SPECIFICATIONS FOR FUTURE TRANSPORTATION FUELS: IMPACTS ON COAL LIQUEFACTION R&D

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STUDY OBJECTIVES AND APPROACH

- **Objectives**
  - Identify and review activities impacting development of future transportation fuels
  - Assemble database of specifications for future transportation fuels

- **Approach**
  - Review current specifications for transportation fuels
  - Summarize ongoing activities on revisions
  - Monitor ongoing joint auto/oil industry test program
  - Summarize California data pertaining to methanol fuels
  - Review database on the "Methanol Rally" program
  - Monitor regulatory activities in planning stages
  - Assess future trends in consumption and demand for fuels
  - Assess impacts of these activities on coal liquefaction R&D.

SUMMARY OF REGULATIONS AND THEIR IMPACT ON TRANSPORTATION FUELS SPECIFICATIONS

	Regulation	Impact
Exhaust Emissions Standards:	Tier I (1993) and Tier II (2003) gm/mi Hydrocarbons 0.25 0.125 NO_x 0.4 0.2 CO 3.4 1.7	Extensive emissions testing required for all fuels
Fuel Volatility:	9-psi gasoline required in ASTM Class C areas in summer (1992)	Limit on volatility affects gasoline blending
Reformulated Gasoline:	Gasoline sold in 9 worst ozone areas by 1/1/95. Oxygen 2.0% min Aromatics 25% max Benzene 1% max	Gasoline composition specifications defined
Oxygenated Fuels:	Gasoline sold in CO nonattainment areas after 11/1/92 (4 mo/yr) must contain at least 2.7% O_2	Oxygenates required

SUMMARY OF REGULATIONS AND THEIR IMPACT ON TRANSPORTATION FUELS SPECIFICATIONS (Continued)

	Regulation	Impact
Clean Fuels/Vehicles:	EPA to certify vehicles operating on clean fuels and set emissions standards (within 18 mo.) Sales of alternative fuels and vehicles required in California (beg. 1995) Fleets of clean vehicles required (beg. 1997)	Clean fuels defined and standards set
Refueling Emissions:	Special nozzles on gasoline pumps plus on-board canisters to be phased in (1993)	
Mobile Source-Related Air Toxics:	EPA study required for benzene, formaldehyde, 1,3 butadiene, and polycylic organic material (POM) et al.	Further restrictions on composition vis-a-vis fuel emissions

Clean Air: Target Cities

The 96 cities and surrounding communities with the worst ozone smog problems and their deadlines for meeting federal standards:

CLASS: EXTREME
DEADLINE: Nov. 2010

Los Angeles

CLASS: SEVERE
DEADLINE: Nov. 2007

Baltimore
New York, nearby N.J. and Conn.

DEADLINE: Nov. 2005

Chicago, nearby Ind. and Wis.
Houston
Milwaukee
Muskegon, Mich.
Philadelphia, nearby N.J., Del. and Md.
San Diego

CLASS: SERIOUS
DEADLINE: Nov. 1999

Atlanta
Bakersfield, Calif.
Baton Rouge, La.
Beaumont, Texas
Boston, nearby N.H.
El Paso, Texas
Fresno, Calif.
Hartford, Conn.
Huntington, W.Va., nearby Ky. and Ohio
Parkersburg, W.Va., nearby Ohio
Portsmouth, N.H., nearby Maine
Providence, R.I.
Sacramento, Calif.
Sheboygan, Wis.
Springfield, Mass.
Washington, nearby Md. and Va.

