Assessment of Criteria Pollutant Emissions from Liquid Fuels Derived From Natural Gas

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NOTICE

EXECUTIVE SUMMARY

The National Renewable Energy Laboratory (NREL) has been asked by the U.S. Department of Energy (DOE) to evaluate emissions of criteria pollutants by diesel fuels produced from natural gas, particularly those produced through variations of the Fischer-Tropsch (F-T) process. The Fischer-Tropsch process is defined as “a hydrogenation of oxides of carbon producing higher hydrocarbons and/or alcohols, the carbon chains of the molecules being predominantly straight and in the range of C_4 and larger.”(1) NREL’s analysis is limited to diesel fuels produced through the F-T process; other gas-to-liquid (GTL) products such as dimethyl ether, methanol, and diglyme, for example, are excluded. DOE expects to initiate a rulemaking to determine if F-T diesel fuels should be designated as alternative fuels under sec. 301(2) of the Energy Policy Act of 1992, which requires among other findings, a finding that the fuels provide “substantial environmental benefits.” Differences in tailpipe emissions of criteria pollutants are a key determinant of overall environmental impacts. It has been suggested that reductions of such tailpipe emissions could be a basis for a finding that the natural gas derived F-T diesel fuels offer substantial environmental benefits.

DOE’s rulemaking is in response to three petitions received by DOE, one from a producer of natural gas-based diesel fuels (Mossgas Pty. Ltd.), and two from developers of technologies related to potential production of F-T diesel fuels (Rentech, Inc. and Syntroleum Corp.)

Key Conclusions

Based on limited data, and consistent with expectations based on fuel properties, F-T diesel fuels appear to provide emission benefits. Distillate produced directly from the Mossgas F-T reactor accounts for only 28%-32% of the total Mossgas diesel. Some 60%-68% of the Mossgas diesel fuel is produced by reforming lighter olefinic hydrocarbons produced by the F-T synthesis into diesel-like distillate paraffinic and aromatic hydrocarbons (“conversion of olefins to distillate,” or “COD,” hence the process will be referred to herein as “F-T/COD”). The F-T and F-T/COD data was insufficient to make quantitative estimates of the emission reductions for the in-use fleet with any statistical significance, but NREL was able to make what it believes to be conservative estimates of potential NO_x reductions based on fuel properties. Conclusions from the data analysis, along with caveats and a discussion of data limitations are summarized below.

- Fischer-Tropsch diesel fuels can be used in conventional vehicles without modification to the engine or fueling system. Thus, alternative fuel vehicles (AFVs) have not been developed for F-T diesel fuel. Emission benefits must be considered based on results for use in conventional vehicles.

- Diesel fuels produced through the F-T processes are typically ultra-low sulfur fuels. Many of these fuels have very low levels of aromatic compounds and very high cetane numbers. However, F-T diesel fuels with aromatic levels and cetane numbers similar to conventional diesel fuel are also possible.

- Research with conventional diesel fuel has shown emission reductions with increasing cetane number and decreasing aromatic content. A reduction in aromatic content from 30% to 10% in conventional diesel fuels has resulted in 0%-5% reductions in the NO_x emission. A cetane number increase of 10 in conventional diesel fuels causes a 2%-5% reduction in NO_x emissions. For F-T diesel fuel, the cetane number is greater than 74, 30 or more points higher than conventional diesel fuel. The aromatic content of F-T fuels is typically zero but can be as high as 10%, compared to 30% for conventional diesel. Thus, the estimated NO_x reduction from Fischer-Tropsch diesel fuel, based on the cumulative effects from decreasing aromatic content to below 10% and increasing cetane number over 74, may range from 6%-20%. Indeed, there are examples in the cited literature showing 20% lower NO_x emissions for F-T diesel fuel versus conventional diesel fuel in certain engines.

- The correlation of diesel fuel properties to particulate matter (PM), hydrocarbons (HC), and carbon monoxide (CO) emissions is less robust. The vast majority of studies found little to no influence on PM, HC, and CO emissions from changes in diesel fuel properties, with the exception of fuel sulfur or addition of oxygenates. Reductions in aromatic content and increases in cetane number can conservatively be expected to have no effect on PM, HC, and CO emissions.

- Test vehicles and engines representing engine and emissions systems that will meet EPA's post-2004 and post-2007 emission standards are not presently available. Emission reductions from F-T based fuels are expected to be lower on those engines than on current generation engines, because the use of exhaust cleanup technologies will be required on virtually all on-highway engines to meet the new heavy-duty emissions standards. A fuel with a very low sulfur content, such as provided by F-T fuel, is required in order for these technologies to be used.

