Assessment of Synfuel Spill Cleanup Options

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April 1982

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ASSESSMENT OF SYNFUEL SPILL CLEANUP OPTIONS

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EXECUTIVE SUMMARY

Production of synthetic fuels (also known as synfuels) will increase in the next two decades because of competitive economics and the demanding world market for primary energy. As more synthetic fuels are produced, the probability of accidental release of synfuels to the environment will also increase. It is possible the control, containment, and cleanup technologies used to combat petroleum spills could be similarly applied to synfuels spills. This report reviews existing petroleum-spill cleanup technologies and determines their limitations should they be used to mitigate the effects of synfuels spills.

The six subsections of this report address program goals:

1. Synfuels Production Estimates to the Year 2000
2. Possible Sources of Synfuel Spills and Volumes of Spilled Fuel to the Year 2000
3. Hazards of Synfuels Spills
4. Assessment of Existing Spill Cleanup Technologies for Oil Spills
5. Assessment of Cleanup Technologies for Synfuel Spills
6. Disposal of Residue from Synfuel Spill Cleanup Operations.

The first goal of the program was to obtain the most current estimates on synfuel production. These estimates were then used to determine the amount of synfuels and synfuel products likely to be spilled, by location and by method of transportation. A review of existing toxicological studies and existing spill mitigation technologies was then completed to determine the potential impacts of synthetic fuel spills on the environment.

CONTENTS

EXECUTIVE SUMMARY	iii
1.0 SYNFUELS PRODUCTION ESTIMATES TO THE YEAR 2000	1.1
2.0 POSSIBLE SOURCES OF SYNFUEL SPILLS AND VOLUMES OF SPILLED FUEL TO THE YEAR 2000	2.1
CRUDE OIL AND PRODUCT SPILLS	2.1
SYNFUEL SPILLS	2.5
SPILL FACTOR DETERMINATION	2.8
COMPUTATION OF SYNTHETIC SPILL VOLUMES	2.10
3.0 HAZARDS OF SYNFUELS SPILLS	3.1
HAZARDS OF SYNFUELS	3.1
Surface Waters and Aquatic Ecology	3.1
Land and Terrestrial Ecology	3.5
BIOMEDICAL EFFECTS	3.5
4.0 ASSESSMENT OF EXISTING SPILL CLEANUP TECHNOLOGIES FOR OIL SPILLS	4.1
RESPONSE PLANS FOR FUEL SPILLS	4.1
CLASSIFICATION OF SPILL TECHNOLOGIES BY SPILL LOCATION	4.4
Surface Water Spills	4.7
Ground-Water Spills	4.8
Spills on Ice and Snow	4.9
Surface Soil Spills	4.9
Subsurface Soil Spills	4.9
CONTAINMENT, REMOVAL, AND STORAGE EQUIPMENT FOR MAJOR SPILLS	4.10
Barriers and Wiers	4.11
Booms	4.14

Dikes and Excavation	.	.	.	.	.	.	.	.	.	4.18
Nozzels	.	.	.	.	.	.	.	.	.	4.20
Separators	.	.	.	.	.	.	.	.	.	4.20
Skimmers	.	.	.	.	.	.	.	.	.	4.20
Sorbents and Gellants	.	.	.	.	.	.	.	.	.	4.23
Dispersants	.	.	.	.	.	.	.	.	.	4.26
5.0 ASSESSMENT OF CLEANUP TECHNOLOGIES FOR SYNFUEL SPILLS	.	.	.	.	.	.	.	.	.	5.1
COAL LIQUIDS	.	.	.	.	.	.	.	.	.	5.3
SHALE OIL AND TAR SANDS	.	.	.	.	.	.	.	.	.	5.4
ALCOHOLS	.	.	.	.	.	.	.	.	.	5.6
6.0 DISPOSAL OF RESIDUES FROM SYNFUEL SPILL CLEANUP OPERATIONS	.	.	.	.	.	.	.	.	.	6.1
TYPES OF RESIDUES	.	.	.	.	.	.	.	.	.	6.1
CHARACTERISTICS OF SPILL RESIDUES	.	.	.	.	.	.	.	.	.	6.1
Recovered Fuel and Oil	.	.	.	.	.	.	.	.	.	6.1
Sorbents and Gellants	.	.	.	.	.	.	.	.	.	6.3
Contaminated Soils and Sediments	.	.	.	.	.	.	.	.	.	6.4
Combustion Residuals	.	.	.	.	.	.	.	.	.	6.4
Contaminated Debris	.	.	.	.	.	.	.	.	.	6.5
METHODS FOR DISPOSING OF SPILL CLEANUP RESIDUALS	.	.	.	.	.	.	.	.	.	6.5
Fuel/Oil Recovery	.	.	.	.	.	.	.	.	.	6.5
Fuel/Oil Reuse	.	.	.	.	.	.	.	.	.	6.6
Landfilling	.	.	.	.	.	.	.	.	.	6.7
Landfarming	.	.	.	.	.	.	.	.	.	6.8
Incineration	.	.	.	.	.	.	.	.	.	6.10
SUITABILITY OF DISPOSAL METHODS FOR SYNFUEL SPILLS	.	.	.	.	.	.	.	.	.	6.11

Effect of Toxicity	6.11
Fuel/Oil Recovery	6.12
Reuse	6.12
Landfilling	6.13
Landfarming	6.13
Incineration	6.14
RECOMMENDED METHODS FOR DISPOSING OF SYN FUEL RESIDUES	6.14
Recovered Fuel and Oil	6.15
Contaminated Soil	6.15
Contaminated Debris	6.15
Spent Sorbents	6.17
Spent Gellants	6.17
Combustion Residue	6.17
RECOMMENDATIONS	6.17
Characterization of Residues	6.17
Performance of Disposal System	6.18
REFERENCES	R.1
APPENDIX A - SYN FUEL PROJECTION ESTIMATES	A.1
APPENDIX B - ACUTE TOXICITY OF SYN FUEL	B.1
APPENDIX C - ACUTE TOXICITY OF ALCOHOLS	C.1
APPENDIX D - TERRESTRIAL EFFECTS	D.1

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•

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•

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FIGURES

1	Synfuels Production Estimates	1.3
2	Toxicity of Synfuels	3.3
3	Acute Toxicity Alcohols	3.4
4	Decision Flow Chart	4.3
5	Improved Spade Dam with Drainage Pipes	4.12
6	Wooden Plate Dam	4.12
7	Straw Bale Barrier	4.13
8	Drilling Through Ice Into Subsurface Pools	4.15
9	Ice Slots and Through-Ice Barriers	4.15
10	Typical Oil Containment Booms	4.16
11	Typical Deployment of Oil Booms and Skimmer	4.17
12	Glance Boom	4.19
13	Moving Bucket Skimmer	4.21
14	Submersion Belt Skimmer	4.21
15	Paddle-Induced Vortex	4.22
16	Cyclone Separator	4.23
17	Barrel Weir Skimmer	4.24
18	Floating Weir Skimmer	4.24
19	Sorption Skimmers	4.25

TABLES

1	Synfuels Production to the Year 2000 in Barrels Per Day, Oil Equivalent	1.2
2	Comparison of Current Production Forecasts Against Past Production Forecasts	1.4

3	Synfuel Product Breakdown and Classification	.	.	.	.	1.5
4	Projections on Products Produced from Synfuels	.	.	.	.	1.6
5	Frequency and Amount of Oil Spilled by Source	.	.	.	.	2.3
6	Types of Oil Discharges	.	.	.	.	2.4
7	Averaged Oil Spill Data for 1977 to 1979	.	.	.	.	2.6
8	Projected Synfuel Spills by Location	.	.	.	.	2.7
9	Spill Factor Calculations	.	.	.	.	2.9
10	Literature Comparison of Spill Factors	.	.	.	.	2.11
11a	Transportation Methods for Synfuels	.	.	.	.	2.13
11b	Transportation Methods for Synfuels	.	.	.	.	2.13
11c	Transportation Methods for Synfuels	.	.	.	.	2.14
11d	Transportation Methods for Synfuels	.	.	.	.	2.14
12	Breakdown Between Crude Oil and Crude Products by Their Method of Transportation	.	.	.	.	2.16
13a	Volume of Syncrudes Products Transported and Spilled by Synfuel and Year (1985)	.	.	.	.	2.17
13b	Volume of Syncrudes and Syncrude Products Transported and Spilled by Synfuel and Year (1990)	.	.	.	.	2.17
13c	Volume of Syncrudes and Syncrude Products Transported and Spilled by Synfuel and Year (1995)	.	.	.	.	2.18
13d	Volume of Syncrudes and Syncrude Products Transported and Spilled by Synfuel and Year (2000)	.	.	.	.	2.18
14	Syncrude Spilled According to Synfuel and Method of Transportation	.	.	.	.	2.19
15	Products Spilled According to Synfuel and Method of Transportation	.	.	.	.	2.20
16	Toxicity of Petroleum Crudes, Shale Oil, and Other Oils and Solvents	.	.	.	.	3.7
17	Summary of Spill-Response Technologies for Spills on Water	.				4.5

18	Spill-Response Methods for Spills on Land	4.6
19	Major Spill Mitigation Techniques Reviewed	4.11
20	Residues Generated During Spill Cleanup Activities	6.2
21	Recommended Methods for Disposal of Synfuel Spill Cleanup Residues	6.16
B.1	Acute Toxicity	B.1
B.2	Acute Toxicity	B.2
B.3	Acute Toxicity	B.3
B.4	Acute Toxicity	B.4
B.5	Acute Toxicity	B.5
B.6	Acute/Chronic Toxicity	B.6
B.7	Acute/Chronic Toxicity	B.7
C.1	Acute Toxicity	C.1
D.1	Terrestrial Effects	D.1

1.0 SYNFUELS PRODUCTION ESTIMATES TO THE YEAR 2000

Production of synthetic fuels will increase in the next two decades due to competitive economics and the world market for petroleum derived fuels. Increasing demand for synfuels has resulted in the need to determine the impact that synfuels production may exert on the environment. In particular, the goal of this program is to determine how to mitigate spills of synfuels and synfuel intermediaries. This chapter estimates synfuels production through the year 2000, and identifies, based on case histories, the synfuels most likely to be spilled. This information will be useful in evaluating cleanup methodologies.

Synthetic fuels are derived from oil shale, coal, tar sands, and biomass. This paper offers production projections for shale oil, directly and indirectly liquified coal, tar sands syncrude, ethanol, and methanol. Direct coal liquefaction processes include solvent refined coal (SRC) II, Exxon donor solvent (EDS), and H-coal. Indirect coal liquefaction processes include Fisher-Tropsch, M-gasoline, and methanol formation. Significant amounts of methanol will probably be made through coal liquefaction.

Projections about synfuels production through the year 2000 are given in Table 1 and Figure 1. Most of the data were obtained from literature published in 1980. Both Table 1 and Figure 1 present average estimates and an overall range of estimates. Average estimates are shown graphically as solid lines, whereas the range limits are shown as dashed lines. Larger ranges indicate greater uncertainty in projected average values. All data are in units of barrels per day, oil equivalent (B/DOE).

Recent production projections are less optimistic than the estimates of three years ago. This is due to the unavailability of necessary equipment and increasing concern about the effect of synfuels development upon the environment. A comparison of current forecast data against past projections forecasts (Table 2) shows that because of this trend in production forecasts, average estimates reported in this paper may be higher than will actually occur (Wakamiya et al. 1979).

TABLE 1. Synfuels Production to the Year 2000 in Barrels Per Day, Oil Equivalent

Synfuel	1985	1990	1995	2000
Direct Coal Liquefaction	15,000 ^(a) (15,000) ^(b)	40,000 (25,000-60,000)	200,000 (150,000-250,000)	506,000 (400,000-625,000)
Indirect Coal Liquefaction	15,000 (15,000)	155,000 (110,000-200,000)	510,000 (350,000-600,000)	823,000 (625,000-1,000,000)
Ethanol	50,000 (38,000,84,000)	183,000 (100,000-290,000)	278,000 (180,000-375,000)	321,000 (185,000-460,000)
Methanol	51,000 (51,000)	69,000 (69,000)	--- ---	819,000 (640,000-1,000,000)
Shale Oil	47,000 (40,000-50,000)	270,000 (40,000-600,000)	685,000 (50,000-1,500,000)	1,560,000 (700,000-3,000,000)
Tar Sands	12,500 (10,000-15,000)	25,800 (0-100,000)	30,000 (10,000-50,000)	70,800 (25,000-125,000)
TOTAL	190,500	742,800	----	4,099,800

(a) Average estimate

(b) Range of estimate shown in parentheses

DIRECT COAL LIQUEFACTION

INDIRECT COAL LIQUEFACTION

ETHANOL

METHANOL

FIGURE 1. Synfuels Production Estimates

SHALE OIL

TAR SANDS

FIGURE 1. (contd)

TABLE 2. Comparison of Current Production Forecasts Against Past Production Forecasts (B/DOE)

Synfuel	Year			
	1985	1990	1995	2000
Shale Oil	47,000(a) (270,000)(b)	270,000 (720,000)	685,000 (2,000,000)	1,560,000 (2,000,000)
Liquefied Coal	30,000 (67,000)	195,000 (292,000)	710,000 (1,500,000)	1,329,000 (1,900,000)

(a) 1980 Estimate

(b) 1978 Estimate

Moreover, actual synfuels production is tied to market demand and political actions. Large-scale government funding of synfuels projects, for example, would increase production to levels above those predicted. The degree to which this would occur is unknown.

To gain an understanding of how synfuel spills might affect human health, it was necessary to determine which synfuel products will be produced and in what quantities. Product distribution data are quite limited, as production is tied to unpredictable consumer demand.

Cowles (1980) gives a limited breakdown of products expected to be produced by shale oil and direct and indirect coal liquefaction processes (Table 3). He estimates that gasoline would account for 51.7% of the total amount of products produced (based on demand); jet fuel, 10.5%; heating oils, 23.8%; and miscellaneous products, 14.0%. From Table 3, it seems that direct coal liquefaction produces heavier (based on relative density) products than indirect coal liquefaction processes. This is due to the nature of the processes themselves. Direct coal liquefaction processes inherently produce heavier products than indirect coal liquefaction processes unless "cracking" operations are performed on the products from direct coal liquefaction processes.

Ghassemi and Iyer (1981) have also evaluated the possible products from synthetic fuel processes (Table 4). Products are classified as synthetic natural gas (SNG), gasoline, liquefied petroleum gas (LPG), naphtha, diesel

TABLE 3. Synfuel Product Breakdown and Classification

<u>Synfuel</u>	<u>Classification</u>	<u>Product(s)</u>
Shale Oil	Gasoline	Gasoline
	Jet Fuel	Jet Fuel
	Heating Oils	Diesel Fuel
	Miscellaneous Products	Residuals, Lubricants, Waxes, LP6
Direct Coal Liquefaction	Gasoline	---
	Jet Fuel	Naphtha
	Heating Oils	Fuel Oils
	Miscellaneous Products	Tar Oils, LPG, Propane, Butane, Solvents
Indirect Coal Liquefaction	Gasoline	Gasoline
	Jet Fuel	---
	Heating Oils	Heavy Fuel Oils, Diesel Fuels
	Miscellaneous Products	Tar Oils, LPG, Methanol

TABLE 4. Projections on Products Produced from Synfuels

<u>Synfuel Process</u>	<u>Product</u>	<u>Quantity Produced (B/DOE)</u>		
		<u>1980-1987</u>	<u>1988-1992</u>	<u>1993-2000</u>
Indirect Coal Liquefaction	SNG	---	32,600	65,200
	Gasoline	---	64,500	579,000
	LPG	---	100	200
	Diesel Fuel	---	2,500	5,000
	Residuals	---	700	1,400
Direct Coal Liquefaction	LPG	---	5,900	44,300
	Naphtha	---	15,400	107,800
	Middle Distillates	---	18,700	130,900
	Residuals	---	10,000	70,000
Shale Oil	Gasoline	57,000	66,700	130,000
	Middle Distillates	13,000	305,100	340,000
	Residuals	7,000	38,100	50,000

fuel, middle distillates, and residuals. Middle distillates include jet fuel, diesel fuel, kerosene, and light fuel oil. Residuals normally include marine fuel oils and lubricants. Several trends are implied by the data in Table 4. First, the only significant liquid synfuels produced up to 1987 will be from oil shale. Second, indirect coal liquefaction processes, once on line, will be used to produce gasoline, whereas shale oil will be used for the production of diesel and jet fuels. Third, direct coal liquefaction processes will produce heavier components, due to the intrinsic nature of the process, similar to the product distribution projected for shale oil.

A comparison of Ghassemi and Iyer's results with those of Cowles indicates that their data are similar, especially in the last time frame (1993 to 2000). Cowles predicted that 51.7% of the synfuel products would be gasoline, 34.3% would be heating and jets fuels, and 14% would consist of miscellaneous products. This compares with Ghassemi and Iyers' forecasts, for the 1993 to 2000 time frame, in which gasoline accounts for 46.5%; heating and jet fuels, 39.3%; and miscellaneous products, 14.2%. Because different product categories were used by the two sources reviewed, some assumptions were made to reduce each data source to a similar basis for comparison. It was assumed that Ghassemi and Iyer's categories for diesel fuel, middle distillate and miscellaneous

products were equivalent to Cowles' categories for heating and jet fuel production. Based on earlier descriptions of what constitutes middle distillate and residual, Ghassemi and Iyer's equivalent for heating and jet fuels contains some miscellaneous products such as lubricants. These products cannot be subtracted from the heating and jet fuels category due to lack of data from the original reference. This error will cause the relative values for Ghassemi and Iyer's heating and jet fuel category to be slightly inflated and the miscellaneous category to be slightly lower than it should be. The miscellaneous products percentage for Ghassemi and Iyer's data was determined by difference.

2.0 POSSIBLE SOURCES OF SYNFUEL SPILLS AND VOLUMES OF SPILLED FUEL TO THE YEAR 2000

Synthetic fuels are expected to become a significant source of energy for the United States by the year 2000. Production forecasts (Table 1) indicate that as much as 25% of all liquid fuels will be of synthetic origin; therefore, it is important to consider the impacts that production and transportation of these materials will have on the environment. The objectives of this chapter are to determine potential synfuel spill locations, determine spill locations where synfuels are most likely to be spilled, and determine the quantity of synfuels likely to be released from these locations.

Synfuels are defined as syncrudes, syncrude intermediaries, and synfuel products. This definition covers all aspects of synfuels from production through refining and finally to product distribution.

Data outlining specific locations where synfuels may be spilled are minimal or do not exist. However, one can approximate synfuels spill incident patterns with historical data on crude oil and crude oil product spills, as long as the correlation is made to account for some significant differences between the two. For instance, crude oils are more likely to be transported over ocean waters than are synfuels, and since a relatively high percentage of crude oils and crude oil products spilled is released through ocean spills, an adjustment is necessary in the release probability estimates for synfuels.

CRUDE OIL AND PRODUCT SPILLS

Information on crude oil spills occurring from 1977 to 1979 was obtained for the most part from U.S. Coast Guard reports published in 1978 and 1979. Data from earlier years do not necessarily reflect current spill-prevention technologies. (The 1980 Coast Guard report was not available at the time this report was prepared.)

Oil spill incidents, by source, are presented in Table 5 for 1977, 1978, and 1979. Data include both the number of incidents and the volume of oil spilled. The general heading of "oil" was defined to include crude oil;

gasoline, other distillates, solvents, diesel oil, fuel oils, asphalt/residual, animal/vegetable oil, waste oil, and other oils. Inclusion of animal/vegetable oil data should not affect the analogy between synfuels and petroleum oils, because animal/vegetable oils are produced in relatively small quantities.