CLASS: MODERATE
DEADLINE: Nov. 1996

Atlantic City, N.J.
Bowling Green, Ky.
Charleston, W.Va.
Charlotte, N.C., nearby S.C.
Cincinnati, nearby Ky. and Ind.
Cleveland
Dallas
Dayton-Springfield, Ohio
Detroit
Grand Rapids, Mich.
Greensboro, N.C.
Jefferson County, N.Y.
Kewaunee County, Wis.
Knox County, Maine
Louisville, Ky., nearby Ind.
Memphis, Tenn., nearby Ark. and Miss.
Miami
Modesto, Calif.
Nashville, Tenn.
Pittsburgh, Pa.
Portland, Maine
Raleigh-Durham, N.C.
Reading, Pa.
Richmond, Va.
Salt Lake City
San Francisco-Oakland-San Jose
Santa Barbara, Calif.
Smyth County, Va.
St.Louis nearby Ill.
Toledo, Ohio
Visalia, Calif.
Worcester, Mass.

CLASS: MARGINAL
DEADLINE: Nov. 1993

Albany, N.Y.
Allentown, Pa., nearby N.J.
Altoona, Pa.
Birmingham, Ala.
Buffalo, N.Y.
Canton, Ohio
Columbus, Ohio
Erie, Pa.
Essex County, N.Y.
Evansville, Ind., nearby Ky.
Fayetteville, N.C.
Greenbrier County, W. Va.
Greenville-Spartanburg, S.C.
Hancock County, Maine
Harrisburg, Pa.
Indianapolis, Ind.
Johnson City-Kingsport-Bristol, Tenn.
Johnstown, Pa.
Kansas City, Mo.-Kan.
Knoxville, Tenn.
Lake Charles, La.
Lancaster, Pa.
Lewiston, Maine
Lexington, Ky.
Lincoln County, Maine
Manchester, N.H.
Montgomery, Ala.
Norfolk, Va.
Owensboro, Ky.
Paducah, Ky.
Poughkeepsie, N.Y.
Scranton, Pa.
South Bend, Ind.
Stockton, Calif.
Sussex County, Del.
Tampa, Fla.
Waldo County, Maine
York, Pa.
Youngstown, Ohio-Sharon, Pa.

Gasoline Reformulation Progress

Industry Initiatives and Government Regulations

	Max. Rvp	Max. (vol.) Aromatics	Max. (vol.) Benzene	Max. Sulfur (ppm)	Min. (wt.) Oxygen
California	9.0	--	--	--	--
S. California - [Arco EC-1]	8.5	20%	1%	300	1.0%
Northeastern States [1]	9.0	--	--	--	--
Colorado	--	--	--	--	2.0%
• - [Diamond Shamrock RG-87]	8.5	20%	1%	300	2.0% [2]
• - [Conoco RXL]	8.5	25%	2%	300	2.5% [3]
• - [Phillips SC Unleaded Plus]	8.5	20%	1%	300	2.0% [2]
Chicago Metro	10.5	--	--	--	--
• - Amoco	9.5	--	--	--	--
Phoenix Metro	--	--	--	--	2.3%
Tucson Metro (non-mandatory)	--	--	--	--	2.3%
Las Vegas Metro	--	--	--	--	2.5%
Reno Metro	--	--	--	--	2.0%
Albuquerque/Bernalillo County	--	--	--	--	2.0%

[1] NESCAUM proposal adopted by MA, RI, CT, NY, ME and NJ. [2] Winter season; 1.0% in summer (May 16 - Sept. 15).
[3] Winter only. **Source:** *Octane Week* and Information Resources, Inc.

U.S. REFINERIES WILL DRASTICALLY ALTER THEIR REFINING PROCESSES BY YEAR 2000

- By the turn of the century, volatility restrictions to control ozone will greatly reduce butane blending to gasoline.

- Petrochemical operations, namely steam cracking for ethylene, will absorb some isomerization feedstock. Isomerate to the pool will be reduced.

- Fluid cat cracking conversion will be reduced via new catalyst technology, primarily to lower aromatics in the cracked distillate fraction used for diesel fuels blending. Increased demand for cracked diesel fractions also will reduce the percentage of cracked gasoline to the pool. However, new catalysts will raise the octane level of the gasoline from cracking. Isoamylenes in light cracked gasoline will become feedstock for TAME manufacture.