- Currently in the United States, on-highway diesel fuel contains a maximum of 500ppm sulfur. In 2006, diesel fuel for on-road use will be capped at 15ppm sulfur, over a 90% reduction. F-T diesel fuels share ultra-low sulfur content with these ”future fuels”. A limited set of data exists comparing F-T diesel fuels and 2006-like ultra-low sulfur diesel (ULSD) fuels. For this small set of data, F-T diesel fuels offer additional emission benefits compared to ULSD for a select set of vehicles and engines.

- A limited amount of test data were submitted by each petitioner, comparing F-T diesel fuels to No. 2 diesel, all of which showed reductions of PM and NO_x with the F-T diesel fuels. None of the petitions included data sets representative of the overall U.S. diesel vehicle population, nor did any include enough separate observations to estimate overall emissions reductions with statistical significance. In the NREL analysis, the petition data was augmented with other published studies on emissions of F-T diesel fuels. This aggregated data set showed regulated emission reductions in nearly every case. However, the data does not include a sufficient variety and quantity of data to quantitatively estimate emissions reductions for the current and future in-use diesel vehicle fleet. Nevertheless, mean emissions reductions were calculated for this data set and on average NO_x emissions decreased by 13%, PM emissions decreased by 11%, CO emissions decreased by 28%, and HC emissions decreased by 22% compared to conventional diesel fuel.

- For the aggregated data set (petitioner submitted data and data from the published studies), a non-parametric test was used to determine if exhaust emissions for F-T diesel fuel could be said to be greater than, less than, or equal to conventional diesel fuel emissions with any degree of significance. The aggregated data set contained at least 50 data points representing emissions from 30 different vehicles and engines, with an average model year of 1993 (range from 1983 to 1999). The analysis shows that all regulated emissions are lower for F-T diesel fuel with greater than 99% confidence. The aggregated data was not a representative sample of the total diesel vehicle population.

- No data have been provided by the petitioners and none identified by NREL relating to durability emissions testing or materials compatibility testing on the F-T diesel fuels. Low sulfur, low aromatic diesel fuels (including F-T) are well known to have low lubricity, which can lead to excessive wear in fuel pumps and in some injector designs. The increased wear in fuel injection equipment can lead to emission deterioration over time. Some commercially-available lubricity additives have been shown to be effective at low treat rates, and additized F-T fuels are able to meet manufacturer specifications for fuel lubricity.

- Test fuels employed in the petitions were not necessarily representative of production from any proprietary process in future plants as distinct from other F-T diesel fuels. The Mossgas

F-T/COD process is fundamentally different from F-T diesel fuel, however, and its fuel shares the beneficial properties of F-T diesel fuel only in part. Mossgas has improved fuel cold flow properties and otherwise attempted to make their F-T diesel fuels more similar to conventional diesel fuel by using post-processing to convert n-alkanes to isoalkanes and aromatic compounds. In doing so, they have traded some environmental benefit relative to 100% F-T diesel fuels.

ABBREVIATIONS AND ACRONYMS

AFV	Alternative fuel vehicles
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
CARB	California Air Resources Board
CBD	Central Business District
CFPP	Cold filter plugging point
CO	Carbon monoxide
COD	Conversion of olefins to distillate
DDC	Detroit Diesel Corporation
DECSE	Diesel Emission Control-Sulfur Effects
DOE	Department of Energy
EGR	Exhaust gas recirculation
EPA	U.S. Environmental Protection Agency
EPAct	Energy Policy Act of 1992
FBP	Final boiling point
FIA	Fluorescent indicator adsorption
F-T	Fischer-Tropsch
FTP	Federal Test Procedure
GM	General Motors
GTL	Gas-to-liquid
H/C	Hydrogen to carbon ratio
HC	Hydrocarbons
HD	Heavy-duty
HHV	Higher heating value
IBP	Initial boiling point
IP	Institute of Petroleum (UK)
LD	Light-duty
LHV	Lower heating value
LSHC	Low-sulfur highly hydrocracked diesel fuel
LTFT	Low temperature flow test
min.	Minimum
max.	Maximum
NO_x	Nitrogen oxides
NREL	National Renewable Energy Laboratory
PM	Particulate matter
PNA	Polynuclear aromatic hydrocarbons or poly-aromatic hydrocarbons
R&D	Research and development
SFC	Supercritical fluid chromatography
ULSD	Ultra-low sulfur diesel
VW	Volkswagen
WOT	Wide open throttle