Tank ships, tank barges, pipelines, fuel transfer locations, and bulk transfer locations are frequent sources of spills. (Offshore oil wells have a high number of spills but were not included in the data base because synfuels will be produced on land.) Refineries reported fewer spills than other sources. Thus, refinery spillage of synfuels is expected to be minimal.

Table 5 also lists the volume of oil spilled by location. High-volume spills occurred on tank ships, tank barges, highways, and of bulk transfer points. Except for tank ships, these sources will probably be responsible for the majority of synfuel releases in the future.

In general, most oil spills are quite small. Leggett et al. (1980) states that over 50% of all oil spills reportedly involved less than 50 gallons of oil. Thus, only a few large spills may account for most of the total volume of oil spilled. In 1978, for example, spillage of oil at bulk transfer locations was an order of magnitude higher than in 1977 and 1979 due to a few large spills at bulk transfer points during 1978 (Table 5). This spill volume to spill incident trend is expected to continue as synfuels are produced and lost through transportation networks.

Crude oil normally accounts for 25 to 30% of the total amount of oil spilled (Table 6). This loss trend is expected to continue with the production and transportation of syncrudes. Several other petroleum products--e.g., diesel fuel, fuel oils, and gasoline--were also spilled in significant quantities. This was due to the relatively large volumes of these products transported as compared with other products produced.

The volume of synfuel products produced will be based on consumer demand. Because the demand for gasoline, diesel, and fuel oils should remain strong (McAfee 1980), significant amounts of these products will be produced from syncrudes. Consequently, the majority of synfuel products spilled will be gasoline, diesel, and fuel oils.

TABLE 5. Frequency and Amount of Oil Spilled by Source (Gallons)

Source	1977				1978				1979			
	No. of Spills	%	Volume	%	No. of Spills	%	Volume	%	No. of Spills	%	Volume	%
Vessels												
Tank Ships	590	4.7	203,660	22.7	724	6.1	327,713	2.3	686	6.5	2,493,546	27.4
Tank Barges	1,099	8.7	1,644,202	18.3	1,077	9.0	3,259,354	22.7	922	8.7	1,152,118	12.7
Dry Cargo Barges	41	0.3	1,395	0.0	26	0.2	41,491	0.3	38	0.4	9,040	0.1
Dry Cargo Ships	417	3.3	71,248	0.8	395	3.3	155,443	1.1	318	3.0	73,428	0.8
Combatants	196	1.6	12,680	0.1	255	2.1	29,928	0.2	150	1.4	7,662	0.1
Other	1,610	12.8	217,282	2.4	1,630	13.6	265,643	1.9	1,368	13.0	276,602	3.1
Total	3,953	31.4	2,150,467	24.0	4,107	34.3	4,079,572	28.4	3,482	33.0	4,012,396	44.1
Land Vehicles												
Rail	58	0.5	138,314	1.5	49	0.4	80,745	0.6	44	0.4	115,750	1.3
Highway	390	3.1	411,934	4.6	406	3.4	399,214	2.8	337	3.2	345,490	3.8
Other	81	0.6	25,334	0.3	78	0.7	23,775	0.2	60	0.6	39,882	0.4
Total	529	4.2	575,582	6.4	553	4.5	503,734	3.6	441	4.2	501,122	5.5
Non-Transport, On/Offshore												
Refinery	115	0.9	68,556	0.8	127	1.1	59,314	0.4	92	0.9	222,628	2.5
Bulk Storage	234	1.9	713,334	8.0	213	1.8	688,373	4.8	211	2.0	318,768	3.5
Onshore Production	164	1.3	320,104	3.6	168	1.4	89,429	0.6	324	3.1	223,076	2.5
Offshore Production	1,094	8.7	84,828	0.9	799	6.7	85,740	0.6	610	5.7	93,318	1.0
Other	983	7.8	1,147,491	12.8	833	7.0	476,706	3.3	707	6.7	339,989	3.7
Total	2,590	20.6	2,344,313	26.0	2,140	18.0	1,399,562	9.7	1,944	18.4	1,197,779	13.2
Pipelines	538	4.3	2,667,766	29.7	448	3.7	1,434,116	10.0	455	4.3	2,128,752	23.4
Marine Facilities On/Offshore												
Fuel Transfer	116	0.9	19,357	0.2	115	1.0	11,556	0.1	115	1.1	57,739	0.6
Bulk Transfer	450	3.6	415,390	4.6	392	3.3	6,059,479	42.2	336	3.2	260,022	2.9
Non-Bulk Transfer	27	0.2	1,182	0.0	24	0.2	16,179	0.1	10	0.1	211,225	2.3
Other	154	1.2	64,017	0.7	144	1.2	238,579	1.7	145	1.4	21,310	0.2
Total	747	5.9	499,946	5.5	675	5.6	6,325,793	44.1	606	5.8	550,296	6.1
Land Facilities	195	1.5	155,923	1.7	230	1.9	127,644	0.9	194	1.8	252,419	2.8
Miscellaneous/Unknown	4,043	32.0	595,384	6.6	3,817	31.9	473,575	3.3	3,434	32.5	448,873	4.9
Grand Total	12,605	100.0	8,979,381	100.0	11,950	100.0	14,343,996	100.0	10,556	100.0	9,091,637	100.0

TABLE 6. Types of Oil Discharges (Gallons)

Materials	1977				1978				1979			
	No.	%	Volume	%	No.	%	Volume	%	No.	%	Volume	%
Crude Oil	2,357	18.7	2,920,236	32.5	2,140	17.9	3,407,519	23.8	1,921	18.5	2,813,094	31.3
Gasoline	858	6.8	1,070,967	12.0	779	6.5	2,874,706	20.0	629	6.0	1,260,966	13.9
Other Distillate	264	2.1	172,095	2.0	307	2.5	1,276,525	8.9	281	2.7	264,985	2.9
Solvents	53	0.4	46,011	0.5	50	0.4	106,000	0.7	38	0.6	7,479	0.1
Diesel Oil	2,637	20.9	1,750,275	19.5	2,768	23.2	1,707,577	11.9	2,530	24.0	1,680,391	18.5
Fuel Oil	1,078	8.6	1,249,518	14.0	1,065	8.9	3,927,047	27.4	941	8.9	887,433	9.8
Asphalt/Tar/Pitch	170	1.3	276,544	3.0	177	1.5	100,753	0.7	152	1.4	155,037	1.7
Animal/Vegetable Oil	71	0.6	108,125	1.2	78	0.7	158,266	1.1	53	0.5	17,590	0.2
Waste Oil	1,575	12.5	484,675	5.4	1,440	12.1	214,811	1.5	1,192	11.3	354,479	3.9
Other Oil	<u>3,522</u>	<u>27.9</u>	<u>900,935</u>	<u>10.0</u>	<u>3,146</u>	<u>26.3</u>	<u>570,792</u>	<u>4.0</u>	<u>2,750</u>	<u>26.0</u>	<u>1,650,183</u>	<u>18.1</u>
Total	12,605	100.0	8,979,381	100.0	11,950	100.0	14,343,996	100.0	10,487	100.0	9,091,637	100.0

Source: U.S.C.G. 1978
U.S.C.G. 1979

SYNFUEL SPILLS

This section hypothesizes the sources and volumes of synfuels spills, based on data for comparable oil spills. To simplify the calculations needed to draw analogies between petroleum spill data and synfuel data, data from Table 5 were averaged (Table 7). In general, yearly fluctuations from these averages are small. One noticeable exception is the release of oil products at bulk transfer marine facilities discussed earlier in the report. Variation from the average was much less for the larger spill categories than for the small spill categories. Therefore, the use of averaged oil spill data should not introduce any large errors in future calculations with the possible exception of bulk transfer storage data.

The last column in Table 7 indicates which sources are also likely to be sources of synfuels spills. Tank barges, bulk transfer points, pipelines, railroads, and highways are the most likely candidates. Tank ships were excluded as significant carriers of synfuels because most synfuels will be produced inland, where there is no need for ships. Most waterborne transport of synfuels will probably be by barges, which have better maneuverability (lower draft requirements) than ships and lower transportation costs (for inland traffic).

Table 8 projects the probable volume of synfuels that will be spilled in the vicinity of refineries, highways, railroads, and marine transfer points. The percentages in Table 8 were extrapolated from oil-spill data found in Table 7. The last column in Table 8 adjusts for skewed data reflecting an unusually large (one magnitude higher) volume of spilled oil at bulk transfer stations in 1978. The percentage from this category was reduced from 28.7% to 10%, and the remaining 18.7% was added to the pipeline category. Placement of this percentage in the pipeline category reflects the belief that synfuels will rely on pipeline transportation more than conventional crude oil and crude oil product transportation. Values from the adjusted category were used in all subsequent calculations requiring a distribution of synthetic fuel sources.

TABLE 7. Averaged Oil Spill Data for 1977 to 1979

Sources of Oil Spills	Spills in Oil Industry (Averages 1977-1979)				Potential Sources of Spills in the Synfuels Industry
	No.	%	Volume (Gallons)	%	
Vessels					
Tank Ships	667	5.7	1,008,000	9.3	
Tank Barges	1,033	8.8	2,018,000	18.7	X
Dry Cargo Barges	35	0.3	17,000	0.2	X
Dry Cargo Ships	377	3.2	100,000	0.9	
Combatants	200	1.7	17,000	0.2	
Other	1,536	13.1	253,000	2.3	
Total	3,848	32.9	3,413,000	31.6	
Land Vehicles					
Rail	50	0.4	112,000	1.0	X
Highway	378	3.2	386,000	3.6	X
Other	73	0.6	30,000	0.3	X
Total	501	4.3	528,000	4.9	
Non-Transport On-Offshore					
Refinery	111	0.9	117,000	1.1	X
Bulk Storage	219	1.9	574,000	5.3	X
Onshore Production	219	1.9	211,000	2.0	
Offshore Production	834	7.1	88,000	0.8	
Other	841	7.2	655,000	6.1	
Total	2,224	19.0	1,645,000	15.2	
Pipelines	480	4.1	2,077,000	19.2	X
Marine Facilities On/Shore					
Fuel Transfer	116	1.0	30,000	0.3	X
Bulk Transfer	393	3.4	2,245,000	20.8	X
Non-Bulk Transfer	20	0.2	76,000	0.7	
Other	148	1.3	108,000	1.0	
Total	677	5.8	2,459,000	22.7	
Land Facilities	206	1.8	179,000	1.7	X
Miscellaneous/Unknown	3,765	32.1	506,000	4.7	
Grand Total	11,701	100.0	10,807,000	100.0	

TABLE 8. Synfuel Spilled by Location

Potential Sources of Synfuel Spills	Volume Percentages of Synfuels Likely to be Spilled Based on Oil Data		Adjusted Volume Percentages of Synfuels Likely to be Spilled Based on Oil Data
	% Incidents	% Volume	% Volume
Vessels			
Tank Barges	33.4	26.0	26.0
Dry Cargo Barges	1.1	0.2	0.2
Land Vehicles			
Rail	1.6	1.4	1.4
Highway	12.2	5.0	5.0
Other	2.4	0.4	0.4
Non-Transport On/Offshore			
Refinery	3.6	1.5	1.5
Bulk Storage	7.1	7.4	7.4
Pipelines	15.5	26.7	45.4
Marine Facilities On/Offshore			
Fuel Transfer	3.7	0.4	0.4
Bulk Transfer	12.7	28.7	10.0
Land Facilities	<u>6.7</u>	<u>2.3</u>	<u>2.3</u>
Total	100.0	100.0	100.0

SPILL FACTOR DETERMINATION

To determine the actual volume of synfuels that might be spilled, we calculated spill factors (volume spilled/volume transported or stored) from oil spill and transportation data for various modes of transportation and storage. These spill factors (based on oil data) were then applied to volumes of synthetic fuels expected to be transported.

Calculation of spill factors involved the use of two data sources on oil transportation and losses in and around U.S. waters. First, the amount of oil spilled, by method of transportation or storage, was acquired from U.S. Coast Guard reports (Table 5) for 1977, 1978, and 1979. Spill factors for synfuels storage areas were necessary because significant amounts of oil are known to be lost at oil storage facilities. Secondly, total crude oil and crude oil products transportation for 1977 and 1978 were obtained from statistics provided by the Association of Oil Pipe Lines (1980). Data for 1979 were not available and, therefore, were calculated from growth trends observed from earlier years. Because the Oil Pipe Line's data were in tons and oil spill data were in gallons, a conversion factor was required. Conversion factors of 6.72 barrels per ton and 42 gallons per barrel were used in converting tons and gallons to barrels. A summary of converted transportation and spill data for 1977 and 1978 is presented in Table 9.

Spill factors are also necessary for storage facilities, and waterways. Spill factors must be calculated for these locations because significant volumes of oil were spilled at these points.

Seasonal changes in demand cause daily fluctuations in throughput at a refinery and, hence, daily fluctuations in spill losses. Unfortunately, accounting for daily variation was beyond the scope of this study. Therefore, calculations are based on the assumption that flow into a refinery equals the flow out. Multiplying the daily volume by the number of days per year resulted in a figure of 5,353,000,000 barrels per year passing through refineries for 1978. (Values of refinery throughput for 1977 and 1979 were unavailable.) Marine facilities' throughput volumes were assumed to be equal to the amount of oil transported by water carriers, since the majority of oil transported by water passes through marine facilities.

TABLE 9. Spill Factor Calculations

Year	Total Crude and Products Transported (bbl/yr)	Breakdown by Mode of Transportation/Storage (bbls/yr)					
		Pipelines	Inland Water Carriers	Motor Carriers	Railroads	Refinery and Bulk Storage	Marine Facilities***
1977	13,818,051,000	6,626,478,400	3,000,812,600	3,998,688,600	197,071,710	---	3,000,812,600
1978	14,170,888,000	6,598,439,200	3,378,793,100	4,021,556,400	172,099,200	5,353,000,000**	3,378,793,100
1979*	14,523,843,000	6,570,518,600	3,756,773,600	4,044,424,600	152,126,690	---	3,756,773,600

Year	Total Crude and Products Transported (bbl/yr)	Spill Breakdown by Mode of Transportation/Storage (bbls/yr)					
		Pipelines	Inland Water Carriers	Motor Carriers	Railroads	Refinery and Bulk Storage	Marine Facilities***
1977	218,795	63,518	51,202	9,808	3,293	13,101	11,903
1978	341,524	34,146	97,132	9,505	1,922	17,802	150,614
1979	216,467	50,685	95,533	8,226	2,756	12,890	13,102

Year	Overall Fraction Spilled (vol/vol)	Spill Breakdown by Mode of Transportation/Storage (bbls/yr)					
		Pipelines	Inland Water Carriers	Motor Carriers	Railroads	Refinery and Bulk Storage	Marine Facilities***
1977	15.5×10^{-6}	9.6×10^{-6}	17.1×10^{-6}	2.5×10^{-6}	17.1×10^{-6}	---	4.0×10^{-6}
1978	24.1×10^{-6}	5.2×10^{-6}	28.7×10^{-6}	2.4×10^{-6}	11.2×10^{-6}	3.3×10^{-6}	44.6×10^{-6}
1979	14.9×10^{-6}	7.7×10^{-6}	25.4×10^{-6}	2.0×10^{-6}	18.1×10^{-6}	---	3.5×10^{-6}
Average	18.2×10^{-6}	7.5×10^{-6}	23.7×10^{-6}	2.3×10^{-6}	15.5×10^{-6}	3.3×10^{-6}	17.4×10^{-6}

* Calculated based on historical trends.

** From National Petroleum Council data

*** Assumed to equal Inland Water Carriers transportation data.

Spill factors, or the fraction of oil transported that was lost to spillage, were calculated by dividing the total amount of oil transported into the total amount spilled. Results of these calculations are presented in the third set of rows in Table 9. The methods of transportation and storage for which spill factors were calculated included pipelines, inland water carriers, motor carriers, railroads, refinery and bulk storage, and marine facilities. Both the overall and specific spill factors (depending on the method of transportation) were determined for 1977, 1978, and 1979 and then averaged. With one exception (marine facilities), the yearly values did not differ significantly from the averaged values. The spill factor at marine facilities was much higher for 1978 than for the other two years. This difference was due to the occurrence of large spills during 1978, but not during 1977 and 1979. Thus, the average value for the marine facilities' spill factor may be larger than it should be. Overall, spill factors ranged from a low of 2.3×10^{-6} for motor carriers to a high of 23.7×10^{-6} for inland water carriers.

Comparative values from the literature are limited. Leggett et al. (1980) provided data on loss fractions per mile for various modes of transportation for crude oil. Spill factors calculated were compared against Leggett's values by multiplying by average trip lengths (dependent on the method of transportation) given by Leggett. Results are presented in Table 10. In general, spill factor values compared quite well. Marine transfer values were the only factors that differed significantly. Calculated spill factor values for marine transfer were much higher than Leggett's values and probably reflect the high-volume spill incidents of 1978 discussed earlier.

COMPUTATION OF SYNTHETIC SPILL VOLUMES

The volumes of synfuels transported or stored, according to their method of transportation and year of production, are summarized in Tables 11a-d. The values given in these tables were based on several assumptions. First, the synfuels production estimates are based on results from Table 1. These estimates are assumed to be accurate, although recent political events could change them drastically. Secondly, knowing the production of synfuels does not allow

TABLE 10. Literature Comparison of Spill Factors

<u>Mode of Transportation</u>	<u>Spill Coefficients (Loss Fraction Per Mile)</u>	<u>Length of Standard Trip (Miles)</u>	<u>Leggett et al., Spill Factor</u>	<u>Calculated Spill Factors</u>
Coastal Tanker	4.221×10^{-10} to 7.146×10^{-8}	1,300	0.463×10^{-6} to 92.9×10^{-6}	23.7×10^{-6}
Tow Boat and Barges	3.963×10^{-9} to 1.06×10^{-7}	1,500	5.95×10^{-6} to 159×10^{-6}	23.7×10^{-6}
Railroad	1.590×10^{-7} to 4.98×10^{-7}	500	79.5×10^{-6} to 249×10^{-6}	15.5×10^{-6}
Pipeline	5.987×10^{-8} to 1.193×10^{-7}	300	17.96×10^{-6} to 53.9×10^{-6}	7.5×10^{-6}
Marine Transfer	---	---	0.058×10^{-6} to 0.682×10^{-6}	17.4×10^{-6}
Storage	---	---	0.380×10^{-6} to 0.688×10^{-6}	3.3×10^{-6}

one to calculate directly the amounts of syncrudes and syncrude products transported and spilled. A syncrude will be transported several times during its evolution from syncrude to final product. Thus, a factor is required to determine the number of products transported versus a fuel syncrude transported. (This factoring was not a problem for ethanol and methanol production, because these synfuels were produced in final form.) As with most analogies used so far, oil transportation data were used in determining the ratio between syncrude transportation and syncrude product transportation. Data from the Association of Oil Pipe Lines for 1978 indicated that, for every barrel of crude oil carried in domestic transportation, 2.08 barrels of petroleum products were transported by domestic transportation. Thus, the total amount of crude petroleum and petroleum products carried by domestic transportation was approximately three times the amount of crude petroleum transported. Applying this factor to synfuels production resulted in column two of Tables 11a-d, the quantity of synfuels estimated to be transported. All quantities are given in barrels per day, oil equivalent (B/DOE).