- Alkylate volume to the pool will be lower because isobutylene feed will be diverted to etherification. Further, some of the alkylate isobutane will be diverted to dehydrogenation to provide additional isobutylene for etherification.

- Reformer severity will be lowered to reduce the formation of light-ends. Volume to the pool will be about the same, but new catalyst technology will increase octane quality incrementally.

- To raise pool octane level to 92.5, 8.5% of MTBE, TAME, and ETBE combined would be required.

Example Unleaded Regular Blend
(Octane And Volatility Distribution)

	Cat Cracked	Alkylate	Reformate	Light S.R.	n-Butane	Blend
Composition, Volume Percent	34.0	16.0	40.0	5.0	5.0	100.0
Gravity, API	57.2	73.1	43.4	77.9	110.0	56.0
Reid Vapor Pressure, API	7.5	9.9	2.9	10.9	51.6	9.6
ASTM Distillation, F						
IBP	95	86	108	90	31	90
10%	126	157	196	115	31	126
20%	141	193	237	126	31	157
50%	214	210	287	148	31	242
90%	372	265	360	186	31	362
EP	430	340	435	258	31	428
(R+M)/2 Octane	85.0	93.7	90.0	63.0	91.9	87.5

Current and Projected Change in U.S. Gasoline Composition

	Volume Percent		
	1988	1995	Octane Range
Blending butanes	7.0	5.5	91-93
Light straight run	3.3	-	55-75
Isomerate	5.0	10.0	80-88
Cat cracked	33.5	34.5	84-89
Hydrocracked	2.0	1.5	85-87
Coker	0.6	-	60-70
Alkylate	11.2	12.5	90-94
Reformate	34.0	33.5	86-96
Ethers	1.4	2.5	106-110
Average clear octane	88.4	89.9	

Reformed Gasolines at Various Severities of Operation
(Octane vs Aromatics)

	Severity		
	Low	Mod.	High
API Gravity	57.9	51.1	45.3
ASTM Distillation			
IBP	93	122	100
10% Evap	139	170	166
50% Evap	221	248	269
90% Evap	313	328	343
EP	391	401	430
Aromatics, Vol%	26.0	43.0	57.0
Octane			
Research	76.6	85.1	97.4
Motor	71.8	77.7	86.1
(R+M)/2	74.2	81.4	91.8

---------Octane No. vs Light Hydrocarbon-----

Severity, RON clean	90	95
Gas Yield, scf/bbl chg		
Hydrogen	967	1015
Methane	55	73
Ethane	55	71
Liquid Yield, vol %		
Propane	3.6	4.9
Isobutane	1.8	2.4
n-Butanes	2.5	3.4
Pentanes Plus	85.6	81.9
Rvp, psi	2.7	3.1

USE OF OXYGENATES BY U.S. REFINERS TO REPLACE AROMATICS

- Petroleum refining industry has essentially removed ethanol and methanol plus cosolvents as oxygenated blending components. They prefer to use methanol and ethanol as MTBE or ETBE.

- MTBE has been widely accepted by U.S. refineries as the primary oxygenate and octane enhancer, with current on-stream capacity exceeding 100,000 BPD.

- ETBE cannot compete with MTBE without a tax subsidy. U.S. Treasury Department has approved extending the 60¢/gal subsidy for ethanol to ethanol used for ETBE production.

- Another ether that is destined to enter U.S. gasoline is TAME. TAME is derived from reacting methanol with isoamylenes. Isoamylenes are produced as part of the cat-cracker stream in finished gasoline. TAME is marketed in Europe as TAME gasoline, a mixture of TAME with light hydrocarbons.

- In the 1990's all three ethers will be used up to 2.5% by U.S. refineries as oxygenated components in gasoline.