UNITS OF MEASURE

° API	Degrees API
°C	Degrees Celsius
cSt	Centistoke
ft-lb	Foot-pound
g/BHP-hr	Grams per brake horsepower hour
g/mi	Grams per mile
g/ml	Grams per milliliter
g/test	Grams per test
L	Liter
mass%	Percent mass
MJ/kg	Megajoule per kilogram
mg/100ml	Milligrams per 100 milliliters
mm	Millimeters
µ	Microns
ppm	Parts per million
psi	Pounds per square inch
rpm	Revolutions per minute
vol%	Percent volume

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INTRODUCTION

Fischer-Tropsch (F-T) diesel fuel has been produced for more than half a century. In 1926, Franz Fischer and Hans Tropsch patented a process, which bears their names, to convert synthesis gas (CO and H_2) to liquid hydrocarbons (2). Historically, the use of F-T fuels has been relatively limited, however Germany refined the F-T process to produce liquid fuels during WWII and South Africa has successfully used domestic resources to produce F-T fuels.

Several companies currently produce F-T diesel fuels. Sasol, a South African company, has been producing Fischer-Tropsch fuels from coal since the 1950's. Mossgas, another South African company, began producing F-T diesel fuels from natural gas in 1992. Shell has been operating a commercial facility in Malaysia since 1993 using natural gas as a feedstock. Other smaller companies have produced Fischer-Tropsch diesel fuels with varying levels of success. Syntroleum, Rentech, Exxon, Mobil, ARCO, and others have produced, at various times, limited quantities of F-T diesel fuel (3).

The National Renewable Energy Laboratory (NREL) has been asked by the U.S. Department of Energy (DOE) to evaluate emissions of criteria pollutants from diesel fuels produced from natural gas through variations of the F-T process. Other GTL products such as dimethyl ether, methanol, and diglyme, for example, are excluded in the analysis. DOE expects to initiate a rulemaking to determine if F-T fuels should be designated as alternative fuels under sec. 301(2) of the Energy Policy Act of 1992, which requires among other findings, a finding that the fuels provide "substantial environmental benefits." Differences in tailpipe emissions of criteria pollutants are a key determinant of overall environmental impacts. It has been suggested that reductions of tailpipe emissions could be a basis for a finding that the natural gas derived diesel fuels offer substantial environmental benefits.

DOE's rulemaking is in response to three petitions received by DOE, one from a producer of natural gas based diesel fuels (Mossgas Pty. Ltd.), and two from developers of technologies related to potential production of such fuels (Rentech, Inc. and Syntroleum Corp.). The two petitions received from the technology developers relate specifically to processes that produce the diesel fuel streams directly from the reaction of the synthesis gas (produced from natural gas by reforming), and maximize diesel fuel within the product stream. Well-established refining processes are used to separate the diesel fuel from other hydrocarbon products and assure diesel fuel quality. These processes are referred to herein as F-T diesel fuel. A number of other companies are also engaged in developing such processes and/or producing such fuels. The Mossgas petition is for fuel from Mossgas's existing plant, which produces a broader slate of hydrocarbons from the F-T synthesis. Distillate produced directly from the Mossgas F-T reactor accounts for only about 28-32% of the total Mossgas diesel. Some 60%-68% of the Mossgas diesel fuel is produced from reforming of lighter olefinic hydrocarbons produced by the F-T synthesis into diesel-like distillate paraffinic and aromatic hydrocarbons ("conversion of olefins to distillate," or "COD," hence the process will be referred to herein as "F-T/COD").

STATUS OF FISCHER-TROPSCH and HIGH QUALITY DIESEL FUELS

GTL and Fischer-Tropsch Fuel Properties

Most states require that conventional diesel fuels meet the ASTM D975 property specifications. Diesel fuels are produced from a variety of crude sources and refinery techniques. The D975 specifications are used as a guideline for limits on several diesel fuel properties. Table 1 gives the fuel property requirements for No.2 low sulfur diesel fuel.