The third section of Tables 11a-d, volume of synfuel transported or stored according to the method of transportation, was determined by using three sets of assumptions. First, calculations assumed that coal liquids, shale oil, and tar sands will use the various modes of transportation (pipelines, inland water carriers, motor carriers, and railroads) in the same relative percentages. Furthermore, it was assumed that these percentages will match the most recent data for the transportation of crude oil and crude oil products published by the Association of Oil Pipe Lines. Their data showed that, in 1978, 46.6% of crude oil and crude oil products was transported by pipeline, 23.8% by inland water carrier, 28.4% by motor carrier, and 1.2% by railroad. Historical trends for the previous ten years indicated that the percentage of crude oil and crude oil products transported by pipelines and water carriers has remained quite constant, although there has been a slight shift (~1%) from railroads to motor carriers. Since railroads are a relatively minor form of transportation for oils, it was assumed that the overall percentages have remained constant. These percentages were then applied to the quantity of synfuels estimated to be transported (column two, Tables 11a-d) for coal liquids, oil shale, and tar

TABLE 11a. Transportation Methods for Synfuels (1985)

Synfuel	1985 Synfuel Production (B/DOE)	Quantity of Synfuels Estimated to be Transported	Volume (B/DOE) Transported/Stored by Method					
			Pipelines	Inland Water Carriers	Motor Carriers	Railroads	Refinery and Bulk Storage	Marine Facilities
Coal Liquids	30,000	90,000	41,940	21,420	25,560	1,080	30,000	21,420
Shale Oil	47,000	141,000	65,710	33,560	40,040	1,690	47,000	33,560
Tar Sands	12,500	37,500	17,470	8,930	10,650	450	12,500	8,930
Methanol*	50,000	50,000	---	4,300	12,400	33,100	50,000	4,300
Ethanol*	51,000	51,000	---	4,390	12,650	33,760	51,000	4,390

* Transportation data from OHM-TADS data base

TABLE 11b. Transportation Methods for Synfuels (1990)

Synfuel	1985 Synfuel Production (B/DOE)	Quantity of Synfuels Estimated to be Transported	Volume (B/DOE) Transported/Stored by Method					
			Pipelines	Inland Water Carriers	Motor Carriers	Railroads	Refinery and Bulk Storage	Marine Facilities
Coal Liquids	195,000	585,000	272,610	139,230	166,140	7,020	195,000	139,230
Shale Oil	270,000	810,000	377,460	192,780	230,040	9,720	270,000	192,780
Tar Sands	25,800	77,400	36,070	18,420	21,980	930	25,800	18,420
Methanol*	69,000	69,000	---	5,930	17,110	45,680	69,000	5,930
Ethanol*	183,000	183,000	---	15,740	45,380	121,150	183,000	15,740

* Transportation data from OHM-TADS data base

TABLE 11c. Transportation Methods for Synfuels (1995)

Synfuel	1985 Synfuel Production (B/DOE)	Quantity of Synfuels Estimated to be Transported	Volume (B/DOE) Transported/Stored by Method					
			Pipelines	Inland Water Carriers	Motor Carriers	Railroads	Refinery and Bulk Storage	Marine Facilities
Coal Liquids	710,000	2,130,000	992,580	506,940	604,920	25,560	710,000	506,940
Shale Oil	685,000	2,055,000	957,630	389,090	583,620	24,660	685,000	489,090
Tar Sands	30,000	90,000	41,940	21,420	25,560	1,080	30,000	21,420
Methanol	-	-	-	-	-	-	-	-
Ethanol*	278,000	278,000	--	23,910	68,940	184,040	278,000	23,910

* Transportation data from OHM-TADS data base

TABLE 11d. Transportation Methods for Synfuels (2000)

Synfuel	1985 Synfuel Production (B/DOE)	Quantity of Synfuels Estimated to be Transported	Volume (B/DOE) Transported/Stored by Method					
			Pipelines	Inland Water Carriers	Motor Carriers	Railroads	Refinery and Bulk Storage	Marine Facilities
Coal Liquids	1,329,000	3,987,000	1,857,940	948,910	1,132,310	47,840	1,329,000	948,910
Shale Oil	1,225,000	3,675,000	1,712,550	874,650	1,043,700	44,100	1,225,000	874,650
Tar Sands	70,800	212,400	98,980	50,550	60,320	2,550	70,800	50,550
Methanol*	819,000	819,000	--	70,430	203,110	542,180	819,000	70,430
Ethanol*	321,000	321,000	--	27,610	79,610	212,500	321,000	27,610

* Transportation data from OHM-TADS data base.

sands. For all synfuel categories, the amount of synfuels passing through refineries and bulk storage was assumed to equal the daily production averages. Synfuels passing through marine facilities were assumed to equal the amount transported by inland water carriers.

Data on methods for transportation of ethanol and methanol were obtained from the Oil and Hazardous Materials Technical Assistance Data System (OHM-TADS) maintained by the Environmental Protection Agency (EPA). This source stated that 66.2% of the ethanol and methanol produced was transported by rail, 24.8% by truck, and 8.6% by barge. Negligible pipeline transportation for ethanol and methanol was indicated. These percentages were applied to total ethanol and methanol production, by year, to compute the volumes carried according to their method of transportation (Tables 11a-d).

Once the volumes of synfuels (both syncrude and syncrude products) were determined, according to their method of transportation, it was necessary to determine the proportion of syncrudes and syncrude products transported by each method of transportation. Again, an analogy between crude oil and crude oil products and syncrudes and syncrude products was made. Relative percentages, by method of transportation, were calculated from Association of Oil Pipe Line data for 1978 and are summarized in Table 12. In general, crude oil tends to be transported by pipelines or water carriers, whereas crude oil products are preferentially transported by motor carriers and railroads. Trends over the past ten years indicated that pipelines are being used to transport relatively more crude oil products than crude oil. Whether this trend will continue in the future is unknown. The volume distribution between oil and oil products, by mode of transportation, was assumed to reflect the expected splits between syncrudes and syncrude products for future synfuel transportation networks.

The splits generated in Table 12 were applied to volumes generated in Tables 11a-d, resulting in the amount of syncrudes and syncrude products expected to be carried by each form of transportation under consideration. These values, presented in Tables 13a-d, were determined for 1985, 1990, 1995, and 2000. Transported volumes were then multiplied by appropriate spill factors, summarized in Table 9, to determine the amount of a particular synfuel likely to be spilled. Spill volumes, given in Tables 13a-d, are shown in parentheses

TABLE 12. Breakdown Between Crude Oil and Crude Products
by Their Method of Transportation

<u>Mode of Transportation</u>	<u>Percentage Crude Oil</u>	<u>Percentage Crude Products</u>
Pipelines	45.58	54.42
Water Carriers	29.04	70.96
Motor Carriers	14.97	85.03
Railroads	7.74	92.26

and lie immediately below the corresponding value for amount of synfuel transported. All data are given in units of barrels per day oil equivalent (B/DOE).

Two additional assumptions were made in compiling Tables 13a-d. First, the split between syncrudes and syncrude products for the "marine facilities" category was assumed to be the same as that for the category "inland water carriers." This assumption follows closely from a similar assumption made earlier that transportation of synfuels through marine facilities was equivalent to the amount transported by water carriers. Secondly, the split between synfuels transported through the category "refineries and bulk storage" was assumed to be 1:2 between syncrude and syncrude products. This assumption was based on a similar ratio (1:2) that existed between the amount of crude oil transported and the amount of crude oil products transported.

Syncrude volumes for ethanol and methanol are not present in Tables 13a-d because ethanol and methanol are themselves assumed to be products. Projections on methanol production for 1995 were not available (Table 1) and therefore, spill volumes associated with the production of ethanol in 1995 could not be determined.

Spill volume data presented in Tables 13a-d were converted to barrels per year, oil equivalent (B/YOE) to obtain yearly losses. Yearly spill loss data for syncrudes and products are presented in Tables 14 and 15, respectively.

By the year 2000, nearly 14,000 B/YOE of syncrudes is expected to be released by the various methods of transportation and storage. Coal liquids and shale oil are expected to be major contributors to syncrude releases. The majority of syncrudes will be lost through pipeline spills, inland water carrier spills, and marine facilities spills.

TABLE 13a. Volume of Syncrudes and Syncrude Products Transported and Spilled by Synfuel and Year (1985)

Synfuel	1985											
	Volume (B/DOE) Transported/Stored by Method											
	Pipeline		Inland Water Carriers		Motor Carriers		Railroads		Refinery and Bulk Storage		Marine Facilities	
	Syncrude (Spilled)	Products (Spilled)	Syncrude (Spilled)	Products (Spilled)	Syncrude (Spilled)	Products (Spilled)	Syncrude (Spilled)	Products (Spilled)	Syncrude (Spilled)	Products (Spilled)	Syncrude (Spilled)	Products (Spilled)
Coal Liquids	19,120 (0.14)	22,820 (0.17)	6,220 (0.15)	15,200 (0.36)	3,830 (0.01)	21,730 (0.05)	84 (0)	996 (0.02)	10,000 (0.03)	20,000 (0.07)	6,220 (0.11)	15,200 (0.26)
Shale Oil	29,950 (0.22)	35,760 (0.27)	9,750 (0.23)	23,810 (0.56)	5,990 (0.01)	34,050 (0.08)	130 (0)	1,560 (0.02)	15,670 (0.05)	31,330 (0.10)	9,750 (0.17)	23,810 (0.41)
Tar Sands	7,960 (0.06)	9,510 (0.07)	2,590 (0.06)	6,340 (0.15)	1,590 (0.00)	9,060 (0.02)	35 (0)	415 (0)	4,170 (0.01)	8,330 (0.03)	2,590 (0.05)	6,340 (0.011)
Methanol	- (-)	- (-)	- (-)	4,300 (0.10)	- (-)	12,400 (0.03)	- (-)	33,100 (0.51)	- (-)	50,000 (0.17)	- (-)	4,300 (0.07)
Ethanol	- (-)	- (-)	- (-)	4,390 (0.10)	- (-)	12,650 (0.03)	- (-)	33,760 (0.52)	- (-)	51,000 (0.17)	- (-)	4,390 (0.08)

TABLE 13b. Volume of Syncrudes and Syncrude Products Transported and Spilled by Synfuel and Year (1990)

Synfuel	1990											
	Volume (B/DOE) Transported/Stored by Method											
	Pipeline		Inland Water Carriers		Motor Carriers		Railroads		Refinery and Bulk Storage		Marine Facilities	
	Syncrude (Spilled)	Products (Spilled)	Syncrude (Spilled)	Products (Spilled)	Syncrude (Spilled)	Products (Spilled)	Syncrude (Spilled)	Products (Spilled)	Syncrude (Spilled)	Products (Spilled)	Syncrude (Spilled)	Products (Spilled)
Coal Liquids	124,260 (0.93)	148,350 (1.11)	40,430 (0.96)	98,800 (2.34)	24,870 (0.06)	141,270 (0.32)	540 (0.01)	6,480 (0.10)	65,000 (0.21)	130,000 (0.43)	40,430 (0.70)	98,800 (1.72)
Shale Oil	172,050 (1.29)	205,410 (1.54)	55,980 (1.33)	136,800 (3.24)	34,440 (0.08)	195,600 (0.45)	750 (0.01)	8,970 (0.14)	90,000 (0.30)	180,000 (0.59)	55,980 (0.97)	136,800 (2.38)
Tar Sands	16,440 (0.12)	19,630 (0.15)	5,350 (0.13)	13,070 (0.31)	3,290 (0.01)	18,690 (0.04)	70 (0)	860 (0.01)	8,600 (0.03)	17,200 (0.06)	5,350 (0.09)	13,070 (0.23)
Methanol	- (-)	- (-)	- (-)	5,930 (0.14)	- (-)	17,110 (0.04)	- (-)	45,680 (0.71)	- (-)	69,000 (0.23)	- (-)	5,930 (0.10)
Ethanol	- (-)	- (-)	- (-)	15,740 (0.37)	- (-)	45,380 (0.10)	- (-)	121,150 (1.88)	- (-)	183,000 (0.60)	- (-)	15,740 (0.27)

TABLE 13c. Volume of Syncrudes and Syncrude Products Transported and Spilled by Synfuel and Year (1995)

Synfuel	1995											
	Volume (B/DOE) Transported/Stored by Method											
	Pipeline		Inland Water Carriers		Motor Carriers		Railroads		Refinery and Bulk Storage		Marine Facilities	
	Syncrude (Spilled)	Products (Spilled)	Syncrude (Spilled)	Products (Spilled)	Syncrude (Spilled)	Products (Spilled)	Syncrude (Spilled)	Products (Spilled)	Syncrude (Spilled)	Products (Spilled)	Syncrude (Spilled)	Products (Spilled)
Coal Liquids	452,420 (3.39)	540,160 (4.05)	146,220 (3.49)	359,720 (8.53)	90,560 (0.21)	514,360 (1.18)	2,980 (0.03)	23,580 (0.37)	236,670 (0.78)	473,330 (1.56)	147,220 (2.56)	359,720 (6.26)
Shale Oil	278,100 (2.09)	679,530 (5.10)	142,030 (3.37)	347,060 (8.23)	87,370 (0.21)	496,250 (1.14)	1,910 (0.03)	22,750 (0.035)	228,330 (0.75)	456,670 (1.51)	142,030 (2.47)	347,060 (6.04)
Tar Sands	19,120 (0.14)	22,820 (0.17)	6,220 (0.15)	15,200 (0.36)	3,830 (0.01)	21,730 (0.05)	80 (0)	1,000 (0.02)	10,000 (0.03)	20,000 (0.07)	6,220 (0.011)	15,200 (0.26)
Methanol	- (-)	- (-)	- (-)	- (-)	- (-)	- (-)	- (-)	- (-)	- (-)	- (-)	- (-)	- (-)
Ethanol	- (-)	- (-)	- (-)	23,819 (0.57)	- (-)	68,940 (0.16)	- (-)	184,040 (2.85)	- (-)	278,000 (0.92)	- (-)	23,910 (0.42)

TABLE 13d. Volume of Syncrudes and Syncrude Products Transported and Spilled by Synfuel and Year (2000)

Synfuel	2000											
	Volume (B/DOE) Transported/Stored by Method											
	Pipeline		Inland Water Carriers		Motor Carriers		Railroads		Refinery and Bulk Storage		Marine Facilities	
	Syncrude (Spilled)	Products (Spilled)	Syncrude (Spilled)	Products (Spilled)	Syncrude (Spilled)	Products (Spilled)	Syncrude (Spilled)	Products (Spilled)	Syncrude (Spilled)	Products (Spilled)	Syncrude (Spilled)	Products (Spilled)
Coal Liquids	846,850 (6.35)	1,011,090 (7.58)	275,560 (6.53)	673,350 (15.96)	169,510 (0.39)	962,800 (2.21)	3,700 (0.06)	44,140 (0.68)	443,000 (1.46)	886,000 (2.92)	275,560 (4.79)	673,350 (11.72)
Shale Oil	780,580 (5.85)	931,970 (6.99)	254,000 (6.02)	620,650 (14.71)	156,240 (0.36)	887,460 (2.04)	3,410 (0.05)	40,690 (0.63)	408,330 (1.35)	816,670 (2.70)	254,000 (4.42)	620,650 (10.80)
Tar Sands	45,120 (0.34)	53,860 (0.40)	14,680 (0.35)	35,870 (0.85)	9,030 (0.02)	51,290 (0.12)	200 (0)	2,350 (0.04)	23,600 (0.08)	47,200 (0.016)	14,680 (0.26)	35,870 (0.62)
Methanol	- (-)	- (-)	- (-)	70,430 (1.67)	- (-)	203,110 (0.47)	- (-)	542,180 (8.40)	- (-)	819,000 (2.70)	- (-)	70,430 (1.23)
Ethanol	- (-)	- (-)	- (-)	27,610 (0.65)	- (-)	79,610 (0.018)	- (-)	212,500 (3.29)	- (-)	321,000 (1.06)	- (-)	27,610 (0.48)

TABLE 14. Syncrude Spilled According to Synfuel and Method of Transportation (B/YOE)

Synfuel	Year	Volume Spilled (B/YOE)						Totals
		Pipeline	Inland Water Carriers	Motor Carriers	Railroads	Refinery and Bulk Storage	Marine Facilities	
Coal Liquids	1985	50	60	4	~0	10	40	160
	1990	340	350	20	4	80	260	1,050
	1995	1,240	1,280	80	11	290	940	3,820
	2000	2,320	2,390	140	22	530	1,750	7,150
Shale Oil	1985	80	80	4	~0	20	60	250
	1990	470	490	30	4	110	350	1,450
	1995	760	1,230	80	11	270	900	3,260
	2000	2,140	2,200	130	18	490	1,610	6,590
Tar Sands	1985	20	20	~0	~0	4	20	70
	1990	40	50	4	~0	10	30	140
	1995	50	60	4	~0	10	40	160
	2000	120	130	7	~0	30	100	380

TABLE 15. Products Spilled According to Synfuel and Method of Transportation (B/YOE)

Synfuel	Year	Volume Spilled (B/YOE)						Totals
		Pipeline	Inland Water Carriers	Motor Carriers	Railroads	Refinery and Bulk Storage	Marine Facilities	
Coal Liquids	1985	60	130	20	7	30	100	340
	1990	410	860	120	40	160	630	2,200
	1995	1,480	3,120	430	140	570	2,290	8,020
	2000	2,770	5,830	810	250	1,070	4,280	15,000
Shale Oil	1985	100	210	30	7	40	150	530
	1990	560	1,180	160	50	220	870	3,040
	1995	1,860	3,010	420	130	550	2,210	8,170
	2000	2,550	5,370	750	230	990	3,950	13,830
Tar Sands	1985	30	60	7	~0	10	40	140
	1990	60	130	20	~0	20	80	310
	1995	60	130	20	7	30	100	340
	2000	150	310	40	20	60	230	800
Methanol	1985	--	40	10	190	60	30	320
	1990	--	50	20	260	80	40	450
	1995	--	--	--	--	--	--	--
	2000	--	610	170	3,070	990	450	5,290
Ethanol	1985	--	40	10	190	60	30	330
	1990	--	140	40	690	220	100	1,180
	1995	--	210	60	1,040	340	150	1,800
	2000	--	240	60	1,200	390	180	2,060

Synfuel product spills are expected to total over 35,000 B/YOE by the year 2000. Nearly 50% of these spills will come from the transportation and storage of products derived from coal liquids and shale oil. Methanol losses, due to increasing production, are expected to total nearly 5000 B/YOE by the year 2000. As with the syncrudes, major spill sources for synfuel products are anticipated to be pipelines, inland water carriers, and marine facilities. Methanol product spillage data for 1995 could not be determined because projections for 1995 methanol production were unavailable.

3.0 HAZARDS OF SYNFUELS SPILLS

This chapter provides a review and summary of available literature on the environmental hazards of petroleum, shale oil, coal liquids, and fuel alcohols. Following a discussion of the acute and chronic toxicity of synfuels, the implications of spills in surface waters are reviewed in terms of the physical, chemical, and biological factors likely to affect the toxicological response of aquatic organisms. The effects of spills in terrestrial habitats are also discussed. Emphasis is given to the potential effects on soils, microorganisms, and vegetation. This chapter also assesses impacts of synfuel spills on humans in terms of biological activities such as mutagenicity, carcinogenicity, and teratogenicity.