OCTANE BLENDING VALUES AND BOILING POINTS OF AROMATICS

Aromatic	Research	Motor	(R+M)/2	Boiling Pt., °F
Benzene	106	88	97	176
Toluene	114	93	103.5	231
p-Xylene	120	98	109	281
m-Xylene	120	99	109.5	282
o-Xylene	105	87	96	291
Ethylbenzene	114	91	102.5	277
C_9 Aromatics	117	98	107.5	---
C_{10} Aromatics	110	92	101	---

OCTANE AND VOLATILITY CHARACTERISTICS OF SELECT OXYGENATES

	Blending Octane*			Blending	Boiling
	RON	MON	(R+M)/2	Rvp, psi*	Point, °F
Methanol	133	99	116	58-62	149
Ethanol	130	96	113	18-22	172
MTBE	118	100	109	8-10	131
ETBE	118	102	110	3-5	158
TAME	111	98	104.5	1-2	187

* Can vary with the hydrocarbon composition of gasoline

Projected Potential Market for New Oxygenate Components in 1995

Component	Production, bpd	Vol % to Gasoline @ 2.7 wt % O_2	Gasoline Market Captured bpd
MTBE	200,000 (committed)	14.8	1,350,000
ETBE	130,000 (committed)	17.2	760,000
TAME	100,000 (potential)	17.2	580,000
Additional Oxygenates**	773,000 (potential)	14.8-17.2	4,830,000
			7,520,000

**May be composed of additional growth in MTBE, ETBE, or TAME or new components such as mixed ethers.

Assumption: All U.S. gasoline must contain 2.7 wt percent oxygen (as ethers), either for emissions control purposes or to supply octane as aromatics are removed.

CHANGES IN DIESEL FUEL SPECIFICATIONS

- EPA concerned about diesel fuel sulfur and aromatics
- SO_x, NO_x, particulates, HC's all related to composition
- Current diesel S content about 0.25% (no present regulation)
- EPA proposed rules to limit diesel S content to 0.05%
- Aromatics may be limited by specifying the cetane number, 45 minimum
- New diesel-fuel standards in California for October 1993
    - S limited to 0.05%
    - Aromatics limited to 10% or 20%, depending on refinery size
- Refinery changes needed to meet new specifications.

U.S. ROAD TRANSPORTATION VEHICLE/FUEL TRENDS

NEAR TERM	MID-1990	LONG TERM
• Gasoline Volatility Reduction	Vehicle Evaporation Emissions Control	Advanced Clean Gasoline Fuel
• Oxygenated Fuels	Tighter Tailpipe Standards	Alternative Vehicles/Fuels
• Enhanced Inspection and Monitoring	Cold Temperature CO Standard	
• Refueling Emissions Controls	Non-Road Engines and Fuels	
• Clean Fuel Buses	Diesel Fuel Control	

ALTERNATE TRANSPORTATION FUELS

- **Methanol**
  - Energy efficiency (Btu/mile) equal to or greater than that of gasoline
  - Less NO_x, less CO, less reactive HC emissions than gasoline
  - More formaldehyde (catalysts being developed) and oxygenated HC (i.e., methanol -- less photochemically reactive)
  - California air quality studies indicate benefits in using methanol instead of gasoline
  - Neat methanol is a cleaner fuel than M85

- **Ethanol**
  - Very similar fuel to methanol
  - Slightly greater emissions compared to methanol
  - More expensive to produce than methanol

- **Natural Gas**
  - Less reactive HC, much less CO, less NO_x than gasoline
  - Total emissions of HC high (due to CH_4, 75-95% of HC emissions)
  - Aldehyde emissions, comparable to those from gasoline.

Fuel Property Comparison

Property	Methanol	Typical Gasoline	Estimated M-85
Combustion, wt %			
Carbon	37.5	87	44.9
Hydrogen	12.6	13	12.7
Oxygen	49.9	0	42.4
API Gravity	46.2	58.8	48.1
Lbs./gallon	6.63	6.19	6.56
Reid vapor pressure PSI	4.60	9-14	---
Boiling Range °F	149	86-410	86-410
Flammability Limits % vapor in air	6-36	1.4-7.6	----
Heat of Combustion (Lower), BTU/gal	58,800	115,000	67,300
(R+M)/2 Octane	100-116*	87-92	98-99
Stoichiometric Air-Fuel Ratio	6.47	14.5	7.67

* Blending value range in gasoline

IMPLICATIONS FOR COAL LIQUEFACTION R&D OF REGULATORY CHANGES AFFECTING TRANSPORTATION FUELS

- Identify coal liquid quality and composition and their relationship to processing conditions and feedstock characteristics.