Table 1. ASTM D975 No.2 Low Sulfur Diesel property requirements

Property	ASTM Test Method	No.2 Low Sulfur Diesel
Flash Point, °C, min.	D93	52
Water and Sediment	D1796	--
Distillation Temperature, °C, T90	D86	282[a]
Kinematic Viscosity, cSt at 40°C, min./max.	D445	1.9/4.1
Ash, mass%, max.	D482	0.01
Sulfur, mass%, max.	D2622	0.05
Copper Strip Corrosion, 3h at 50°C	D130	No. 3
Cetane Number, min.	D613	40[b]
One of the following must be met :		
(1) Cetane Index, min.	D976	40
(2) Aromatics, vol%, max.	D1319	35
Cloud Point, °C, max.	D2500	[c]
Carbon Residue, 10% bottoms, Mass%, max.	D524	0.35

a: If the cloud point is less than –12°C, the T90 requirement shall be waived, the minimum flash point shall be 38°C, and the minimum viscosity shall be 1.7 cSt.

b: Low ambient temperature or high altitude operation may require higher cetane numbers.

c: The cloud point will be determined by the region where the fuel is used.

A review of the technical literature found data for several F-T diesel fuels; Table 2 gives the properties for these fuels. A blank entry in the table indicates the property was not reported. When reported in the literature, the properties of conventional diesel fuel are also shown, as a comparison to the F-T and GTL diesel fuels. In Table 2, “2D” is conventional No.2 diesel fuel, “CARB” refers to diesel fuel meeting the California Air Resources Board requirements for sale in California, “Cert. Diesel” is EPA Certification diesel fuel, and “10% Aro.” is nominally 10% aromatic content diesel fuel. Data from the test fuels in the petitions to DOE have also been included.

Typically, the density, sulfur content, and aromatic content are lower in F-T diesel fuels relative to conventional diesel fuels. The viscosity, distillation temperature, and energy content are similar for conventional diesel fuel and F-T diesel fuels. With the exception of the Mossgas F-T/COD fuel, F-T diesel fuels have cetane numbers much higher than typical diesel fuels. The cetane number of F-T diesel fuels is often reported as >74. This is because common practice in measuring cetane number is to use an upper cetane number standard with a value of 74. The actual cetane number of Fischer-Tropsch diesel fuels could be even higher than 74, the typically reported value, and for certain fuels composed entirely of normal paraffins could be as high as 100.

Fuel property data in Table 2 for several F-T diesel fuels from Sasol, Shell, and Exxon-Mobil gives an indication of the variability of the products. The Sasol diesel fuels vary in the aromatic and sulfur content because they were produced using two different low temperature slurry phase distillate processes. The Shell Fischer-Tropsch diesel fuels are very similar. The Exxon-Mobil diesel fuels are examples of different cuts of the refinery stream, as seen in the range of distillation temperatures. Variations in fuel properties cannot be attributed only to differences between fuel producers, but are also strongly related to the operating conditions and post-processing of the fuel.

As fuel properties change, exhaust emissions may also change. Limited work has been performed with Fischer-Tropsch diesel fuels to study the effect of changing fuel properties and the resultant emissions effects. However, a comparatively large amount of work has been done to examine the effect of conventional diesel fuel properties on the emissions. The results from conventional diesel fuel R&D can be used to make inferences about the potential environmental benefits of F-T diesel fuel and to try to predict how product variations can be expected to change engine out emissions. Previous diesel fuel studies found that the most important fuel properties were sulfur content, density, distillation temperature, cetane number, and aromatic content.

Table 2. Properties of Fischer-Tropsch, GTL, and conventional diesel fuels. Fuels are grouped together to show fuels compared side-by-side in the emissions studies discussed below.

