesel fractions were closer to specification. The highest quality product, produced at the most severe conditions, had a cetane index of 44.0, -33°C pour point, and contained 4.8 ppm nitrogen. Although the specific gravity (0.8816) and viscosity (4.93 cSt @ 40°C) were higher than typical ADO, it may be possible to adjust the end point of the diesel to ensure that these requirements are met. In comparison with

the kerosene fraction, the syncrude diesel would require minimal treatment at a petroleum refinery.

The residue fractions (20-30 wt%) of the hydrotreated topped stabilized products were found to be suitable for either FCC treatment (7 ppm basic nitrogen) or use as lubricating base stocks.

It was apparent that a synfuel, produced from a blend of stabilized naphtha and hydrotreated topped oil, would not attract a premium price due to the relative unsaturation of the kerosene fraction. However, with a deregulated market now operating in Australia, it is possible that such a synfuel would be attractive to local refiners due to the high value of the naphtha and diesel fractions as blendstocks.

CONCLUSIONS

The most significant technical problems relate to initial stabilization of the oil due to high loadings of heteroatoms and metals. These problems are independent of the overall upgrading scheme chosen. Therefore in answering the question - finished products or synfuel? - influencing factors will be market related rather than technical.

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