- Develop new catalytic process for refining direct-liquefaction products into a blending component that could substitute for a petroleum-based aromatics stream.

- Integrate coal liquefaction process concepts (i.e., direct and indirect, oxygenate synthesis, etc.) into a coal refinery to produce coal-based transportation fuels.

- Establish emissions characteristics of coal-derived fuel components and their mixtures with gasoline.

- Focus catalyst and process research on direct synthesis of ethers (MTBE, ETBE, etc.) from coal-derived syngas.

- Develop lower-severity coal liquefaction process to produce fuel components better suited for future transportation fuel specifications.

- Develop specifications and process for producing high-density jet fuel from coal liquids.

- Produce additives from coal liquids for making neat methanol fuels.

DEVELOP IMPROVED ANALYTICAL TECHNIQUES AND OBTAIN MORE DATA ON THE COMPOSITIONS OF COAL LIQUIDS AND PRODUCTS

- Different liquefaction processes produce coal liquids with different properties
- Same process with different operating conditions can maximize specific product from syncrude to naphtha
- It will become more important in the future to understand coal liquid compositions
    - Coal liquid quality as related to product quality, both for gasoline blending components as well as coal liquid fuels
    - Coal liquid composition as related to potential emissions upon combustion
- Better analytical techniques suited to coal liquids need to be developed.

REPRESENTATIVE HYDROCARBON ANALYSES OF COAL LIQUIDS

Description Approximate Boiling Range, °F	ITSL Wyodak* 300-725	ITSL ILL. No. 6* 750°F EP	H-COAL ILL No. 6** 750°F EP	H-COAL Wyodak** 785°F EP
Hydrocarbon Type, LV % Saturates				
C(N)H(2N + 2) Paraffins	3.7	0.0	4.4	9.5
C(N)H(2N) Monocycloparaffins	9.5	11.0	11.9	27.0
C(N)H(2N - 2) Dicycloparaffins	7.3	7.7	8.4	9.1
C(N)H(2N - 4) Tricycloparaffins	4.7	5.5	19.9	10.4
Total Naphthenes	**21.5**	**24.2**	**40.2**	**46.5**
Total Saturates	**25.2**	**24.2**	**44.6**	**56.0**
Monoaromatics				
C(N)H(2N - 6) Alkylbenzenes	6.9	15.3	15.7	16.3
C(N)H(2N - 8) Benzocycloparaffins	7.5	10.7		
C(N)H(2N - 10) Benzodicycloparaffins	10.1	9.2	3.7	2.1
Diaromatics				
C(N)H(2N - 12) Naphthalenes	13.0	16.4	9.6	3.9
C(N)H(2N - 14)	6.3	6.5		
C(N)H(2N - 16)	14.2	9.2		
Triaromatics				
C(N)H(2N - 18)	9.6	4.6		
C(N)H(2N - 22)	5.1	2.3		
Tetraaromatics				
C(N)H(2N - 24)	0.0	0.0		
C(N)H(2N - 28)	0.0	0.0		
Total Aromatics	**72.6**	**74.2**	**55.4**	**44.0**
C(N)H(2N - 4) S Thiophenes	0.0	0.0		
C(N)H(2N - 10) Benzothiophenes	2.2	1.6		
C(N)H(2N - 16) S Dibenzothiophenes	0.0	0.0		
Total Sulfur Compounds	**2.2**	**1.6**		
% C	89.0	89.0	86.2	86.2
% H	10.5	10.7	11.3	12.7
0, ppm	3900	1800	18000	8500