HAZARDS OF SYNFUELS

Hazards of synfuels will depend not only on the fuels' toxicity but also on their physical properties, e.g., density and solubility, and the environment in which they are spilled. This section deals with the aquatic and terrestrial effects of synfuels spills.

Surface Waters and Aquatic Ecology

Oils spilled in the aquatic environment will spread over the waters' surface. Less viscous oils [SRC, H-coal product, light distillates (No. 2, DMF, JP-5)] will spread more rapidly than many petroleum crudes and heavy distillates (No. 6). If the densities of oil and water are nearly equal, significant mixing will occur. Turbulence will also promote this process.

Oils derived from coal or shale, and probably tar sands, contain greater concentrations of phenols and anilines than their petroleum counterparts (White, Schweighardt, and Shuty 1977-1978, Paudler and Cheplen 1979). These compounds, which are highly toxic to aquatic organisms, will dissolve from light oils and distillates within minutes of a spill. These same compounds will dissolve much more slowly from raw syncrudes and heavier distillates. Aromatic hydrocarbons (toluene, naphthalene), which are the principal soluble components of petroleum, dissolve more slowly and reach lower equilibrium

concentrations than phenols and anilines and, therefore, are less important contributors to initial (acute) toxicities (DOE 1981). Dissolution will be more rapid in well-mixed water bodies, such as streams, rivers, and coastal waters, but will be slower in lakes, reservoirs, and estuaries.

Sunlight may also cause photochemical changes in spilled coal liquids and petroleum, resulting in increased initial toxicities. Gehrs et al. (1981) determined that oxidants were produced in water underlying two coal liquids at rates comparable to a petroleum-based No. 2 fuel oil. On the contrary, no oxidants were produced from irradiation of a petroleum crude.

Depending on the density of oil spilled and the rates of dissolution and evaporation, some or all of the spilled product may sink and become associated with the sediments. However, on a comparative basis, the chemical forms of these materials, their ultimate fate in sediments, and their eventual effects on aquatic organisms, are all questions yet to be answered. Impacts will be most severe in proximity to the spill site. For spills into rivers and streams, a "pulse" of suspended and solubilized material will be transported downstream at approximately the velocity of stream flow. Insoluble materials will contaminate shorelines and bottom sediments. Many solubilized components of oil, either synthetic or petroleum, will be acutely lethal and result in the death of all or most organisms in the immediate vicinity of the spill. In the case of coal and shale liquids, phenols and anilines and some hydrocarbons will contribute to initial (acute) toxicity. For petroleum, aromatic hydrocarbons account for the initial or acutely lethal response of affected organisms.

As the "pulse" of contaminated water moves downstream, however, the concentration of pollutants will be reduced by dilution, volatilization, photolysis, decomposition, adsorption to sediment, and uptake by organisms. Eventually, the decline in concentration downstream will result in sublethal responses rather than mortality. Some organisms may recover after the initial insult (DOE 1981).

For a spill on a lake or reservoir, contaminants will be dispersed mainly by diffusion. This will result in an area of total mortality surrounded by concentric zones of lesser impact. Selective mortality and sublethal effects may be expected in those areas farthest from the spill site.

The degree of acute toxicity for synfuels can be ranked as shown in Figure 2, based on data generated by Giddings and Washington (1981); Giddings (1980); Becker et al. (1981); Gehrs (1980); Giddings et al. (1980); States et al. (1982); and Cowser (1981b). Detailed results of the toxicity studies used in preparing this figure are presented in Appendix B. The toxicity is based on aquatic effects of organisms such as Selenastrum capricornutum, Microcystic aeruginosa, Daphnia magna, and so forth. Petroleum crude and refined petroleum products are used as reference material in establishing relative toxicity. Figure 2 shows that crude petroleum is less toxic than refined petroleum products. The lighter refined petroleum products are more toxic than the heavier. Studies summarized by Figure 2 also indicate that refined shale oil products are similar in toxicity to petroleum products. The crude and hydrotreated crude shale oils are more toxic than their derived products; however, hydrotreated shale oil is less toxic than the crude. Data from Gehrs (1980), Strand and Vaughan (1981) and States et al. (1982) indicate that raw distillates and fuel blends of coal liquids are more than two orders of magnitude more toxic than comparable petroleum products. Hydrotreatment of coal liquids will reduce this toxicity.

Acute toxicity of aliphatic alcohols to aquatic organisms will increase with ascending molecular weight as shown in Figure 3. Anderson (1944), Gillette, Miller, and Redman (1952), and Thirumurthi and Gloyna (1965) all noted these trends. Detailed results from their studies are given in Appendix C.

FIGURE 2. Toxicity of Synfuels

FIGURE 3. Acute Toxicity Alcohols

Fish placed in toxic concentrations of ethanol display restlessness, increased respiratory rate, loss of equilibrium, and narcosis. When transferred to water containing no toxicant, they recover readily (Liebmann 1960) which suggests that the toxic effects are reversible. At concentrations up to 10^3 mg/l, methanol does not inhibit oxygen use by sewage micro-organisms (Hermann 1959). Allyl alcohol is not toxic to saprophytic micro-organisms up to 125 mg/l, but 150 mg/l causes a temporary inhibition of microbial growth. Kharitonova and Yakolic (1968) found that nitrifying micro-organisms are not affected by 100 ppm allyl alcohol, and after 4 to 5 days of acclimation, were able to oxidize 125 mg/l.

Longer-term impacts (chronic effects) would largely be attributed to the less soluble components of the oils, particularly higher molecular weight hydrocarbons (DOE 1981). Significant quantities of spilled product will mix with gravel and sediments of the water body and pose a long-term hazard as toxic components are leached. Polynuclear aromatics (PNAs) associated with fine sediments are not likely to solubilize in quantities to become acutely lethal, but may be accumulated and concentrated by organisms.

Unfortunately, little or no comparative data regarding longer term effects are available. What is available is limited to the studies of States et al. (1982) and Cowser (1981b), which again suggest that coal liquids (SRC-II, H-coal) are significantly more toxic than petroleum (No. 2, No. 6 fuel oils) over chronic exposure regimes (Appendix B).

Land and Terrestrial Ecology

The impact of oils spilled on soils depends on soil texture (infiltration characteristics), time since the spill occurred, and the rate of physical, chemical, and biological degradation of hydrocarbons (DOE 1981). In comparative degradation studies, Gehrs et al. (1981) determined that the number of oil-degrading organisms increased significantly in soils following addition of a petroleum crude or a shale oil. However, coal oil degrading micro-organisms were undetectable both at the start of the experiment and three months later. The U.S. Department of Energy (1981) suggests that phenolic compounds present in coal liquids are acutely toxic to micro-organisms, and that they may eradicate microbial communities that aid in the degradation of heavier hydrocarbons. Accordingly, there is the implication that coal liquids will remain in the soil for longer periods of time than petroleum or shale liquids. When phenolics decrease to concentrations at which hydrocarbon metabolizing micro-organisms survive, biodegradation of spilled coal liquids will begin. However, the time frame for this process depends upon several factors, including magnitude of the spill, ambient temperatures, rates of leaching, and site-specific conditions. Lysimeter studies conducted by Cline, Rickard, and Thiede (1982) confirm that coal liquids do not readily degrade (Appendix D). Although germination of barley occurred during a second growing season following amendment of soils with coal liquids (SRC-II), grain production was still significantly suppressed at all test concentrations (0.15, 1.48 and 14.84 l/m²), suggesting a relatively slow change in toxicological properties due to microbiotic and other degradative processes.

BIOMEDICAL EFFECTS

Spills of synfuel materials may affect human populations in a number of ways. A synfuel or some of its constituents may enter drinking water (directly or indirectly) or the food chain. People may be exposed by skin contact or by inhalation of vapors or aerosols either at the time of the spill or during subsequent cleanup operations. People also may be exposed to synfuels as a result of fire accompanying a spill. It is, therefore, desirable to estimate the impacts of spills on humans to determine the necessity for cleanup measures

and the appropriate precautions to be used. It must be recognized, however, that the toxicological data base for many of the materials likely to be encountered is limited, since the synfuel technologies are not fully developed. Products refined from synfuels will be considered as comparable in toxicity to similar products prepared from petroleum crudes unless the data indicate otherwise. This same view is expressed by Leggett et al. (1980). Products derived from the same source (i.e., coal or shale oil) but through different processes are grouped according to boiling ranges for purposes of toxicity, unless information is available to indicate that larger differences occur. When chemical composition is available, but actual toxicity data are not, the composition is examined to aid in evaluating the potential toxicity. Generally, the potential toxicity of a synfuel is considered relative to that for petroleum crude or products derived from petroleum. Methanol and ethanol were not included in this section because they are items of commerce whose spillage and biomedical impacts are well documented.

Toxicological and biomedical data on synfuels are limited. A summary of available data (Table 16) shows that petroleum crudes (used as a reference material) have little or no in vitro mutagenic activity (microbial or cell transformation) and a very low degree of acute toxicity in animals. However, petroleum crude is capable of producing a carcinogenic response (although the activity is rather low).

Crude shale oil is both more mutagenic and carcinogenic than petroleum crude and exhibits teratological activity. Hydrotreatment of crude shale oil results in almost complete abolition of mutagenic activity. However, a very low level of carcinogenic activity seems to remain. Jet fuel and diesel marine fuel prepared from shale oil do not appear to be carcinogenic but they are relatively potent skin irritants. Jet fuel and diesel marine fuel prepared from petroleum crude also did not exhibit carcinogenic activity but they, too, were potent skin irritants.

The high boiling point materials (heavier fractions) derived from direct coal liquefaction are both more mutagenic and carcinogenic than petroleum crude and possess teratogenic activity. Hydrotreatment of the fuel blend (mixture of middle distillate and heavy distillate) from SRC-II reduced the mutagenic

TABLE 16. Toxicity of Petroleum Crudes, Shale Oil, and Other Oils and Solvents

Material	Acute Toxicity LD ₅₀ (g/kg)	Microbial Mutagenicity*	Mammalian Cell Trans- formation*	Carcino- genicity*	Skin Irritation*	Teratology*	References
Petroleum Crude (Wilmington and Recluse)	>12	0	1 (Very Low)	1			Pacific Northwest Laboratory 1979
Shale Oil, Raw	9	1	1	2		1	Cowser 1981a and Pacific Northwest Laboratory 1979
Shale Oil, Hydrotreated		0		1			
JP5 - Shale Oil				0	1		
JP8 - Shale Oil				0	1		
DFM - Shale Oil				0	1		
							Cowser 1981a
JP5 - Petroleum				0	1		
JP8 - Petroleum				0	1		
DFM - Petroleum				0	1		
SRC-I							
Light Oil	3	0	0			0	
Wash Solvent	0.5	0	0			0	
Process Solvent	3	1	1			1	Pacific Northwest Laboratory 1981
Product		1					
Coke							
SRC-II							
Naphtha	3	0	0	0		0	
Middle Distillate	3	0	0			0	
Heavy Distillate	3	1	1	4		1	Pacific Northwest Laboratory 1979
Fuel Blend (2.9:1, MD:HD)		1	1				
Fuel Blend, Hydrotreated, Low		1					
Fuel Blend, Hydrotreated, High		0					
Heavy Gas Oil		1		3-4			
EDS							
Naphtha		0	0	0			
Heavy Gas Oil		1	3				
Vacuum Gas Oil		1	3				Calkins et al. 1982
Residue		1	3				
Solvent		1	3				

* Scale of 0 to 4

activity. In contrast, the lower boiling point fractions are generally devoid of mutagenic and carcinogenic activity and do not exhibit teratologic activity.

Indirect coal liquefaction processes are expected to produce a slate of products with less biological activity than those produced by direct liquefaction. Unfortunately, biological data for these materials are not available. The Sasol plant in South Africa has been the only major user of indirect liquefaction technology and has not produced any toxicological data. An examination of the product slate from Sasol indicates that reformed liquid products probably have little biological activity. However, there are a number of by-products, such as asphalt and creosote, which might contain biologically active materials. More information on these materials are needed to make an adequate evaluation of their potential hazards.

The following general conclusions can be made from Table 16:

- high boiling point materials derived from direct coal liquefaction are more biologically active (as measured by mutagenesis, teratogenesis, and carcinogenesis) than petroleum crudes
 - crude shale oil is more biologically active than petroleum crudes but less active than high boiling point coal liquids
 - hydrotreatment of high boiling coal liquids and shale oil reduces, but does not eliminate, their biological activity
 - lower boiling point (550°F) materials derived from direct coal liquefaction appear to possess little mutagenic, teratogenic, or carcinogenic activity, but their acute toxicities are higher than that of petroleum crude or shale oil. The volatile components of the lighter distillates may produce an acute reaction if inhaled
 - refining of synthetic crudes may reduce the mutagenic, teratogenic, and carcinogenic activity to that of refined petroleum products.
- The investigations of JP-5 and DFM prepared from shale oil appear to substantiate this when mutagenesis and carcinogenesis are evaluated.

4.0 ASSESSMENT OF EXISTING SPILL CLEANUP TECHNOLOGIES FOR OIL SPILLS

As readily available sources of petroleum decline, the development and production of synthetic fuels will become more important, necessitating a review of containment and cleanup technologies currently available for the removal of potential spills occurring during the transportation of fuels to their final marketplace. The economics and safety of handling synfuels (two parameters not yet well defined) will determine if synfuels are upgraded onsite or off-site. Consequently, the exact breakdown of synthetic liquids spilled can only be estimated (see Chapter 2). Because synfuels are potentially more toxic than their counterparts in the petroleum industry, the safe and efficient cleanup of synfuel spills is very important. This chapter examines cleanup technologies currently available based on the environment in which a pollutant is released. Since the majority of data currently available on containment and control of spills deal with petroleum spills, this review will assume that petroleum spill cleanup technologies will be used for mitigation of synthetic fuel spills.

This chapter has been divided into three sections: 1) general response actions for fuel spills; 2) classification of containment and cleanup technologies by spill location; and 3) a discussion of available containment and cleanup technologies.

RESPONSE PLANS FOR FUEL SPILLS

To evaluate spill containment and cleanup technologies, one must review contingency plans and methods of response. Such a review helps aid in understanding how best to deploy spill mitigation technologies. The first section of this chapter discusses the technologies that follow directly from spill response guidelines and contingency plans.

Contingency planning provides an orderly method by which to respond to oil spills. Without contingency plans, disorderly responses to spills would be inevitable, resulting in two avenues of increased impact to the environment. First, disorganization lengthens the time a spill will be in contact with the

environment. Second, if inadequate preliminary planning exists, it is possible that ineffective containment technologies will be employed. For these reasons, contingency planning is important.

Contingency planning takes on added significance in the case of synfuel spills due to the potentially increased toxicity and solubility of these liquids in comparison with comparable petroleum products. A response team should be available and able to respond quickly and effectively to a spill.

Although an existing federal response network should be used to manage synfuel spill mitigation operations, modifications to the network will be necessary to account for the potentially high toxicity of synfuels. In some cases, it may not be advisable to use local personnel because of health and safety reasons; instead, as with hazardous chemical spills, highly trained response teams should be brought to the spill site. In this case, locally trained personnel could serve support roles in which they do not come into direct contact with the syncrude.

In almost all situations, the on-scene coordinator (OSC) will have to make decisions about which containment and cleanup options to use once he arrives on-site. Usually, these decisions are made through the use of a flow chart (Figure 4), which is based on a similar flow schematic by Huibregtse et al. (1977). The immediate concern for the OSC will usually be containment of the spill, except when a spill poses an immediate threat to the safety of the local population. In these emergency situations, spills may be diluted and dispersed in the local environment to minimize the possibility of loss of human life, in spite of the probable environmental damage this action may cause.

The flow chart shown in Figure 4 lists several options for response actions. The most acceptable response, both environmentally and economically, would be to reclaim and recycle spilled materials. If this option cannot be used the following technologies are available, in order of preference:

FIGURE 4. Decision Flow Chart

onsite treatment, remote treatment, containment and fixation, and dispersion. When the spill is large in volume, it is often economically preferable to treat onsite because of the transportation costs associated with remote treatment. Fixation may be accomplished by chemical and physical means, depending on the type of material spilled. Dilution and dispersion are viable mitigation techniques if the diluted material has been determined not to be hazardous. For example, dilution and dispersion are very effective in minimizing the impacts of acid and caustic spills.

As seen in Figure 4, numerous decision points lead to the final choice of which treatment technologies will be used. Normally, the OSC has access to technical data bases such as the Oil and Hazardous Materials-Technical Assistance Data System (OHM-TADS) and the U.S. Coast Guards' CHRIS manual to help them in making such decisions. In general, the OSC will act so as to minimize the danger to human health and then to the environment when making decisions associated with spillage of hazardous materials. Often, these two concerns--human health and environmental damage--are jointly affected and the OSC must use his experience when making a decision on which containment and treatment technologies to use.

CLASSIFICATION OF SPILL TECHNOLOGIES BY SPILL LOCATION

Spill locations are assumed to cover five categories: surface waters, ground waters, ice and snow, surface soils, and subsoils. These categories encompass most areas in which materials are spilled. Surface water spills have been further broken down into three areas associated with the density and solubility of spilled materials: floatable, soluble or miscible, and sinkable. Containment, removal, and storage technologies are reviewed for both large and small spills for the locations listed above.