Property	**Method**	**Sasol** [4,5]	**Sasol** [4]	**CARB** [4]		**Sasol** [11]	**CARB** [11]	**2 D** [11]		**"F-TA"**[14]	**"F-TB"**[14]	**10% Aro.** [14]
Density, 15°C	ASTM D4052	0.7769	0.7779	0.8303		0.7698	0.8342	0.8450			0.7823	0.8245
API Gravity	ASTM D287	50.6	50.3	38.7		52.3	38.1	36.0		51.8	49.3	40.1
Distillation, °C	ASTM D86											
IBP		189	185	203		159	204	182		163.9	227.7	194.5
10%		209	208	218		181	217	214		183.3	255.7	209.0
50%		256	257	249		244	246	257		243.9	290.2	247.4
90%		331	332	290		334	309	308		332.2	324.2	307.1
95%												334.4
FBP		356	358	351		352	342	334		352.2	335.3	343.9
Flash Point, °C	ASTM D93					59	77	72		59	101	72
Viscosity, 40°C (cSt)	ASTM D445	2.43	2.42	2.42		2.08	2.52	2.41		2.08	3.35	2.45
Cetane Number	ASTM D613	> 73.7	73.3	49.4		> 74.8	52.6	46.2		> 74	> 74	50
Cetane Index												
Sulfur, ppm	ASTM D4294	10 **	20 **	280		< 5 **	130	300				
	ASTM D5453									3.5	< 1.0	19
SFC Aromatics (vol%)	ASTM D5186	2.68	2.46	9.91		0.7	9.5	24.5		0.60	0.16	10.9
PNA						0.12	1.04	5.46		0.11	0.05	2.5
FIA Aromatics	ASTM D1319											
Aromatics										0.7	0.6	9.9
Olefins										1.2	0.6	3.5
Saturates										98.1	98.8	86.6
C, H, O, mass%	ASTM D5291											
Carbon										84.8	84.9	86.2
Hydrogen						15.1				15.2	15.1	13.8
Nitrogen												
Oxygen			0.3							~ 0	~ 0	~ 0
Cloud Point, °C	ASTM D2500					-19	-31	-19		-20	1	-18
CFPP, °C	IP309					-25	-40	-22		-28		
LTFT, °C	ASTM D4539									-20		-28
H/C ratio, mol/mol						2.14						
HHV, MJ/kg	ASTM D240					46.7	45.9	45.3		47.1	47.1	46.1
LHV, MJ/kg	ASTM D240									43.9	43.9	43.2

* below detection limit

** Fuel sulfur was determined by ASTM D4294. This method is appropriate for fuels with a sulfur level of 150 ppm or higher. It has been recommended that this method no longer be used for determining fuel sulfur in ultra-low sulfur diesel fuel.

Table 2, continued. Properties of Fischer-Tropsch, GTL, and conventional diesel fuels. Fuels are grouped together to show fuels compared side-by-side in the studies emissions discussed below.

Property	Method	Syntroleum [8]	Syntroleum [12]	Mossgas [9]	2D [9]	ExxonMobil [16]					Unknown Source [7]	2D [7]
						Typical F-T	280-700 Cut	300-700 Cut	280-800 Cut	280-900 Cut		
Density, 15°C	ASTM D4052			0.8042		0.731	0.768	0.772	0.778	0.785	0.7845	0.838
API Gravity	ASTM D287			44.0								
Distillation, °C	ASTM D86											
IBP				229.9	188	194	136	173	174	174		
10%				235.3	212	231						
50%				254.7	256	286	252	257	273	291		
90%				323.7	307	327						
95%							330	332	375	390		
FBP				361.2	331	338						
Flash Point, °C	ASTM D93			97		60	41.1			69.5		
Viscosity, 40°C (cSt)	ASTM D445	1.92	2.2	2.98		2.66					3.57	
Cetane Number	ASTM D613	>64	>67	48.9		74	70	71.8	71.8		73.7	
Cetane Index	ASTM D4737						80.2	81.0	80.2	82.3		
	ASTM D976											48.7
Sulfur, ppm	ASTM D5453			< 10								350Ŧ
	ASTM D129										< 50**	
	ASTM D2622					0	0	0	0	0		
SFC Aromatics (vol%)	ASTM D5186			9.18		0.26	0	0	0	0	0.1	24.7
PNA				0.21								
FIA Aromatics	ASTM D1319											
Aromatics					24.7							
Olefins					1.5							
Saturates					73.8							
C, H, O, N, mass%	ASTM D5291											
Carbon				83.95	86.11						84.91	86.11
Hydrogen				14.43	13.37						14.94	13.37
Nitrogen					< 0.03							
Oxygen				1.59								
Cloud Point, °C	ASTM D2550			< -60			-36	-36	-33			
CFPP, °C	IP309						-45	-46	-33	-15		
LTFT, °C												
H/C ratio, mol/mol												
HHV, MJ/kg	ASTM D240			46.8	~45.7							
LHV, MJ/kg	ASTM D240			43.7	~43.0						43.9	43.1

** Sulfur was determined using ASTM D129. This method is used for the determining sulfur in petroleum products with greater than 100ppm sulfur. Additionally, the method is known to have a bias of 50 ppm higher than the actual fuel sulfur level.

Ŧ Typical Specification

Table 2, continued. Properties of Fischer-Tropsch, GTL, and conventional diesel fuels. Fuels are grouped together to show fuels compared side-by-side in the emissions studies discussed below.