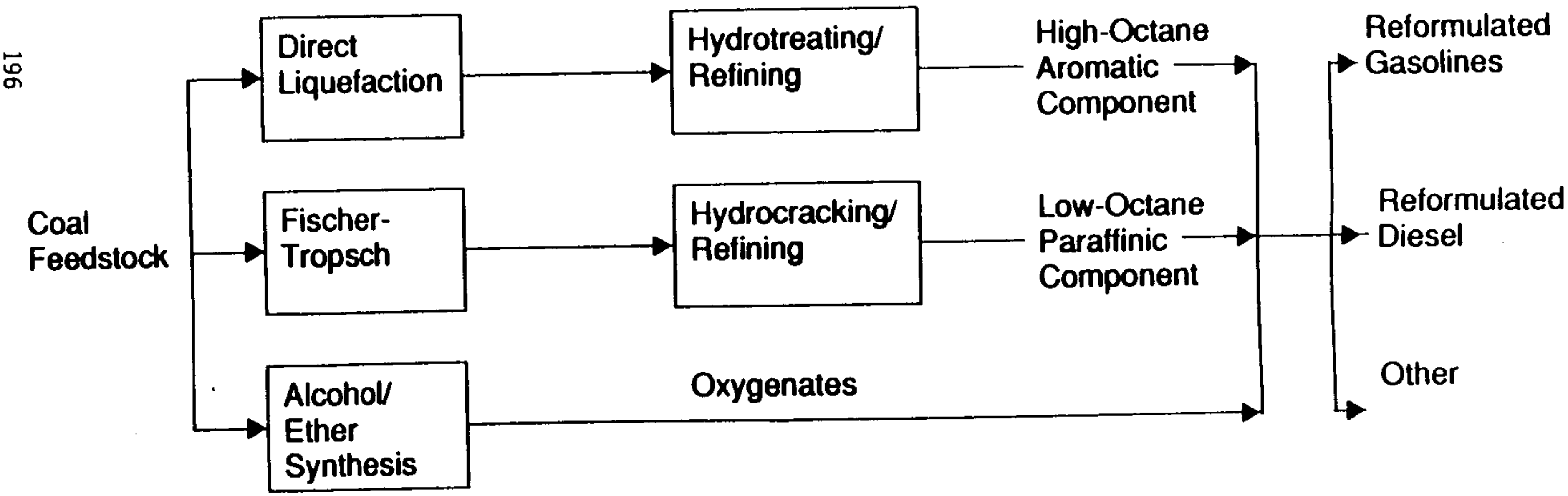
* 22-Component mass spectrometric analysis
** 9-Component mass spectrometric analysis

INTEGRATION OF COAL LIQUEFACTION PRODUCTS WITH PETROLEUM REFINING OPERATIONS

- Combine isobutanol produced from coal-derived synthesis gas with isobutane stream produced from n-butanes for MTBE production.
- Extract toluene and xylene components from coal liquids for refinery blending.
- Future changes in naphtha reforming operations can open an opportunity for substituting aromatic coal liquids as octane enhancers.
- Future shortages of H_2 in refining industry for product upgrading can be mitigated with H_2 from coal-derived synthesis gas.

MORE EXACTING SPECIFICATIONS WILL REQUIRE COAL LIQUEFACTION REFINERY TO PRODUCE NEW TRANSPORTATION FUELS

- Different processes produce different types of products which must be blended, perhaps with additives such as oxygenates.



- Different blending schemes (analogous to a petroleum refinery) need to be evaluated.