Containment, removal, and storage spill-response technologies are presented in Tables 17 and 18 by spill location and size. Inputs for these tables were obtained from Fussell et al. (1981) and Huibregtse et al. (1977). The selection of a containment and cleanup technologies used (Tables 17 and 18) will depend on the hazards of the spilled synfuels, chemical compatibility with equipment used, and weather conditions. Mitigation of larger spills will

TABLE 17. Summary of Spill-Response Technologies for Spills on Water

SPILL LOCATION	LARGE SPILLS AND INITIAL OPERATIONS			SMALL SPILLS AND POLISHING OPERATIONS		
	CONTAINMENT	REMOVAL	STORAGE	CONTAINMENT	REMOVAL	STORAGE
FLOATING	DAM	NOZZLES (SUCTION) SPRAY HERDING METHODS	TANKS, SEPARATORS, TRANSPORT VEHICLES	BALES		NORMALLY SPILL VOLUME IS TOO SMALL FOR STORAGE TO CONSIST OF ANYTHING BUT PLASTIC SHEETS LAID ON NEARBY LAND
DITCHES				BARRIERS AND WEIRS PNEUMATIC BARRIER	SORBENT SKIMMER AND FILTER	
STREAMS	BARRIER AND WEIR PNEUMATIC BARRIER	NOZZLES (SUCTION OR SKIMMERS		SORBENT AND NET OR BALES		
CANALS AND SLOW RIVERS (≤ 1.2 m/s)	BOOMS STRAW BARRIER	NOZZLES (SUCTION OR SKIMMERS		BOOMS	SORBENT SKIMMER AND FILTER	
FAST RIVERS (> 1.2 m/s)	BOOMS	SKIMMERS SORBENTS & NOZZLES	SORBENT AND NOZZLES			
	SORBENT AND NET BARRIER		SORBENT AND NET BARRIERS			
LAKES	BOOM AND SWEEP	SKIMMER	TANKS, SEPARATORS, TRANSPORT	BOOM OR SWEEP OIL HERDERS	SORBENT AND SWEEP SKIMMERS AND FILTERS	
	COMBUSTION					
ESTUARIES	BOOM	SKIMMER				
	DISPERSE (IF PERMITTED)			DISPERSE (IF PERMITTED)		
SOLUABLE OR MISCIBLE	SEALED BOOMS DIVERSION OF FLOW	NOZZLES (SUCTION)	TANKS, SEPARATORS TRANSPORT VEHICLES	SEALED BOOMS DIVERSION OF FLOW GELLING AGENTS	NOZZLES (SUCTION)	TANKS, SEPARATORS, TRANSPORT VEHICLES
DITCHES AND STREAMS						
LARGER WATER BODIES	DISPERSE (IF PERMITTED)			DISPERSE (IF PERMITTED)		
SINKING IN WATER	NATURAL AND ARTIFICIAL EXCAVATIONS DIKES DREDGING		TANKS, SEPARATORS, TRANSPORT VEHICLES	NATURAL AND ARTIFICIAL EXCAVATIONS DIKES DREDGING		TANKS, SEPARATORS, TRANSPORT VEHICLES
ALL WATERBODIES						
GROUNDWATER	"DEPRESSION" WELLS, TRENCHES	PUMPING WASHING FLOODING	SEPARATORS PORTABLE TANKS AND DRUMS	"DEPRESSION" WELLS TRENCHES	PUMPING	SEPARATORS PORTABLE TANKS
ICE AND SNOW	ICE AND SNOW BARRIERS BOOM	EXCAVATION SKIMMERS SORBENTS SEPARATORS	SEALED PIT SEPARATORS	ICE AND SNOW BARRIERS	SORBENTS	SEALED PITS
		COMBUSTION				

TABLE 18. Spill-Response Methods for Spills on Land

SPILL LOCATION	LARGE SPILLS			SMALL SPILLS AND POLISHING OPERATIONS		
	CONTAINMENT	REMOVAL	STORAGE	CONTAINMENT	REMOVAL	STORAGE
SUBSOILS	DITCHES EXCAVATION EXCAVATION AND WASHING DISK AND ENHANCE BIOLOGICAL DEGREDAION		PLASTIC SHEETS LINED PITS SEPARATORS	EXCAVATION AND WASHING BIOLOGICAL DEGREDAION		STORE ON PLASTIC SHEETS AND MOVE TO REMOVAL SITE
SURFACE SOILS	DAMS DIKES SORBENTS (SAND, SOIL) FOAMED CONCRETE FOAMED POLYURETHANE	NOZZLES (SUCTION) EXCAVATION SORBENTS ORGANIC FELTS STRAW DILUTION (IF PERMITTED)	PLASTIC SHEETS LINED PITS PORTABLE TANKS, DRUMS	SORBENTS (SAND, SOIL) FOAMED CONCRETE FOAMED POLYURETHANE	EXCAVATION STRAW SORBENTS	PLASTIC SHEETS PORTABLE TANKS AND DRUMS LINED PITS
	COMBUSTION BIOLOGICAL DEGREDAION			BIOLOGICAL DEGREDAION		

normally require the use of more heavy equipment and less sophisticated technologies due to the large volumes of materials handled. On the other hand, smaller spills may be contained and cleaned up using smaller equipment and more sophisticated technologies for spill disposal because of the smaller volumes handled. The following paragraphs discuss the data in Tables 17 and 18.

Surface Water Spills

Containment of spills floating on surface waters normally depends on the size of the water body and whether or not the water is moving at an appreciable velocity (~ 1.2 m/s). Dams, barriers, and booms are commonly used for containment of spills in ditches, streams, canals and slow moving rivers. Due to the smaller areas under consideration, barriers and booms can often be deployed by hand and do not require the use of heavy equipment. For fast moving rivers, lakes and estuaries, containment options are booms, barriers, and sorbents. The faster the river the stronger the boom needed and the deeper its skirts must be. Net barriers with sorbent are another option to contain spills on fast flowing rivers. Combustion can be used to mitigate spills on lakes, although it is not normally recommended because of logistical problems.

Spill removal techniques are standard for surface water spills and depend mainly on where the spill occurs. For ditches, streams, canals and slow rivers, suction nozzles are usually used for spill removal. Occasionally, spray herding methods and skimmers are used. Removal of spilled materials from fast rivers, lakes, and estuaries is normally completed using skimmers and, less often, sorbents. Sorbents tend to be more applicable for smaller spills.

Storage facilities for the recovered spilled materials are typically tanks, separators and transport vehicles. Plastic sheets can be used for temporary storage of recovered materials, particularly if the spill is relatively small in volume. In all cases, the storage facilities are normally considered to be temporary for spilled materials until a decision on a final disposal method has been made.

Spills on water of soluble, miscible, or sinkable materials are much more difficult to contain than surface floating spills. If the water body on which

the spill occurs is small enough, diversion dikes and sealed booms can be used for containment. If a material is released to a larger water body, the spilled materials will often be diluted before any containment techniques can be employed. In these latter situations, it is especially important to minimize the amount of materials reaching the water body and prevent any further releases, since no effective containment methods exist once the material reaches the water.

Once contained, the spilled material can be removed by nozzles (suction), excavation, and dredging. Nozzles are used for liquids removal, and excavation is used for removing contaminants from dikes and containment basins. Dredging is used for removing sunken materials; however, the high cost of this technique normally limits its use to extremely hazardous materials such as PCBs. After the contained materials are removed, they are stored in tanks, separators, and transport vehicles pending final disposition.

Ground-Water Spills

Spills of materials reaching the ground water can often be contained by employing either depression wells and the second, construction of trenches. "Depression" wells are often used where the ground water is far from the surface and involves construction of a well down to the ground-water level downstream from the spill location. By pumping an adequate amount of water from the well, the local ground water can be lowered, allowing oil to accumulate in the depressed ground-water area. Oil flows by gravity to this depressed ground-water area where it is collected and removed. Where ground waters are near the soil surface, trenches are constructed and booms are placed across the ditch to contain spilled materials. Contained materials can then be removed either by pumping, washing or flooding. Pumping is normally the preferred removal option (Fussell et al. 1981). Washing and flooding are discussed in later sections. As with surface water spills, storage facilities for ground-water spills will consist of portable tanks, separators, and transport vehicles. Separators are, in addition to being effective storage facilities, often required in spill removal situations to separate water from the spilled material.

Spills on Ice and Snow

Spills are contained on ice and snow by ice and snow barriers and booms. Besides being effective barriers, ice and snow barriers also act as sorbents, binding up spilled materials. Once bound, the contaminated ice and snow can be removed and stored in lined pits, where they are allowed to melt. At that point the materials can be removed with conventional skimmers, nozzles, and sorbents. Materials gathered by booms are usually removed by nozzles or skimmers for final disposal.

Surface Soil Spills

Spills on surface soils may be contained by dams, dikes, sorbents, foamed concrete, and foamed polyurethane. Dams and dikes are typically more effective on impervious soils. Sorbents and foamed materials are effective in containing small spills on porous soils but become costly if used on larger spills.

Spills can be removed from surface soils by using nozzles (suction), excavation, sorbents, and possibly dilution. The use of sorbents and organic felts, the more sophisticated techniques, is usually reserved for smaller spills because of cost and logistics. If the contaminants are biodegradable, often the spill materials are disked into the ground, fed nutrients and allowed to degrade. The petroleum industry refers to this method as "landfarming." Landfarming is not effective at highly toxic or high-volume spills, however, as the material could overwhelm local microbial populations. Combustion, another spill removal option, is normally not used because of environmental restrictions.

Materials gathered during containment and removal operations can be stored in lined pits, portable tanks and drums, and on plastic sheets. Selection of a storage facility is usually based on availability. Hazardous materials must be stored in an approved storage device.

Subsurface Soil Spills

It is usually not possible to contain spills in subsoils. However, the degree of contamination can be minimized by eliminating the source of spilled

materials. If the contaminated zone lies above an impervious zone (e.g., clay), lateral movement of shallow spill zones can be stopped by digging trenches around the spill site. Care should be taken to avoid penetrating the impervious zone or else the spill material may move downward into the ground water.

Removal techniques for subsurface soil spills include excavation, excavation and extraction, and in situ biological degradation. Biological degradation is not a true removal technique (see earlier discussion in surface spills section), but often it is very effective in ultimately restoring the spill site to pre-spill conditions. Excavation will probably be used only if the spills are small or if the material spilled is considered hazardous. If the site can be surrounded by trenches, sumps will be spaced through the trench(s) and spilled material collected at these points. Artificial flooding might be effective in moving contaminants more quickly to sump areas. Pumps would then be used to remove collected materials from the sumps.

Storage facilities for materials collected during excavation, excavation and extraction, and pumping operations will include portable tanks and drums, separators, lined pits and plastic sheets. The choice of a storage facility will depend on whether or not the removed material is a liquid or a solid. When pumping operations are used, separators may be required, because surface and subsurface waters will probably be collected. Lined pits and plastic sheets will be used to store solid material only until the removed material finally can be disposed of.

CONTAINMENT, REMOVAL, AND STORAGE EQUIPMENT FOR MAJOR SPILLS

The following text describes, in detail, the major containment, removal, and storage options available to alleviate oil spills on land and water. Where possible, advantages and disadvantages of the equipment described are given. If the equipment can be used to combat both land and water spills, possible peculiarities concerning these two applications are addressed. The techniques discussed in this chapter are identified in Table 19 along with their major area(s) of application (containment, removal, and/or storage).

TABLE 19. Major Spill Mitigation Techniques Reviewed

<u>Technique</u>	<u>Application(s)</u>
Barriers and Weirs	Containment, Removal
Booms	Containment
Dikes and Excavation	Containment, Removal
Nozzles (suction)	Removal
Separators	Removal, Storage
Skimmers	Removal
Sorbents and Gellants	Containment, Removal

Barriers and Wiers

Earthen dams, spade dams, wooden plates, straw bales, nets, and pneumatic and wire fencing barriers are mostly used to contain surface spills to waterways. Occasionally, they are used to stop movements of surface spills to land and snow and ice (Fussell et al. 1981; Huibregtse et al. 1977). Wiers are used in conjunction with certain types of barriers, though not with all barriers. Barriers and wiers offer excellent capacity for collecting and containing spilled materials and do not clog easily. They are disadvantageous in that they can be used only on small, shallow, and smooth waters.

The most common barriers are dams made of earth, metal, wood, and straw (Figures 5, 6, and 7). Dams act as gravity separators because the subsurface outlets that run through the base of the dam allow water to continue flowing past the dam. Floating contaminants are removed from the surface of the water by nozzles, skimmers, sorbents, or other available materials. Spade and wooden dams work the same way as earthen dams, except that the dam itself is constructed differently. Spade dams consist of a metal spade hammered into a ditch that seals the sides of the ditch but allows water to pass beneath it. Wooden dams are used on larger streams and consist of planks and boards placed against a cross stream matrix, which extends a finite distance into the stream. Water passes the planks, but the floating spill is trapped behind the wooden barrier until it can be removed. Straw bale barriers are constructed exactly the same as wooden plank dams, except that the straw is used in place of wooden planks. Straw bale barriers offer the additional advantage of being sorbent to spilled materials. After the bales are saturated they can be removed and burned.

FIGURE 5. Improved Spade Dam with Drainage Pipes

FIGURE 6. Wooden Plate Dam

FIGURE 7. Straw Bale Barrier

Net and wire barriers consist of sections of net or wire that are stretched across a stream or small river and anchored to the river bottom and shorelines. They are normally used in conjunction with sorbent materials. Often, several nets are used in tandem. Net and wire barriers have the advantage over other barriers in that they do not impede stream flow. Often, weirs are placed downstream of net and wire barriers to produce a quiescent zone that minimizes drag on these relatively low-strength barriers.

Pneumatic barriers employing subsurface air diffusers are available for containing spilled materials; however, they are rarely used because of operational difficulties. Diffusers and compressors for these systems are often difficult to obtain, and any significant wind or current will render this technique ineffective. Furthermore, the technique is effectively limited to shallow waters because of compressor limitations.

Barriers are often used to contain spills on ice and snow (Allen 1979) in areas where the spill has reached subsurface waters. Drilling holes through

the ice will cause local upwelling to the surface, where surface barriers can be effectively placed to contain upwelled spilled materials (Figure 8). Through-ice barriers and ice slots (Figure 9) may be employed to contain a moving slick. Removal techniques previously discussed are then used to recover the oil.

Booms

Booms are used to contain spilled materials on all types of waters and can be either fixed in place (for use on streams and rivers) or made mobile (for use on lakes and oceans). Typical floating containment booms are shown in Figures 10 and 11. Any material that can be made into a barrier is a likely candidate for a boom. Sealed booms are available for small spills of soluble and miscible materials. Booms typically have a fence or skirt extending above and below the water's surface; the skirt forms the containment section. Tension on support chains or cables can be increased or decreased to give the skirt members the proper angle to the contaminant stream to maximize containment. The effectiveness of a boom is limited by waves, winds and currents. Most booms fail because, as the spill material is contained, the current carries portions of the material under the boom. A series of booms may have to be deployed to effectively contain most of the spilled material. Booms are advantageous because they come in many varieties and they are effective on large spills. Disadvantages may be imposed by poor weather conditions. Wave action greater than 2 to 4 ft and currents greater than 0.7 knots, for example, tend to render booms ineffective (Huibregtse et al. 1977). Also, it is sometimes difficult to obtain the proper boom and deployment systems at a particular spill site.

The use of booms on rivers presents an especially difficult situation. Most rivers will not accommodate boom placement from bank to bank and perpendicular to flow, because the force of the flowing water can break the boom up. As a result, booms must be deployed at angles to the direction of river flow. The angle is determined by calculating the force of the river and the strength of the particular boom used (Fussell et al. 1981). One end of the boom is either anchored to the bank, if the distance is short enough, or to the river bottom; the other end is secured to the opposite bank. The boom

FIGURE 8. Drilling Through Ice Into Subsurface Pools

FIGURE 9. Ice Slots and Through-Ice Barriers

FIGURE 10. Typical Oil Containment Booms

FIGURE 11. Typical Deployment of Oil Booms and Skimmer

moves the spill toward the shore, where it can be collected and removed by skimmers and absorbents. A number of booms are often deployed in series, because some of the spilled materials are carried under the boom skirts by the current. If a river is wide enough, floating booms may be used.

Booms are sometimes used to contain oil spills in icy waters, too, although the success of the technique tends to be less. If ice flows accumulate inside the boom, the ice may stress the sides or even sink the boom. Most conventional containment booms will break apart under the severe loading of ice and current. Air floatation booms can be damaged by sharp pieces of ice, and anchor points will frequently fail, particularly if large rocks or well-rooted trees are not present. If the containment boom fails for any of these reasons, oil and ice will pass under or over the boom.

If light ice flows are present, one possible containment strategy is to use two booms. A heavy-duty, porous boom would first be used to separate and divert the ice within a flow; a second, nonporous boom would be deployed downstream to divert the ice-free oil to a suitable, quiet-water recovery site.

Tsang and Vanderkooy (1979) have researched the feasibility of developing a flexible boom similar to the glance booms used by the timber industry (Figure 12). The boom would be constructed of a sturdy body and a number of short fins or rudders. When the fins are gradually closed (winched towards shore), the force of the current on the fins would bring the boom gradually into the flow. Should a large ice pack strike the boom, the boom would yield until the ice pack slides off and would then redeploy itself. Openings are provided in the boom so that the oil slick can pass through it and then be recovered by conventional methods.

Dikes and Excavation

Dikes and excavation are used for containing and removing surface and subsurface spills. Dikes are made from sandbags or excavated materials. Excavation, which can be both a containment and removal technique, is usually completed using heavy equipment such as a bulldozers or earth movers. The objective of using these technologies is to minimize the spread of spilled materials by removing the contaminated soils before further spreading occurs.

FIGURE 12. Glance Boom

In general, excavation should be used only when danger to drinking water supplies exists (Fussell et al. 1981). Except for soils contaminated by hazardous wastes, the excavated soils are encouraged to support biological activity (Mathers 1980), which breaks down the spilled materials. Excavated soils that contain sufficient levels of hazardous wastes will have to be treated or hauled to a secure landfill. Dikes are advantageous because they can be made from materials available at the site of the spill, and excavation is advantageous because it requires only common construction equipment. Excavation is disadvantageous because it disrupts the natural soil (in particular, it increases the soils' permeability). Care must be taken during excavations to ensure that impermeable soil layers are not penetrated, so that the spill remains confined.

Nozzles (Suction Pumps)

Nozzles or suction pumps are used to remove contained liquid spill materials. Selection of the proper pump is often difficult and should be based on flow requirements, total dynamic head, suction conditions, viscosity, solids content, power source, mobility requirements, corrosivity, and whether or not explosives and flammables will be pumped (Huibregtse et al. 1977). Huibregtse et al. (1977) has described in detail the procedure for selecting the proper pump size and the reader is referred to this report for more information on the subject.

Separators

Recovered spill materials often contain significant amounts of water when they are removed from a spill site. The water can be separated from the contaminants by gravity separation. Temporary separators can be fashioned from road and rail tankcars, rigid or flexible tanks, lined pits, or drums, as long as a residence time of 20 min can be maintained (Fussell et al. 1981). Often, these separators can be used in series to greatly improve discharged water quality. A variety of chemical additives is available for materials that do not separate well to enhance separation. In most cases, decanted water should be filtered through a sorbent medium before being discharged back to the environment.

Skimmers

Skimmers are used to pick up floating materials with as little water as possible. A wide variety of skimmers is currently available. According to Fussell et al. (1981), the factors that should be evaluated prior to selecting a skimmer include capacity, size, weight, oil-to-water recovery ratio, effectiveness on different materials, behavior in choppy waves and in the presence of debris, maintenance needed, ease of operation, manpower required, auxiliary equipment needed, and availability and cost. For emergency use, it is best to use portable and easily operated skimmers.

On large waterbodies such as lakes and estuaries, moving bucket (Figure 13) and submersion belt (Figure 14) skimmers are the most commonly used. These

FIGURE 13. Moving Bucket Skimmer

FIGURE 14. Submersion Belt Skimmer

two skimmers are usually used in conjunction with containment booms. On smaller water bodies, the most popular skimmers are suction, paddle-induced vortex, barrel weir, floating weir, and the cyclone separator skimmers. Both the paddle-induced vortex (Figure 15) and the cyclone separator (Figure 16) use angular acceleration to concentrate the contaminants in a zone from which the contaminants are then pumped to appropriate storage facilities.

Suction head skimmers work in much the same manner as vacuum cleaners. When held above the spilled material, the suction head draws the contaminant into the nozzle and back to storage facilities. Weir skimmers (Figures 17 and 18) are normally used in small, slow flowing streams. In both cases, the weir acts to provide a quiescent settling zone to enhance gravity separation. Localized pumping creates a depression in which the spilled material collects and is removed. Sorption skimmers (Figure 19) are used to collect oil spills on water. Typically, the sorbent material is an oleophilic material, which preferentially absorbs oil over water (Shaw and Dorrlor 1977). The sorbed materials are then removed by scrapers or squeeze rollers, collected, and pumped to storage facilities.

FIGURE 15. Paddle-Induced Vortex

FIGURE 16. Cyclone Separator

If large spills are involved, it is often better to use many small skimmers as opposed to a few large skimmers. This is because the smaller skimmers can be placed more strategically than larger skimmers.