Property	Method	Shell [6,10,15]	CARB [6]	2D [10]	Cert. Diesel[15]	10% Aro.[15]	Unknown Source [13]	CARB [3]	Typical Syntroleum	Typical Mossgas RFD1	Typical Mossgas RFD2	Typical Mossgas RFD3	Typical Rentech
Density, 15°C	ASTM D4052	0.7845	0.8337	0.8473	0.8476	0.8302	0.7803	0.8379	0.771	0.8125	0.8103	0.8102	
API Gravity	ASTM D287	54							52.0				
Distillation, °C	ASTM D86												
IBP		210	175	173	177.8	179.4	222	191	160	221.7	225.8	81.3	
10%		260	213	237	217.2	216.1	257	215	199	236.6	235.8	238.5	
50%		600	268	299	267.8	247.8	288	253	256	254.9	255.3	250.8	
90%		331	332	336	315	315	324	308	316	322.5	324.0	317.5	
95%				347									
FBP		338	363	358	338.9	347.8	337	330	350	360.4	362.6	363.3	
Flash Point, °C	ASTM D93	72			67	57.2	98	72	64	100.5	102.5	20.0	74
Viscosity, 40°C (cSt)	ASTM D445	3.57		3.97	2.7	2.5	3.204	2.457	2.1	2.784	2.781	2.175	1.96
Cetane Number	ASTM D613	> 74	53.7	49.1	47.4	48.2	81.1	48.4	> 74	53.0	49.4	49.3	
Cetane Index	ASTM D4737				48.3	49.4							67
Sulfur, ppm	ASTM D5453	*		98	430	57	0	175	*	< 10	< 10	< 10	< 0.001
	ASTM D129		100										
SFC Aromatics (vol%)	ASTM D5186	0.3		16.32			1.2	20.1		16.4	15.6	15.9	< 10
PNA		0.2	18.1	4.09			0.0	5.1		< 0.1	< 0.1	< 0.1	
FIA Aromatics	ASTM D1319												
Aromatics		0.1			31.9	7.5			*				
Olefins		0.1			1.5	2.1			*				
Saturates		99.8			66.6	90.4			> 99				
C, H, O, N, mass%	ASTM D5291												
Carbon		84.91					84.77	86.48					
Hydrogen		14.97					15.12	13.48					
Nitrogen		0.67						9					
Oxygen		~ 0					0.11	0.05					
Cloud Point, °C	ASTM D2500	3			-16	-29	0	-24	< -17				
CFPP, °C		0								-25	-23	-24	
LTFT, °C													
H/C ratio, mol/mol													
HHV, MJ/kg	ASTM D240	47.2	45.7				43.9	45.9		46.5	47.3	45.9	47.8
LHV, MJ/kg	ASTM D240	44.0	42.9				47.2	42.6					

*below detection limit

Table 2, continued. Properties of Fischer-Tropsch, GTL, and conventional diesel fuels. Fuels are grouped together to show fuels compared side-by-side in the emissions studies discussed below.

Property	**Method**	**Fuels Tested in Syntroleum Petition**					**Fuel Tested in Mossgas Petition**			
		Syntroleum [39]	**Swedish City 1** [39]	**CARB** [39]	**2D** [39]		**2D**	**Mossgas RFD**	**Mossgas COD**	**Rentech**
Density, 15°C	ASTM D4052	0.7716	0.8194	0.8341	0.8455					0.7753
Density, 20 °C								0.8055*	0.8007*	
API Gravity	ASTM D4052	51.90	41.2	38.1	35.86		37.4			51.0
Distillation, °C	ASTM D86									
IBP							187			186
10%							212			212
50%							255			245
90%							306	319.8	321.1	309
95%							318	> 365	360.8	
FBP							331			318
Flash Point, °C	ASTM D93							95	100	77
Viscosity, 40°C (cSt)	ASTM D445							2.710	2.974	2.01
Cetane Number	ASTM D613	73.6	52.4	51.4	46.7			53.3	51.4	
Cetane Index	ASTM D976	74.1	50.1	47.9	46.6		48.7			73
Sulfur, ppm	ASTM D2622	0.5	<10	155	300			< 10	< 10	
	ASTM D129									< 0.01**
SFC Aromatics (vol%)	ASTM D5186	0.7						16.9	10.1	
PNA		0.08								
FIA Aromatics	ASTM D1319									
Aromatics		0.6	3.7	8.1	28.3		24.7			3.9
Olefins		0.8	1.7	1.8	1.4		1.5			5.8
Saturates		98.6	94.6	90.1	70.3		73.8			90.3
C, H, O, N, mass%	ASTM D5291									
Carbon							86.11	83.98		
Hydrogen							13.37	14.46		
Nitrogen							< 0.03			
Oxygen								1.59		
Cloud Point, °C	ASTM D2500							-15	< -36	
CFPP, °C										
LTFT, °C										
H/C ratio, mol/mol										
HHV, MJ/kg	ASTM D240	47.2	46.2	46.0	45.5		48.5	46.6		48.0
LHV, MJ/kg	ASTM D240	44.0	43.2	43.1	43.9		45.5	43.5		