FUTURE TRANSPORTATION FUELS WILL COMPETE AND BE EVALUATED ON BASIS OF EMISSIONS

Background

- Typical Emissions Data (grams/mile)

Vehicle Type	Reactive HC			CO	NO_x
	Total	Exhaust	Evaporative		
Gasoline	0.39	0.35	0.04	1.40	0.66
Methanol	0.34	0.25	0.09	1.00	0.45
CNG	0.19	0.19	0	0.10	0.44
Electricity	0.006	0.006	0	0.008	0.07

Current Work

- Auto/Oil Industry Joint Research Program for Development of Cleaner-Burning Motor Vehicle Fuels

- Develop data regarding potential reduction in emissions and improvement in air quality from
  - Reformulated gasoline in existing vehicles
  - M85 in flexible-fuel vehicles
  - Future gasolines in future vehicles
  - Other alternative vehicle/fuel systems

- Fuel Variables
  - Gasoline -- aromatics, olefins, 90% temp, Rvp, MTBE
  - Other -- methanol, ethanol, ETBE

Impact on Coal Liquefaction

- Database needed on coal liquid compositions related to emissions -- both quantity and speciation

Atmospheric Reactivity and Vapor Pressure
(Hydrocarbons and Oxygenates)

Compound	Atmospheric Reactivity*	Blending Rvp, psi**
n-Butane	2.7	60
Isopentane	3.6	21
n-Pentane	5.0	16
Isohexane	5.0	7
n-Hexane	5.6	5
Benzene	1.3	3
Toluene	6.4	0.5
M-xylene	23.0	0.3
Butene-2	65.0	50
Pentene-1	30.0	16
2-Methyl 2-Butene	85.0	15
Methanol	1.0	60
Ethanol	3.4	18
MTBE	2.6	9

*Gas phase reaction rate with the hydroxyl (OH) radical.
**Values will vary with blendstocks.

POTENTIAL CONCEPTS FOR PRODUCING ETHERS FROM COAL-DERIVED SYNGAS

ETHER PRODUCT	CATALYST	CONDITIONS	SELECTIVITY
Isobutanol (MTBE)	Cu/ZnO/Al_2O_3 promoted with K, Ce	300°C, 10-13 MPA	25%
Isobutanol (MTBE)	Zr/Zn/Mn/Li/Pd	327°-477°C, 10 MPA	60%
MIBE	Rafion-H resins	160°C, 7.6 MPA	42%
DME	Cu/ZnO, Gamma Alumina	292°-300°C, 6 MPA	97%

A UNIQUE MARKET FOR COAL-DERIVED TRANSPORTATION FUELS IS HIGH-DENSITY JET FUEL

- Current fuels are paraffinic (based on petroleum)
  - low density and volumetric heat content (PAR<NAP<ARO)
  - poor fluidity properties (high freezing point, high viscosity)

- Naphthenic fuels have significant advantages
  - high volumetric heat content
  - good fluidity properties
  - low volatility (reduced emissions) and high flash point (safety)
  - acceptable flame characteristics
  - minimum changes in fuel specifications
  - suitable for both jet and diesel engines as a "unifuel"

- Coal has better properties as feedstock for jet fuel
  - aromatics (2- and 3-ring) in abundance
  - coal liquids easily converted to wholly naphthenic fuel

- Economic studies show that coal liquids are more economical to refine than future heavy crudes.

METHANOL FUEL ADDITIVES

An Alternate, Higher Value-Added Route to Introducing Coal Liquid Components into Nation's Fuel Supply

<u>Background</u>

- Neat methanol (M100) has many advantages for achieving low emission levels
- Problems with M100
  - Difficult vehicle cold starting, especially at low ambient temperatures
  - Poor fuel lubricity
  - Flammability of saturated vapors in storage tanks
  - Low flame luminosity
  - Toxicity by inhalation, absorption through the skin, or ingestion.
- Additives proposed to alleviate these problems

<u>Current Work</u>

- Work being done by Southwest Research Institute sponsored by California
- Additive nominees
  - 2.2 vol % butane
  - 2.8 vol % toluene
  - 0.12 wt % lubricity additive
  - 0.0012 wt % Bitrex
  - 0.007 wt % odorant

<u>Potential</u>

- Use aromatic coal liquid component in place of toluene to address flammability limits, luminosity, possible odorant