Sorbents and Gellants

Sorbents and gellants absorb contaminants from relatively small spills. The sorbents may be rigid and flexible organic foams, organic felts, vegetable fibers, strips of plastic film, netting, or clay granules (Fussell et al. 1981). Gelling agents are composed of compounds, each directed at solidifying a class or range of compounds (Michalovic et al. 1976). When selecting a sorbent or gellant one should consider the material's capacity, retention effectiveness, cost, manageability, and disposal. Generally, sorbents are preferable to gellants, which have several disadvantages. First, gellants are hard to obtain. Second, the gelled materials usually cannot be removed by pumping and must be hauled to an appropriate disposal site. Third, gellants

FIGURE 17. Barrel Weir Skimmer (Static Type)

FIGURE 18. Floating Weir Skimmer

DRUM SKIMMER

DISC SKIMMER

BELT SKIMMER

ROPE SKIMMER

FIGURE 19. Sorption Skimmers

are more costly than equally effective sorbents. Bahloul et al. (1979) has developed a gellant, that, once recovered, can be regenerated and used again. However, he advocates that the gellant be used only on small spills due to the high cost of the gellant. Fussell et al. (1981) also recommend using sorbents over gellants whenever possible.

Many sorbents are marketed and generally available. However, in emergency situations, straw, sawdust, wood chips and some peats can be used as sorbents. These natural substances are not as effective as synthetic materials, however, because natural materials do not preferentially absorb substances spilled on water. Thus, their capacity to remove spilled materials is inferior.

Dispersants

Many commercial dispersants are available for dispersion of spilled materials, particularly for hydrocarbons. Toxicity of dispersants, less of a factor now than it has been in the past, restricts the applications of these materials to large waterbodies and usually only after the exhaustion of alternative options.

5.0 ASSESSMENT OF CLEANUP TECHNOLOGIES FOR SYNFUEL SPILLS

A major objective of this study was to determine potential gaps in spill mitigation technologies and determine data needed in order to close these technology gaps. The previous chapter outlined existing spill mitigation technologies for conventional hydrocarbon spills. This chapter outlines those technologies likely to be used to mitigate synfuel spills, identifies potential technology gaps and outlines areas where research may be needed in order to close technology gaps.

In summary, technologies currently available will be used to contain and cleanup potential synthetic fuel spills. Modifications in cleanup equipment, which includes booms, barriers, skimmers and sorbents, may be necessary in order to overcome any differences between conventional oil spills and synthetic fuel spills. Differences may include:

- Differences in physical and chemical properties between conventional oils and synfuels.
- Differences in the effects of chemical constituents on the materials of fabrication used to construct cleanup and containment equipment.
- Differences in toxicity between conventional oils and synfuels which may require greater worker protection through improvements in equipment design.

One of the major physical differences between synfuels and conventional petroleum products is density. Many of the synfuels will have considerably higher densities than their conventional crude oil counterparts. When some of the heavier synfuel products are spilled onto water the possibility that these materials may sink is greater than that for conventional products. Once these materials sink, existing surface water mitigation techniques would become ineffective. Dredging or vacuuming of the sediments would be possible; however, the impact of disturbing the sediments, cost of these types of operations, and the availability of such equipment (often low) near a spill site make this option unlikely. If the densities of oils and syncrudes are

approximately the same, and the synfuels are immiscible in water, conventional oil spill mitigation equipment should be adequate to remove spillage from surface water spills.

Chemically, many of the synfuels are similar to conventional hydrocarbons; however, they often contain a relatively higher percentage of unsaturated hydrocarbons along with nitrogen and oxygen containing compounds. Because synfuels contain higher percentages of these compounds, they may be more reactive than their petroleum counterparts and may be incompatible with materials used in constructing conventional containment and cleanup equipment. *However, no extensive research has been conducted on the compatibility of materials with synfuels and future research should address this area.*

Increased toxicity of the synfuels in comparison to their petroleum counterparts, particularly the direct coal liquefaction products, will require increased awareness of safety features in equipment design, although the extent to which this will be necessary is unclear. It is possible to reduce the toxicity of the heavy fractions from direct coal liquefaction processes through process changes such as hydrotreating. Thus, it may be possible to reduce toxicity to sufficient levels, through process changes, such that equipment modification and revisions to operating instructions are not necessary. Until more complete toxicological studies are completed decisions on process changes cannot be made. *If the toxicity of synfuels is not reduced, then specially equipped and trained personnel may be required to mitigate the effects of synfuel spills.* Training would involve teaching techniques and procedures which minimize inhalation and dermal contact.

The following paragraphs discuss problems associated with particular synfuel sources which may require modifications to conventional spill mitigation equipment or usage procedures. Synfuels will be discussed according to one of three categories; 1) coal liquids, 2) shale oil and tar sand liquids, and 3) alcohols. Shale oil and tar sand liquids were combined into a single category because spill cleanup technologies for these fuels should be similar based on their physical and chemical properties.

COAL LIQUIDS

Coal liquids are defined as products or product intermediaries from direct or indirect coal liquefaction facilities. Generally indirect coal liquefaction products will be physically and chemically similar to petroleum products and are not expected to have the higher toxicity problems that exist with some of the direct coal liquefaction products. This is because indirect coal liquefaction processes, such as Fischer-Tropsch, build complex hydrocarbons from synthesis gas through controlled addition reactions which are similar to conventional petroleum refinery products. Thus existing technologies should be adequate to control, contain and cleanup spills of indirect coal liquefaction products (see Section 4.0 for location-specific methods).

Direct coal liquefaction processes, which include solvent refined coal (SRC-I and SRC-II), Exxon donor solvent (EDS) and H-coal, will potentially produce products which are much more toxic than conventional crude oil products (Giddings and Washington 1981, Gray and Drucker 1981). Preliminary experimental work on direct coal liquefaction products from SRC-I and SRC-II laboratory and pilot plant experiments has shown that the higher density (heavy) fractions have much greater toxicity than their petroleum counterparts. If these observations are corroborated by further research then either the conversion process will have to be modified or equipment and cleanup practices will have to be changed to ensure greater worker protection during cleanup operations. Experimental data also indicate that SRC products are relatively higher in unsaturated and oxygen and nitrogen containing compounds. It is not known if these particular compounds will be incompatible with existing equipment materials of construction. *Tests should be performed to determine if materials currently used in construction of oil spill mitigation equipment will be compatible with direct coal liquefaction fuels. Data on toxicity of direct coal liquefaction fuels are required in order to determine the extent to which existing cleanup equipment and procedures will have to be modified in order to ensure worker safety.*

Conventional containment and cleanup technologies are expected to be used for spillage of direct coal liquefaction products to surface waters provided safety and materials compatibility criteria are met. The relatively high

density of the heavier constituents in direct coal liquids may result in surface water spills which sink, in which case conventional containment and cleanup techniques would be ineffective. Once the spilled material sinks, dredging and vacuuming become the major spill removal options available. However, dredging and vacuuming often severely disrupt bottom sediments and disperses contaminants to a greater extent than if they were left undisturbed. *A need exists for a technology which could effectively remove sunken spill material from bottom sediments.* Spills which remain on the surface should be amenable to containment and cleanup methods such as booms, barriers, skimmers and suction nozzles; the method used will depend on the size of the waterbody, the volume of material spilled, atmospheric conditions and the velocity of any currents which exist. Specific methods are outlined in Table 17. Spills onto soils may be removed by excavation or possibly left to be degraded in-situ by microbial action. *Biodegradation by land spreading may not be a viable option because of the high toxicity of direct coal liquefaction products and the negative impact this would have on microbial populations.* In addition, if the contaminated soil could be designated as a hazardous waste, the additional burden of removing excavated soil to a secure landfill would be incurred. For those spills which enter the sub-soil and could potentially degrade groundwater quality, interceptor ditches and/or depression wells will have to be employed. Sumps placed in the ditches and the wells would then be pumped to remove and cleanse contaminated waters.

SHALE OIL AND TAR SANDS

Both oil shale and tar sands produce a synthetic crude (syncrude) similar to and in some way superior to conventional crude oils. Syncrude from oil shale has an overall specific gravity which is greater than many crude oils but lacks the very heavy boiling fractions (residuals) found in crude oil. The lack of heavy fractions results from the process limiting temperature reached during the extraction of shale oil from oil shale.

Because shale oil production will exceed tar sand oil production by an order of magnitude for the next 20 yr, the majority of this section pertains to anticipated shale oil spill cleanup technologies. When tar sand liquids

production reaches significant commercial production levels, it is anticipated that spill mitigation technologies used will be similar to those used for shale oil spills based on similar physical and chemical characteristics between the two materials.

Initial shale oil recovery will take place primarily in Colorado, Utah and Wyoming, regions which are relatively dry. Transportation of shale oil and its derivatives will be by pipeline and motor carrier. These two factors support the assertion that most shale oil spills will be to surface soils. Rivers, lakes and streams could also be affected by spill releases but the probability of a spill to land is greater than one to watercourses.

Shale oil toxicity is reported to be intermediate between conventional hydrocarbons and direct coal liquefaction liquids (Giddings and Washington 1981). *The degree to which spill mitigation equipment will have to be modified to account for the toxicity and reactivity of shale oil is unknown; however, personnel should minimize direct contact with spilled shale oil during containment and cleanup operations.*

Neither increased toxicity nor incompatibility of materials, two problem areas identified for mitigation of direct coal liquefaction spills, should be as severe of problems for mitigation of shale oil spills. Small land spills could be excavated but in situ biological degradation, promoted by soil aeration, may be the most viable and cost effective option available, provided surface and groundwaters are not endangered. Larger spills will require containment equipment and the subsequent removal of free liquid by suction nozzles. The relatively high viscosity of shale oil, in comparison to most crude oils, could require heavy duty pumps for the suction nozzles. The high viscosity of shale oil could also be beneficial since this property would retard movement of the oil toward groundwater. Spills of shale oil or shale oil products into small streams, rivers, and lakes could be contained using booms, barriers and wiers. Larger river and lake spills could be contained using booms, skimmers, and barriers containing sorbent materials. Once contained, the spilled materials could be removed using suction nozzles, sorbents and belt skimmers. Groundwater contamination, probably not a large problem area, could be cleaned up using depression wells if required.

ALCOHOLS

Two alcohols, methanol and ethanol, will be produced as synthetic fuels. A large amount of the methanol produced will come from coal liquefaction processes, particularly indirect coal liquefaction facilities. Both methanol and ethanol are toxic; however, regulations and procedures outlining cleanup methods for alcohol spills are well established (OHM-TADS).

Normal cleanup options for spillage of alcohol(s) to soil surfaces include containment and removal of free-standing liquid using barriers and suction nozzles, use of absorbents, dilution with water, on in situ biological degradation. Because alcohols are relatively volatile, evaporation will, over time, become a large factor in spill removal. Since these alcohols are quite volatile, water is often sprayed over a spill site to minimize the presence of toxic vapors and to prevent ignition of the flammable material. Workers should wear approved safety goggles and have respiratory apparatus available in order to minimize their exposure to toxic vapors. Small spills can be biodegraded quite rapidly provided the spill does not saturate the soil to an extent that the microbial population is overwhelmed. Periodic disking of the contaminated soil should enhance biological degradation.

Because alcohols such as methanol and ethanol are miscible in water (OHM-TADS), it is unlikely much can be done once alcohol(s) are spilled into a watercourse. Aeration, where technically feasible, may enhance biodegradation. The main priority with alcohol spills is to prevent further spillage. Dilution of the spill with water will often prevent excessive damage to aquatic life except near the spill zone itself. The extent of damage from a spill to water will depend on both the size of the spill and the size of the watercourse to which the spill has occurred.

6.0 DISPOSAL OF RESIDUES FROM SYNFUEL SPILL CLEANUP OPERATIONS

Previous chapters have predicted synfuel-spill volumes for the next 20 yr and discussed the methods available for cleaning up such spills. This chapter outlines ways to dispose of the residues resulting from cleanup activities.

TYPES OF RESIDUES

No techniques have been developed expressly for the cleanup of synfuel spills. The types of residue resulting from cleanup efforts will depend on the cleanup technique used and the location of the spill (Table 20).

CHARACTERISTICS OF SPILL RESIDUES

The spill cleanup residues identified in Table 20 have been classified as recovered fuel and oil, sorbents, gellants, contaminated soil and sediments, combustion residues, and contaminated debris. A general description of these residues, their characteristics, and what affects them is given in the following sections.

Recovered Fuel and Oil

Fuel and oil residues are composed of weathered fuel or oil and assorted contaminants that have been picked up during the recovery operations. The exact composition of the residue from a particular spill will depend on the medium from which the spill was removed, the type of recovery device employed, the fuel or oil's original characteristics, and the length of time between the spill and recovery activities. Fuels or oils recovered from spills on water will usually contain large amounts of water, either as an emulsion or as entrained water trapped during recovery. Residues recovered from water may also be contaminated by aquatic plants or other small floating debris. Fuel or oil recovered from spills on land is usually contaminated with soil, rocks, leaves, twigs, and other small debris.

TABLE 20. Residues Generated During Spill Cleanup Activities

<u>Spill Location</u>	<u>Spill Cleanup Technique</u>	<u>Residuals</u>
Land	Trenching, Diking, Recovery of Pooled Liquid	Recovered Fuel, Contaminated Soil, Contaminated Debris
	Excavation	Contaminated Soil
	Soil Flooding or Flushing	Recovered Fuel and Water
Groundwater	Pumping	Recovered Fuel and Water, Contaminated Soil
	Trenching, Recovery of Pooled Liquid	Recovered Fuel and Water, Contaminated Soil
Surface Water	Surface Separation or Recovery	Recovered Fuel and Water, Contaminated Debris, Gellants
	Adsorption	Contaminated Sorbents, Contaminated Debris
	Combustion	Combustion Residue, Contaminated Debris

The water content of residues may vary considerably, depending on the recovery device employed. McCracken and Schwartz (1977) found that residue collected by floating suction-head skimmers was 80% water and 20% hazardous material. Residue from self-adjusting weir-type skimmers was 70% water and 30% hazardous material; residue from an advancing endless belt-type skimmer was 90% water and 10% hazardous material; and residue from oleophilic rope-type skimmers was 20% water and 80% hazardous material.

Fuels and oils can be recovered from soils by flushing the hydrocarbons from the soil using water and then by employing a recovery device to separate them from the water. Residues recovered by this process would be similar to residues recovered from water, with the composition depending on the recovery device employed.

Highly viscous hydrocarbons are easier to recover than low-viscosity oils and, therefore, they are less likely to become contaminated during recovery. On water, low-viscosity fuels spread out quickly to form thin slicks, which

are difficult to recover without entrapping water. In general, the water content of residues increases with decreasing viscosity of the spilled material (McCracken and Schwartz 1977). The exact influence of viscosity will, of course, depend on the particular recovery device. On land, the viscosity will also influence the extent and rate that the spilled material tend to percolate into the soil. Viscous fuels will remain on the surface, thus making recovery easy. The degree of soil contamination should decrease with increasing viscosity.

The length of time between a spill and the start of recovery operations may influence the physical and chemical characteristics of the material recovered. Weathering and evaporation are two time-dependent phenomena that can change the character of residues. After several days exposure to the environment, the volatile distillate components of No. 4, 5, and 6 fuel oils will evaporate, leaving a solid or semi-solid and persistent residue (Kim et al. 1974). Prompt recovery, however, can result in residues having very similar characteristics to the original product.

An effect similar to evaporation occurs when water soluble fuel components dissolve. If fuels or oils containing water soluble components are left on water for long periods, these components can leave the fuel, changing the characteristics of the residue that remains. Leary (1975) reported that medium boiling hydrocarbons ($\sim 500^{\circ}\text{F}$) are subject to the highest loss by dissolution. More volatile fractions are lost to evaporation before they can dissolve, while higher boiling fractions are less soluble.

Sorbents and Gellants

Oil residues collected by sorbents or gellants will contain parts of the spent sorbents or gellants. The relative amounts of oils, water, and sorbent present in the residue will depend on the type of sorbent used. Leary (1975) reported that oil adsorption capacity ranged from 4 lb oil/lb sorbent for straw, corncobs, and vermiculite, to as much as 80 lb oil/lb dry sorbent for polyurethane foam. The percent of oil retained by sorbents ranged from 65% for polyethylene fiber to 98% for straw. These results indicate that natural

sorbents (e.g., straw or vermiculite) hold little water but produce large quantities of spent sorbent. Synthetic sorbents (e.g., polyurethane foam), on the other hand, contain relatively high amounts of water.

Gellants will affect the composition of a residue. The amount of gellant present will depend on the material being recovered. According to Bahloul (1979), the optimal ratios of volume of gellant to volume of fuel ranges from 0.1 to 0.2. Higher dosages are needed for No. 2 fuel oil than for aviation gasoline. The chemical composition of the gel that Bahloul tested in lab was 70% Amine D, 15% ethyl alcohol, and 15% benzyl alcohol.

Contaminated Soils and Sediments

Contaminated soils and sediments are oil- or fuel-laden soils that are collected during the excavation or dredging of spill-affected areas. The amount of contamination present in soils will depend both on the properties of the oil or fuel and the characteristics of the soil. Conditions corresponding to slow movement through the soil, such as slightly permeable soils and viscous hydrocarbons, will result in relatively small volumes of highly contaminated soil. In the worst case, the entire pore volume of the soil will be occupied by the hydrocarbon. Conversely, permeable soils and non-viscous hydrocarbons will result in greater volumes of less contaminated soils. In such cases the soil may contain only traces of contamination. Sediments are typically contaminated only by those fractions that sink, such as tars, unless strong mixing is provided (e.g., tidal action or rapids).

Combustion Residuals

Combusting oil or fuel spills creates a residue of combustion products and unburned products that must be recovered and disposed of. Peterson, Yano, and Orgill (1975) estimated that a residue consisting of 2 to 10% of the original volume remained after combustion of crude oil on water. This residue consisted of a heavy tar-like substance, high in soot, which could easily be removed from the surface of the water.

If combustion promoters or wicking agents are employed, they may also be present in the residue. One commercially available promoter consisting of

extremely fine particles of fumed silica is applied in dosages of 0.1 to 0.5% by weight. After combustion, this material forms a nontacky hardened residue similar in appearance to tar paper, which is easily collectable (Peterson, Yano, and Orgill 1975).

Combustion may also be employed to clean up spills on land. In these cases, the residues will consist of soil contaminated with heavy combustion residues.

Contaminated Debris

Contaminated debris refers to a wide variety of materials contaminated during spills that must be collected and disposed of. The exact nature of the debris will depend on where the spill has occurred. Debris may be virtually any item that is contaminated during a spill or spill cleanup operation. Common examples include tree stumps and branches, dead animals, aquatic and shoreline vegetation, vehicle wreckage, and clothing and equipment used during cleanup.

METHODS FOR DISPOSING OF SPILL CLEANUP RESIDUALS

The following section describes various alternatives for disposing of residues from spill cleanup operations. Methods described are fuel/oil recovery, fuel/oil reuse, landfilling, landfarming, and incineration. The operation of each of these methods is described, as well as factors that affect operation, and the suitability of the methods on specific residues and applications. The advantages and disadvantages of each method are also described.

Fuel/Oil Recovery

Recovering fuel or oil is not an ultimate disposal method in itself, but rather a pretreatment method to precede other disposal techniques. The method involves recovery of oil or fuel from spill cleanup residues so that it can be used beneficially or disposed of. Usually, this involves the separation of oil or fuel from water, debris, sorbents, or gellants. Separation from water is usually accomplished with separators such as the API oil-water separator. Emulsified mixtures may have to be treated with emulsion breakers prior to

treatment. Small debris such as leaves or twigs may be removed by screening. Oil can be recovered from large debris by placing the debris on a platform in a pit and allowing the oil to flow down off of the debris to a collector. Oil or fuel can be recovered from various sorbents using processes designed for these products. For example, oil is recovered from polyurethane foam or polyethylene fabric sorbents by running the sorbent through a series of rollers and squeezing the oil free. If gellants have been used to aid in spill cleanup, the oil or fuel can be recovered from the gellant and the gellant can be reused. Centrifuges are used to separate the harvested gel into the recovered hydrocarbon and a carbamate salt (Bahloul et al. 1979).