** Sulfur was determined using ASTM D129. This method is used for the determining sulfur in petroleum products with greater than 100ppm sulfur. Additionally, the method is known to have a bias of 50 ppm higher than the actual fuel sulfur level.

Fuel Property Effects on Diesel Exhaust Emissions

Sulfur Content

Fuel sulfur is emitted as engine out SO_2 by diesel engines. The SO_2 may further oxidize to SO_3 and rapidly combine with water to form sulfuric acid in the exhaust. Sulfuric acid forms droplets that are collected on the particulate matter (PM) filter and thus contribute to PM emissions in engines without aftertreatment. PM samples are analyzed for sulfate to determine the magnitude of the sulfuric acid emission. Approximately 1%-2% of the fuel sulfur is converted to engine out sulfate emissions (17). The fuel sulfur to sulfate conversion is independent of the amount of sulfur in diesel fuel, thus reductions in fuel sulfur correspond to reductions in the sulfate fraction of the PM emission (17) for engines without aftertreatment.

Diesel PM is nominally composed of soot, sulfate, and particle-bound organic matter (17). Large PM emission reductions were observed when on-road fuel sulfur was decreased from 3,000 ppm to 500 ppm in the early 1990s (17). Reductions below 500 ppm fuel sulfur can further lower PM emissions, but with diminishing returns as sulfur content becomes very low. (18, 19)

Due to ever stricter emissions standards, diesel engine manufacturers are being required to reduce exhaust emissions. In addition to reducing engine-out sulfate emissions, several technologies for reducing emissions are enabled by fuel with ultra-low sulfur content (<15 ppm) and these are discussed below.

Exhaust gas recirculation (EGR) systems are used to reduce engine out NO_x emissions and may face durability issues in heavy-duty diesel engines, even with low (<500 ppm) sulfur fuel. The corrosiveness of the sulfuric acid formed from sulfate in the exhaust can significantly shorten the life of the EGR system and other engine components (17). Thus, the more sulfur in the fuel, the greater the risk of EGR system corrosion. Using ultra-low sulfur diesel fuels and management of the engine control system lessens this problem.

Exhaust aftertreatment systems such as diesel particle filters, NO_x adsorbers, and catalysts are also sensitive to fuel sulfur level. The DOE sponsored Diesel Emission Control-Sulfur Effects (DECSE) program examined the effect of fuel sulfur (3, 16, 30, 150, and 350ppm fuels) on several types of exhaust aftertreatment technologies, including oxidation catalysts, particle filters, NO_x adsorbers, and lean NO_x catalysts (20).

Diesel oxidation catalysts and diesel particle filters both contain catalytic metals whose function is to cause combustion of soot and organic matter (21). However, these oxidation catalysts can also convert SO_2 to SO_3, leading to an increase in the sulfate emission (17). For properly designed diesel oxidation catalysts, a significant reduction in particle bound organic matter can be obtained without increasing sulfate emissions, even for diesel fuels with sulfur levels of 500ppm. For catalyzed diesel particle filters, the increase in the sulfate emission for 500ppm sulfur fuel can negate the advantages of soot and organic compound combustion by the aftertreatment system. Very low fuel sulfur content, typically 30ppm and less, is required to obtain the PM emission reductions possible with PM filters.

Fuel sulfur has not been shown to affect the engine-out HC and CO emissions from diesel engines (19). The DECSE program found small effects of fuel sulfur on HC emissions, but these effects were not statistically significant (20). Even with a diesel oxidation catalyst, the effect of changing fuel sulfur on the HC and CO emissions was negligible.