Recovery is suitable for all residues too contaminated for direct reuse or for desired disposal methods. The main advantage of the method is that it allows a wider range of possible disposal methods to be used. The primary disadvantage is the higher costs associated with additional treatment. This cost may be offset, however, by the use of disposal methods offering cost recovery.

Fuel/Oil Reuse

Reuse of recovered fuel or oil is the most desirable method of disposal both from an environmental and economic point of view. This method allows beneficial use of what would otherwise be a waste material and also offers the opportunity for cost recovery. Recovered oil or fuel may be reused for its original purpose or an alternate purpose, depending mainly on the degree of weathering. Crudes or products recovered immediately after a spill may still be usable for their original purpose. This is especially true of heavy products such as residual fuel oil, which does not undergo rapid loss of volatile or soluble components. Recovered oil or products that have been weathered significantly may still be usable, though not for their original purposes. If a refinery is near a spill site, weathered crudes can be blended with other crudes and refined. If this is not possible, weathered crude may still be suitable for use as residual fuel oil or road oil (Kim et al. 1974). Recovered residual and distillate fuel oil may be cleaned and burned as fuel.

Reuse, as a disposal technique, is most suitable for oils and fuels that have been recovered from cleanup residues. The technique may, however, be

suitable for other residues. For example, residue consisting mainly of oiled soil can be used as a road base (Sterns et al. 1977).

The main advantages of reuse are that it eliminates the need for less environmentally acceptable disposal methods and that it allows resource recovery. The method may also allow cost recovery. The chief disadvantage is that reuse usually must follow recovery or some other pretreatment method. Facilities for pretreatment may not be available at many locations. In addition, the economics of this option are not always favorable. For example, the reprocessing costs of low-value products often exceed the value of the final product, especially when dealing with small volumes (Kim et al. 1974).

Landfilling

Landfilling has historically been the most popular method of disposing of spill cleanup debris. This method has involved burial of residues both in facilities normally operated for the disposal of other wastes (e.g., municipal refuse and in facilities especially constructed for spill debris disposal). *Although widely practiced in the past, the use of landfilling should be lessened in the future by solid waste management regulations developed pursuant to the Resource Conservation and Recovery Act (RCRA, PL 94-580).* Under these regulations, most synfuel spill cleanup residues would likely be classified as hazardous wastes. As such, landfilling would have to be conducted at secure landfill sites licensed by the Environmental Protection Agency (EPA) that are specifically constructed to prevent migration of contaminants. If not classified as hazardous waste, residues would still have to be disposed of in landfills meeting the siting and performance criteria spelled out in Subtitle D of RCRA. The overall impact of RCRA on spill residue disposal will probably be to limit disposal to existing licensed facilities. This should eliminate the use of landfills constructed solely for disposal of the residue from a spill except under emergency situations.

Landfilling is most suitable for non-liquid residues, such as contaminated debris. If large debris such as tree limbs or trunks are to be disposed of, it may be necessary to reduce the debris size first by shredding or chipping. Landfilling is generally not a desirable method for disposing of liquid

waste, such as oil-water emulsions, due to the high potential of subsurface migration of contaminants. If other absorbent wastes are also present (e.g., municipal refuse), landfilling of liquid residues may be acceptable. In addition, landfilling is probably best suited for small quantities of residue.

Disposal of spill cleanup debris at an existing landfill offers several advantages, namely, minimal equipment needs, minimal site preparation, low initial cost, and high availability of sites (Sittig 1979). These advantages stem from a facility that is already available and in operation. If residues must be disposed of in a secure hazardous waste landfill, the cost and availability advantages would be much less. Disadvantages are due to possible environmental consequences. Because oil and oil products are degraded very slowly (if at all) in an anaerobic landfill, landfilling of contaminated residues creates a long-term threat regarding the migration of contaminants from the landfill and necessitates long-term environmental monitoring at the site.

Landfarming

Landfarming was developed as a disposal method for petroleum refinery wastes. This method involved the controlled application of wastes to the soil followed by slow degradation of the wastes by soil micro-organisms. The operating procedure generally involves plowing the soil to loosen it, adding necessary nutrients, spreading the waste on the surface of the soil and allowing it to weather several weeks, and then rototilling or plowing the waste into the soil (Farlow et al. 1977). Oily wastes do not ordinarily contain adequate nutrients so supplements must be added. Brown et al. (1981) reported that each waste has an optimum carbon to nitrogen (C:N) ratio, and that addition of nitrogen to reach the optimum ratio will improve degradation. Stearns, Ross, and Morrison (1977) reported that typical application rates for oily wastes are 2 to 6 in./yr in cool climates and 6 to 12 in./yr in warmer climates. Brown et al. (1981) found that maximum degradation of oily wastes occurs when the oil accounts for only 1% (by weight) of the soil mass. Oily wastes are commonly plowed to a depth of about 6 to 8 in. The soil is then replowed several times a year to promote aeration.

Landfarming has been shown to be an effective and environmentally sound method of disposing of oil-containing wastes. Stearns, Ross, and Morrison (1977) reported results showing average degradation rates after 1 yr of landfarming to be 58% for No. 6 fuel oil, 62% for crude oil, 68% for used crankcase oil, and 87% for No. 2 fuel oil. Landfarming of oily wastes does not appear to cause plant toxicity problems, and plants are often grown on the treated soil to reduce erosion. Plant growth inhibition is largely due to the inability of the plant roots to obtain sufficient oxygen and moisture, which would occur only with overapplication of wastes (Stearns, Ross, and Morrison 1977). Cresswell (1977) reported that normal crops can be grown with 5 to 10% oil in the soil. Several studies have reported no subsurface migration of contaminants away from landfarm areas (Cresswell 1977 and Weldon 1979).

Many spill cleanup residues are similar to oily wastes, which means that landfarming should be suitable for the disposal of many types of residue. Residues should be either liquid or semi-solid to facilitate application and incorporation into the soils. Solid debris would not be suitable. In fact, large debris must be removed to avoid possible damage to tilling equipment. Non-degradable residues such as plastic sorbents should also be removed. The inclusion of degradable sorbents such as straw is not desirable, because these materials can exert a relatively high nitrogen demand during degradation, which can then slow the degradation of the oil (Stearns, Ross, and Morrison 1977).

Environmental factors may affect the suitability of landfarming at a given location. For example, the effect of temperature on landfarm performance can be significant. Brown et al. (1981) reported that biodegradation rates of oily wastes in soils doubled between 10°C and 30°C. Although landfarming in cold climates is possible, warmer climates are preferable.

The main advantage of landfarming is that it results in relatively rapid destruction of wastes, compared to other land disposal methods, reducing the long-term threat of adverse environmental impacts. Another advantage is that the land may be reclaimed for alternate uses after landfarming operations have been completed. Landfarming of wastes can also result in improved soil properties. A major disadvantage is high operating costs compared to other methods.

This is due primarily to the labor intensiveness of the method. Landfarming also presents a higher potential for volatile losses of wastes than other methods. Depending on the residues, this may or may not be important. The method may also require storage of residues before application because of inclement weather or limited land application area. A further disadvantage is the possibility of introducing trace contaminants into the food chain from the residues.

Incineration

Incineration is an accepted disposal method for a number of wastes, and may also have application to spill residue disposal. Mercer et al. (1979) reviewed the applicability of several types of incinerators to combustion of spill cleanup residues. Open pit incineration was commonly practiced in the past during spill cleanup, but has become largely unacceptable because of the uncontrolled release of gaseous effluents. An alternative to open pit incineration is the use of a portable brush burner (Wise and Brunk 1977), which employs a fan to increase air flow to the fire and also allows injection of fuel oil into the debris to improve combustion. Multiple hearth incinerators are very useful, since they can burn residues having high moisture contents. These incinerators can accept sludges, tars, solids, and liquids. Rotary kiln incinerators are very versatile and are suited to the ultimate disposal of virtually any form of combustible wastes. Peterson, Yano, and Orgill (1975) recommended the use of all-metal, non-refractory rotary kiln incinerators for burning large volumes of oil spill residues, especially those heavily contaminated with oil. Fluidized bed incinerators are suitable for a wide variety of wastes, but this technology is relatively new. Liquid combustors are available, but are useful primarily for destruction of combustible liquid wastes. The above incinerators may be either mobile, for use at the spill site, or stationary, for use at a waste disposal facility.

Incineration is suitable for virtually all combustible spill-cleanup residues. On-site incineration using mobile incinerators is especially suitable for disposal of residues from large spills in remote locations. In such cases, the volume of material often precludes landfarming or landfilling while

transportation costs preclude reuse. Leary (1975) recommended incineration for disposing of small quantities of residue from spills of all types of oil or fuel. The method is especially desirable when alternate methods are not economical with small volumes. Incineration is not suitable for non-combustible residues such as contaminated soil or rocks. Certain noncombustible residues, such as spent inorganic sorbents, may be incinerated, but a large volume of ash requiring further disposal will be produced.

Several important advantages are gained by incinerating spill-cleanup residues. Incineration technology is generally well proven and equipment is readily available. The technique is broadly applicable to most organic wastes. It is the only method that can readily accept toxic organics and ensure that their destruction is total. The method is relatively rapid and can handle large volumes of wastes without requiring large land areas. A disadvantage is that the process is relatively expensive and relatively complex compared to other methods. Air pollution control is also required and may present a problem if residuals are contaminated with hazardous materials. Lastly, ash is produced during incineration and must be disposed of (although the volume and hazard are generally quite low).

SUITABILITY OF DISPOSAL METHODS FOR SYNFUEL SPILLS

This section discusses the suitability of the disposal methods discussed above to the disposal of synfuel residues. The greater toxicity of synthetic crudes and products is cause for special concern. As such the following discussion focuses on the effects that synfuels might exert on various disposal methods.

Effect of Toxicity

Preliminary investigations of the toxicity of synthetic crudes and products suggest that these materials may be more toxic than their petroleum counterparts (Chapter 3). Because of this higher toxicity, special precautions may be necessary with all disposal methods. For example, care must be taken to avoid inhaling fumes when handling residues containing coal liquids that have low boiling points (PNL 1979). In addition, the lighter fractions of

both coal and shale liquids can cause skin irritation and inflammation (Cowser 1981a and PNL 1981). Special protective clothing should be worn by workers when they handle residues containing these materials. Higher-boiling-point synfuel products do not exhibit acute toxicities, in general, but may exhibit mutagenic or carcinogenic properties (Calkin et al. 1982, Cowser 1981a, and PNL 1981). This is especially true for coal liquids. During disposal of heavier residues, care must be taken to minimize worker contact with residuals.

Fuel/Oil Recovery

Most data suggest that the quality of recovered synfuels and petroleum fuels should be similar. Recovered fuels and oils may contain certain amounts of water in the form of emulsions. The surface tension of a fuel determines the degree to which it will emulsify the water. *Adequate data on the surface tensions of synthetic fuels do not exist to determine if synthetic fuels will emulsify to a greater or lesser extent than petroleum fuels when spilled on water.* Water is also introduced to the recovered fuels during the operation of recovery devices. The amount of water contaminating the recovered fuel depends to a large extent on the viscosity of the fuel (McCracken and Schwartz 1977).

Other factors affecting residue quality are evaporative loss and dissolution. Data presented by Bland and Davidson (1968) and Reynolds, Niedzwiecki, and Clark (1980) show that petroleum products tend to be high in paraffinic hydrocarbons while synthetic fuels are high in aromatic hydrocarbons. Paraffins typically have higher vapor pressures than aromatics and are, therefore, subject to greater evaporation loss. Aromatics, on the other hand, tend to have greater water solubilities than paraffins and would be subject to greater loss by dissolution. The overall impact of these two processes is very site- and case-specific, however, and no generalizations can be made.

Reuse

The toxicity of recovered synfuel products will not affect their rerefining or reuse as fuel, but might affect their use as a road oil. Synfuel products exhibiting high toxicity should not be reused if public exposure or contact are involved.

Landfilling

Synfuels residues must be landfilled with greater care than petroleum residues. The more acute toxicity of synthetic fuels is due primarily to the presence of aromatic compounds such as phenols and anilines, which are so soluble that they can easily migrate from land disposal sites if groundwater flow reaches the residues. The chronic toxicity and mutagenicity of synfuels are caused mainly by the heavy fractions. In an anaerobic landfill environment, these materials will degrade very slowly (if at all) and, therefore, will pose a long-term environmental threat.

Landfarming

Results of several studies on landfarm treatment of oily wastes and refinery wastes suggest that the method may be very suitable for degrading synfuel spill cleanup residues. The degradation rates of synthetic fuel residues should be approximately the same or somewhat slower than those of petroleum residues because of the relative proportions of various hydrocarbons in the two materials. Petroleum products typically contain high concentrations of paraffins, while aromatics form the bulk of most synfuels. Weldon (1979) showed that landfarming degraded paraffins in oily refinery waste more readily than aromatics, although good removal of both was achieved. Similar results were obtained by Cresswell (1977), who investigated landfarm treatment of crude oil, refinery wastewater treatment sludge, and refinery oily wastes. With crude oil, the paraffin fraction degraded first, followed shortly by the aromatics. After 41 months, over 80% of both the paraffins and aromatics had been degraded. With oily wastewater treatment sludge, 88% of the paraffins and 85% of the aromatics were degraded after 18 months. In all cases, asphaltic fractions degraded at a much slower rate. This investigation also showed that all oil fractions tended to stay tightly bound to the soil and did not migrate.

Results obtained by Donnelly and Brown (1981) indicate that landfarming may be effective in reducing the mutagenicity of synfuel residues. They measured the mutagenic activity of soils to which various amounts of API separator sludge had been added. Landfarming reduced the mutagenic activity of the

wastes for all cases studied. The mutagenic activity of the aromatic fractions were reduced to a greater extent than that of the paraffin fractions. In addition, only low levels of mutagenic activity were detected in leachate water collected after waste application.

Wetherold, Rosebook, and Cunningham (1981) investigated the volatilization of hydrocarbons following landfarming of oily sludges. Their results showed that from 0.01 to 3.2 wt% of the applied oil was volatilized. Because aromatics are lower in vapor pressure than are paraffins, lower volatilization losses may be expected from synfuels than from petroleum products.

Incineration

Incineration is an appropriate disposal method for residues containing synthetic fuels, because it completely destroys toxic constituents. Incineration must be performed under controlled conditions, however, to ensure complete destruction of toxic materials. Open burning, while commonly used in the past to dispose of oil-spill residues, is not suitable for synfuel residues. Open burning does not guarantee the destruction of the toxic components of synfuels and can serve as a means of spreading these contaminants throughout the environment.

RECOMMENDED METHODS FOR DISPOSING OF SYNFUEL RESIDUES

In the previous sections, spill cleanup residues for various spill locations and cleanup methods were identified and characterized. Methods for disposing of spill residues were also described, both in general terms and with respect to synfuel spills. Drawing from the information presented in these previous sections, methods for the disposal of synfuel spill cleanup residues are recommended.

Six general classes of spill residues were identified earlier; these are recovered fuel and oil, contaminated soil, contaminated debris, spent sorbents, spent gellants, and combustion residuals. In this section, disposal methods are recommended for residue resulting from the cleanup of synthetic crudes, synthetic distillate products, and synthetic residual products. Residues were

broken down into these three classes because properties affecting disposal are relatively constant within these groups. Table 21 presents a summary of recommended disposal methods for the various residues.

Recovered Fuel and Oil

Recovered crude should be shipped to a refinery, blended with a similar fresh crude, and refined. If this action is not possible because quantities are too small or distances to refineries are too great, the residues should be incinerated (small quantities) or landfarmed (large quantities). Landfilling should be employed only as a last resort.

Recovered distillate products will probably be unsuitable for reuse as originally intended. If possible, they should be combined with residual products for use as a low-grade fuel. Otherwise, incineration is recommended. Landfarming is not recommended because of the high potential for worker exposure to residues that may be acutely toxic. Landfilling should be employed only if no other methods are feasible.

Recovered residual products will probably be suitable for reuse as originally intended or for reuse as a low-grade fuel. Otherwise, incineration or landfarming should be employed, depending upon the availability of facilities and economic considerations. Again, landfilling is not recommended.

Contaminated Soil

Soil contaminated with any type of synthetic crude or product should be landfarmed if possible. If suitable conditions exist, landfarming may be accomplished in situ by applying proper amounts of nutrients and moisture to the soil and rototilling it regularly. If landfarming is not possible because of climatic considerations, landfilling should be practiced, though this will be costly. Incineration is not recommended because of the large amounts of inorganic material present. Indirect reuse, such as use as a road surface, is not advised because of toxicity considerations.

Contaminated Debris

Landfilling is recommended for disposal of inorganic debris. If possible, large debris should be shredded or chipped to reduce volume. For large

**TABLE 21. Recommended Methods for Disposal of Synfuel Spill Cleanup Residues
(Listed in Order of Preference)**

Cleanup Residue	Disposal Method by Synthetic Fuel		
	Synthetic Crude	Synthetic Distillate Products	Synthetic Residual Products
Recovered Fuel/ Oil	1. Refine with fresh crude 2. Incinerate (small quantities) or landfarm (large quantities)	1. Blend with residual products, use as fuel 2. Incinerate	1. Use as fuel 2. Incinerate or landfarm
Contaminated Soil	1. Landfarm (in situ if possible) 2. Landfill	1. Landfarm (in situ if possible) 2. Landfill	1. Landfarm (in situ if possible) 2. Landfill
Contaminated Debris-Inorganic	1. Landfill	1. Landfill	1. Landfill
Contaminated Debris-Organic	1. Landfarm (large quantities) or incinerate (small quantities) 2. Landfill	1. Landfarm (large quantities) incinerate (small quantities) 2. Landfill	1. Landfarm (large quantities) or incinerate (small quantities) 2. Landfill
Spent Sorbents	1. Recover and reuse 2. Landfill (inorganic) or landfarm or incinerate (organic)	1. Recover and reuse 2. Landfill (inorganic) or landfarm or incinerate (organic)	1. Recover and reuse 2. Landfill (inorganic) or landfarm or incinerate (organic)
Spent Gellants	1. Recover and reuse 2. Incinerate or landfarm	1. Recover and reuse 2. Incinerate or landfarm	1. Recover and reuse 2. Incinerate or landfarm
Combustion Residuals	1. Landfill	1. Landfill	1. Landfill

quantities of small or shredded organic debris, landfarming is recommended, though large amounts of nutrients may be required to degrade both the synfuel and the debris. Small quantities of small or shredded organic debris may be incinerated. If these methods are not suitable or if large debris cannot be shredded, landfilling can be used.

Spent Sorbents

Recovery and reuse is the recommended disposal practice for all types of spent sorbents. If this is not possible, nonreusable inorganic sorbents should be landfilled. Nonreusable organic sorbents should be incinerated or, if they are readily degradable, landfarmed.

Spent Gellants

Recovery and reuse is recommended for the disposal of all spent gellants. If this is not possible, gellants should be incinerated or landfarmed, depending on the availability of facilities and the economics of disposal. Landfilling is suggested only if no other method is suitable.

Combustion Residue

The recommended method for disposing of all combustion residue is landfilling. Incineration and landfarming are not expected to be effective methods, because the residues will probably contain large amounts of refractory organics.

RECOMMENDATIONS

Several recommendations for additional are presented below. The objective of continuing work would be to provide data that were needed for this report but which are presently unavailable. In general, additional work is needed to determine the characteristics of spill cleanup residues and the performance of disposal systems.

Characterization of Residues

Additional characterization of some spill cleanup residues is needed. The effect of weathering on spill residuals should be studied, particularly

with respect to toxicity and physical properties. If the acute toxicity of synfuels is associated with water-soluble fractions (phenols, anilines), then residuals recovered from spills to water could exhibit greatly reduced toxicity compared to fresh products. Similarly, if the toxic components of residues are volatilized quickly following spills, there may be little hazard associated with volatile losses during disposal operations. The impact of emulsification on residual characteristics should also be studied. All of these factors could affect how residuals can be disposed of.

The performance of actual spill cleanup systems should be field tested using synthetic fuels. This would allow more accurate determination of the actual characteristics of cleanup residuals. Any operational difficulties related to synfuel spill cleanup (e.g., exposure of workers to toxic vapors) could also be identified.

Performance of Disposal System

The results of this study suggest that landfarming may be a highly promising method for the treatment of synfuel spill residuals. Currently, however, little is known about how such systems perform. The only current work identified in this area is a study of the biodegradation of several synfuels (Gehrs et al. 1981). It is recommended that bench-scale treatability studies be undertaken to assess the performance of landfarming of synfuels. Measurements of volatile losses of toxic components during simulated landfarming conditions would allow potential hazards of this method to be better assessed.

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APPENDIX A

SYNFUEL PROJECTION ESTIMATES

APPENDIX A

SYNFUEL PROJECTION ESTIMATES

COAL LIQUEFACTION

A) Direct -- SRC II, Exxon Donor Solvent, and H-Coal

<u>Year</u>	<u>Production (Barrels/Day, Oil Equivalent)</u>	<u>Reference</u>
1985	15,000 34,000*	Princiotta 1980 DOE 1979
1987	50,000	<u>Synfuels Newsletter</u> , 1980c
1990	25,000-50,000 40,000-60,000 34,000* 25,000-50,000*	DOE 1980b Princiotta 1980 DOE 1979 Hagler, Bailey, and Co. 1980
1992	300,000	<u>Synfuels Newsletter</u> 1980;
1995	270,000* 150,000-250,000	DOE 1979 Hagler, Bailey, and Co. 1980
2000	400,000-625,000 400,000-600,000	Princiotta 1980 Hagler, Bailey, and Co. 1980

* Both direct and indirect

COAL LIQUEFACTION

b) Indirect -- Fisher-Tropsch, M-Gasoline, and Methanol

<u>Year</u>	<u>Production (Barrels/Day, Oil Equivalent)</u>	<u>Reference</u>
1985	15,000	Princiotta 1980
1987	100,000	<u>Synfuels Newsletter 1980c</u>
1990	110,000-195,000*	DOE 1980a
	500,000*	Oil and Gas Journal 1979a
	1,000,000**	<u>Engineering News Record 1980</u>
	225,000**	<u>Synfuels News Letter 1980f</u>
	125,000-200,000	Princiotta 1980
	125,000-175,000	Hagler, Bailey, and Co. 1980
1992	400,000	<u>Synfuels Newsletter 1980c</u>
1995	350,000-560,000*	DOE 1980a
	475,000-600,000	DOE 1980b
	475,000-600,000	Hagler, Bailey, and Co. 1980
2000	640,000-1,000,000*	DOE 1980a
	<3,000,000**	<u>Engineering News Record 1980</u>
	1,200,000 (boiler fuel from coal only)	<u>Synfuels Newsletter 1980j</u>
	1,000,000 (both direct and indirect to MeOH only)	<u>Synfuels Newsletter 1980i</u>
	625,000-1,000,000	Princiotta 1980
	675,000-1,000,000	Hagler, Bailey, and Co. 1980
2005	240,000 (Colorado only)	<u>Synfuels Newsletter 1980e</u>
2020	4,000,000**	<u>Synfuels Newsletter 1980j</u>

* Calculated

** Both direct and indirect

COAL GAS

<u>Year</u>	<u>Production (Barrels/Day, Oil Equivalent)</u>	<u>Reference</u>
1985	20,000-34,000 45,000 20,000-33,500	DOE 1980b DOE 1979 Hagler, Bailey, and Co. 1980
1987	80,000	<u>Synfuels Newsletter</u> 1980c
1990	600,000 159,000 88,000-176,000 245,00000-575,000	<u>Oil and Gas Journal</u> 1979a DOE 1979 Rothberg 1980 Hagler, Bailey, and Co. 1980
1992	350,000	<u>Synfuels Newsletter</u> 1980c
1995	400,000 775,000-1,155,000	DOE 1979 Hagler, Bailey, and Co. 1980
2000	950,000-1,500,000	Hagler, Bailey, and Co. 1980

ETHANOL

<u>Year</u>	<u>Production (Barrels/Day, Oil Equivalent)</u>	<u>Reference</u>
1985	64,000-84,000	DOE 1980a, DOE 1980b
	40,000	<u>Chemical and Engineering News</u>
		1979
	37,800	<u>Synfuels Newsletter 1980f</u>
	40,000-50,000	<u>Princiotta 1980</u>
	41,400-62,100*	<u>Synfuels Newsletter 1980c</u>
1990	175,000-290,000	DOE 1980b
	100,000**	<u>Oil and Gas Journal, 1979a</u>
	100,000**	<u>Automotive Industries 1980</u>
	100,000	<u>Synfuels Newsletter 1980i</u>
	180,000-250,000	<u>Princiotta 1980</u>
1995	180,000-375,000	DOE 1980b
2000	185,000-460,000	DOE 1980b
	190,000-450,000	Princiotta 1980

* Calculated

** From biomass only

METHANOL

<u>Year</u>	<u>Production (Barrels/Day, Oil Equivalent)</u>	<u>Reference</u>
1985	51,000*	<u>Oil and Gas Journal</u> 1979b
199	69,000*	<u>Oil and Gas Journal</u> 1979b, <u>Synfuels Newsletter</u> 1980i
1995	-	
2000	1,000,000 (from coal only) 637,000 (maximum)	EPA 1980 <u>Synfuels Newsletter</u> 1980d
2020	2,400,000 (from coal only)	<u>Synfuels Newsletter</u> 1980e

* Calculated

SHALE OIL

<u>Year</u>	<u>Production (Barrels/Day, Oil Equivalent)</u>	<u>Reference</u>
1985	40,000-50,000 50,000 40,000-50,000	DOE 1980a DOE 1980c Hagler, Bailey, and Co. 1980
1987	237,000	<u>Synfuels Newsletter</u> 1980c
1990	105,000-275,000 350,000 400,000 600,000 200,000-400,000 175,000 400,000 (maximum) 40,000-50,000 55,000-312,000 50,000-200,000 100,000-275,000	DOE 1980a Oil and Gas Journal 1979a Automotive Industries 1980 <u>Synfuels Newsletter</u> 1980k <u>Synfuels Newsletter</u> 1980j <u>Synfuels Newsletter</u> 1980i <u>Synfuels Newsletter</u> 1980i <u>Energy Resources and Technology</u> 1980 EPA 1980 DOE 1980c Hagler, Bailey, and Co. 1980
1992	800,000	<u>Synfuels Newsletter</u> 1980c
1995	430,000-600,000 880,000 1,500,000 450,000 380,000-850,000 50,000-600,000 425,000-600,000	DOE 1980a <u>Synfuels Newsletter</u> 1980g <u>Synfuels Newsletter</u> 1980k <u>Synfuels Newsletter</u> 1980j EPA 1980 DOE 1980c Hagler, Bailey, and Co. 1980
2000	700,000-1,500,000 3,000,000 800,000-1,950,000 850,000-1,700,000 700,000-1,400,000	DOE 1980a <u>Synfuels Newsletter</u> 1980k EPA 1980 <u>Synfuels Newsletter</u> 1980b Hagler, Bailey, and Co. 1980
2005	1,500,000 2,000,000 (Colorado only)	<u>Synfuels Newsletter</u> 1980j <u>Synfuels Newsletter</u> 1980e
2020	2,600,000	<u>Synfuels Newsletter</u> 1980j

TAR SANDS

<u>Year</u>	<u>Production (Barrels/Day, Oil Equivalent)</u>	<u>Reference</u>
1985	10,000-15,000	Princiotta 1980
1990	0-10,000	DOE 1980b
	100,000	<u>Synfuels Newsletter</u> 1980g
	20,000	<u>Synfuels Newsletter</u> 1980j
	15,000-20,000	<u>Princiotta 1980</u>
	10,000	Rothberg 1980
	0-10,000	Hagler, Bailey, and Co. 1980
1995	10,000-50,000	DOE 1980b
	10,000-50,000	Hagler, Bailey and Co. 1980
2000	25,000-50,000	DOE 1980b
	70,000-125,000	Princiotta 1980
	55,000-100,000	Hagle, Bailey and Co. 1980

APPENDIX B

ACUTE TOXICITY OF SYNFUEL

TABLE B.1. Acute Toxicity

Organism	Index of Effect	Duration Exposure	Crude Shale (WSF) (1)	Shale JP-5 (WSF) (1)	Shale (DFM) (2) (WSF) (1)	Petroleum No. 2 (WSF) (1)	Petroleum JP-5 (WSF) (1)	Petroleum No. 6 (WSF) (1)	References
<i>Selenastrum capricornutum</i>	Photosynthetic rate (% control) in 10% dilution of stock WSF	4-hr	21%	101%	106%	91%	109%	97-106%	Giddings and Washington (1981)
<i>Microcystis</i>	Photosynthetic rate (% control) (in 10% dilution of stock WSF)	4-hr	10%	--	--	98%	--	88-103%	Giddings and Washington (1981)

(1) Each WSF prepared by adding oil to distilled water in a 1:8 (oil-water ratio) and stirring gently for 16 h in dark; then separating from oil and filtering (Whatman No. 41) before testing.

(2) Diesel fuel marine

TABLE B.2. Acute Toxicity

Organism	Index of Effect	Duration Exposure	Shale Derived		Petroleum Derived		References
			JP-5 (WSF) (1)	DFM ⁽²⁾ (WSF) (1)	JP-5 (WSF) (1)	DFM (WSF) (1)	
Selenastrum capricornutum	Photosynthetic rate (% control) in 10% dilution of stock WSF	4-hr	100%	>100%	>100%	90%	Giddings (1980)
Selenastrum capricornutum	Photosynthetic rate (% control) in 100% dilution of stock WSF	4-hr	100%	80%	90%	0%	Giddings (1980)

(1) Each WSF prepared by adding oil to distilled water in a 1:8 (oil-water ratio) and stirring gently for 16 h in dark; then separating from oil and filtering (Whatman No. 41) before testing.

(2) Diesel fuel marine

TABLE B.3. Acute Toxicity

<u>Organism</u>	<u>Index of Effect</u>	<u>Duration Exposure</u>	<u>SRC (WSF)⁽¹⁾ TOC, mg/L</u>	<u>Prudhoe Bay Crude (WSF)⁽¹⁾ TOC, mg/L</u>	<u>References</u>
Chironomus tentans	Mortality LC ₅₀	24-hr	9.18-10.04	19.0 ⁽²⁾	Becker et al. (1981)
Daphnia magna	Mortality LC ₅₀	48-hr	2.03-2.44	8.0 ⁽²⁾	Becker et al. (1981)
Pimephales promelas	Mortality LC ₅₀	96-hr	8.75-9.44	13.4 ⁽²⁾	Becker et al. (1981)

(1) Mixing regime for stock solution: 1) water to oil ratio - 99:1, 2) mixing time - 4 hr, 3) non-filtered, and 4) yield 1000 mg/L TOC (SRC).
 (2) Concentration at which no effect was observed at the end of 24 hr.

TABLE B.4. Acute Toxicity

Organism	Index of Effect	Duration Exposure	Crude Shale (WSF) ⁽¹⁾	Shale JP-5 (WSF) ⁽¹⁾	Shale (DFM) (WSF) ⁽¹⁾	References
<i>Selenastrum capricornutum</i>	Photosynthetic rate (% control) in 10% dilution of stock WSF	4-hr	30%	100%	>100%	Giddings (1980)
<i>Selenastrum capricornutum</i>	Photosynthetic rate (% control) in 100% dilution of stock WSF	4-hr	0%	100%	80%	Giddings (1980)

Organism	Index of Effect	Duration Exposure	Crude Shale (WSF) ⁽¹⁾	HDT ⁽³⁾ Crude (WSF) ⁽¹⁾	References
<i>Selenastrum capricornutum</i>	Photosynthetic rate (% control) in 10% dilution of stock WSF	4-hr	20%	80%	Giddings (1980)
<i>Microcystis aeruginosa</i>	Photosynthetic rate (% control) in 10% dilution of stock WSF	4-hr	10%	70%	Giddings (1980)

(1) Each WSF prepared by adding oil to distilled water in a 1:8 (oil-water ratio) and stirring gently for 16 h in dark; then separating from oil and filtering (Whatman No. 41) before testing.

(2) Diesel fuel marine

(3) Hydrotreated

TABLE B.5. Acute Toxicity

Organism	Index of Effect	Duration Exposure	SRC-II (WSF) ⁽¹⁾	H-coal ⁽²⁾ Distillate (WFS) ⁽¹⁾	H-coal ⁽³⁾ Distillate (WFS) ⁽¹⁾	H-coal ⁽⁴⁾ Fuel Oil (WSF) ⁽¹⁾	Crude Shale ⁽¹⁾ (WSF) ⁽¹⁾	Petroleum No. 2 ⁽¹⁾ (WSF) ⁽¹⁾	References
Selanastrum capricornutum	Lowest % of WSF causing significant photo-synthetic inhibition	4-hr	1	1	1	0.1	10	100	Gehrs (1980)
Microcystis aeruginosa	Lowest % of WSF causing significant photo-synthetic inhibition	4-hr	1	1	10	1	1	100	Gehrs (1980)

(1) Each WSF prepared by adding oil to distilled water in a 1:8 (oil-water ratio) and stirring gently for 16 hr in the dark; then separating from oil and filtering (Whatman No. 41) before testing.

(2) Raw, without hydrotreating

(3) Medium severity hydrotreatment

(4) Vacuum overhead

TABLE B.6. Acute/Chronic Toxicity

Organism	Index of Effect	Duration Exposure	SRC (WSF) ⁽¹⁾	No. 6 (WSF) ⁽¹⁾	No. 2 (WSF) ⁽¹⁾	Reference
Selenastrum capricornutum	Inhibition of growth	4-hr	1%	>100%	100%	Giddings et al. (1980) ⁽²⁾
Microcystis aeruginosa	Inhibition of growth	4-hr	1%	100%	100%	Giddings et al. (1980) ⁽²⁾
Daphnia magna	Mortality LC ₅₀	48-hr	0.31%	>100%	6.7%	Giddings et al. (1980) ⁽²⁾
Daphnia magna	Mortality LRCT	24-hr	0.3%	>100%	>100%	States et al. (1982) ⁽³⁾
		21-day	0.06%	25%	25%	
Daphnia magna	Inhibition of reproduction LRCT	21-day	1%	25%	50%	States et al. (1982) ⁽³⁾

(1) Dilution (%) of stock solution producing equal biological effects.

(2) Mixing regime for stock solution: 1) water to oil ratio - 8:1, 2) mixing time - 16 hr, 3) filtered oil droplets, 4) yield 5000 mg/l TOC (SRC), 19 mg/l TOC (No. 6), and 105 mg/l TOC (No. 2).

(3) Mixing regime for stock solution: 1) water to oil ratio - 99:1, 2) mixing time - 4 hr, 3) non-filtered, 4) yield 1000 mg/l TOC (SRC).

TABLE B.7. Acute/Chronic Toxicity

Organism	Index of Effect	Duration Exposure	H-Coal	H-Coal	H-Coal	Petroleum			References
			Raw Distillate (WSF) (1)	Product Blend (WSF) (1)	Product (WSF) (1)	Marine Diesel (WSF) (1)	No. 2 (WSF) (1)	No. 6 (WSF) (1)	
<i>Selenastrum capricornutum</i>	Lowest concentration of WSF that inhibited photosynthesis significantly (P=0.05)	4-hr	1	1	--	100	100	>100	Cowser (1981)
<i>Microcystis aeruginosa</i>	Lowest concentration of WSF that inhibited photosynthesis significantly (P=0.05)	4-hr	1	--	--	--	100	100	Cowser (1981)
<i>Daphnia magna</i>	Percent concentration of the water extract estimated to have killed 50% of test organisms	48-hr			4.64(2) 1.04(3)	30.34			
<i>Daphnia magna</i>	Highest concentration (%) at which no significant effects on reproduction (P=0.05) were observed	28-day			0.29(2) 0.12(3)	10.0			

(1) Each WSF prepared by adding oil to distilled water in a 1:8 (oil-water ratio) and stirring gently for 16 h in dark; then separating from oil and filtering (Whatman No. 41)

(2) Atmospheric-still-bottoms (syncrude mode)

(3) Atmospheric-still-bottoms (fuel-oil mode)

APPENDIX C

ACUTE TOXICITY OF ALCOHOLS

TABLE C.1. Acute Toxicity

Organism	Index of Effect	Duration Exposure	mg/					References
			Methanol	Ethanol	Propanol	Butanol	Amyl	
Chlorella pyrenoidosa	Toxic concentration	5-day	31,000	27,200	11,200	8,500	--	Thirumurthi and Gloyna (1965)
Semolitus atromaculatus	Critical range	24-hr	8,000 - 17,000	7,000 - 9,000	200 - 500	1,000 - 1,400	350 ⁽¹⁾ - 500	Gillette et al. (1952)
Daphnia magna	Threshold of immobilization	32-hr	32,000	17,400	--	--	881 ⁽²⁾	Anderson (1944)

(1) n-amyl

(2) iso-amyl

APPENDIX D

TERRESTRIAL EFFECTS

TABLE D.1. Terrestrial Effects (Phototoxicity)

Organism	Index of Effect	Duration Exposure ⁽¹⁾	Control	SRC-I Solid		SRC-II Liquid ⁽⁴⁾			References
				Layered ⁽²⁾	Mixed ⁽³⁾	0.15 L/m ²	1.48 L/m ²	14.84 L/m ²	
Hordeum vulgare	Length of flowering culms (cm)	Growing-season	75.4	60.5	71.0	75.9	42.7	36.8	Cline et al. (1982)
	Length of seed heads (cm)	Growing-season	8.3	6.7	8.1	8.4	4.5	3.0	Cline et al. (1982)
	Dry matter produced (g)	Growing-season	35.33	--	--	24.03	2.5	0.40	Cline et al. (1982)
	Dry weight of grain produced (g)	Growing-season	14.53	5.80	10.16	--	--	--	Cline et al. (1982)

(1) 1979 in the case of SRC-I solids; 1980 in the case of SRC-II liquid.

(2) 1-cm layer of pellets layered over a 6-cm soil column covered by a 3-cm layer of soil.

(3) 1:1 mixture of soil and pellet layered 3-cm deep over a 7-cm soil column.

(4) 2.9:1 middle to heavy distillate added to soil column in a layer 10-cm below soil surface.

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