NO_x adsorber durability was found to diminish with increasing fuel sulfur content. At fuel sulfur levels as low as 3 ppm, the performance of a NO_x adsorber was found to deteriorate (20). This occurred because the catalyst/sorbent used in these technologies is also active for SO_2 to SO_3 oxidation. Therefore, the SO_3 formed poisons the surface sites that are active for adsorption and reduction of NO_x.

The DECSE program has effectively shown that the lower the diesel fuel sulfur content, the larger the regulated emissions reductions possible for the types of diesel aftertreatment devices studied. Ultra-low sulfur diesel fuels may also enable passive regeneration or less frequent active regeneration of trap and filter devices. Fischer-Tropsch diesel fuels have near zero sulfur levels. The very low sulfur content of these fuels causes reductions in the engine-out particulate matter emission and will potentially enable higher conversion efficiencies of sulfur sensitive exhaust aftertreatment devices.

Sulfur in the natural gas feedstock is removed during the manufacture of synthesis gas, resulting in near zero sulfur content in the fuel (22). It is unlikely that the fuel sulfur will vary from the near zero levels in F-T diesel fuels due to process variations, but the fuel could pick up sulfur if introduced into the petroleum distribution infrastructure. As noted in Table 2, some studies used outdated methods to determine the sulfur content in F-T diesel fuel (specifically D4294 and D129). Newer studies have used the more appropriate D5453 and D2622 methods for sulfur determination. The results from these studies confirm that Fischer-Tropsch diesel fuels contain near zero levels of fuel sulfur.

Cetane Number

The cetane number is a measure of the autoignition quality of a diesel fuel. A higher cetane number indicates a shorter time delay between the fuel injection and ignition. A number of studies have examined the effect of changing cetane number on emissions (17).

Increasing cetane number may decrease or have no effect on hydrocarbon and carbon monoxide emissions from diesel engines. Engines emitting less than 0.2 g/BHP-hr HC and 0.7 g/BHP-hr CO are relatively insensitive to changes in cetane number, regardless of engine age. Both HC and CO emissions benefits were observed for higher emitting engines (17).

Increasing the cetane number reduces NO_x emissions at light and moderate loads. This is because increasing cetane number reduces ignition delay, thereby reducing the time available for mixture formation and the amount of fuel consumed in pre-mixed combustion. This leads to lower NO_x formation rates because pressure rises more slowly, allowing more time for heat transfer and cooling by dilution and mixing. However, in recent technology engines, fuel injection timing has been highly retarded to reduce NO_x by reducing or eliminating pre-mixed combustion altogether. Thus, the NO_x emission reduction attributable to increases in cetane number varies with the age of the engine, or the emission standard in effect for its year of manufacture. Older, higher NO_x engines experience a greater reduction due to increased cetane number than newer, lower NO_x engines (17, 23). In newer engines, the NO_x reduction with an increase of 10 cetane numbers is around 2%. In older engines, NO_x reductions due to an increase of 10 cetane numbers may be as high as 5% (23).

The particulate matter emissions do not show overall changes with cetane number (17). The effect of cetane number is highly engine specific, with increases, decreases, and no change reported for many different types of engines.

Cetane number is measured on a scale of 0 to 100. Normal C_{16} paraffin, n-hexadecane, is assigned a value of 100. Normal paraffins, such as n-hexadecane readily combust at high temperatures and pressures, like those found in a diesel engine (25). As shown in Table 2, many Fischer-Tropsch diesel fuels are composed almost wholly of paraffins. For a "straight-run" F-T diesel, with minimal post processing, these are all normal paraffins (22). The cetane number of individual paraffins varies, but a F-T diesel fuel that is predominately paraffinic will typically have a high cetane number. Variations in the types of paraffinic compounds in the fuel may result in small changes in cetane number, but the overall effect on exhaust emissions is not expected to vary.

A common variation in the hydrocarbon compounds in F-T diesel fuels is the presence of branched paraffins formed from the normal paraffins by cracking and isomerizing. Branched paraffins have lower cetane numbers than n-paraffins (25). Both Sasol (5) and Mossgas (9) produce F-T diesel fuels with branched and normal paraffins. The presence of branched paraffins in F-T diesel fuel is used to improve the cold flow properties. Table 2 provides a good example of the effect of branching on cold flow properties. Shell (5, 9, 14) produces a “raw” F-T diesel product fuel with a very high paraffin content (99.8%) and relatively poor cold flow properties, evidenced by a cloud point of 3°C. The highly branched Mossgas COD (9) diesel fuel has a cloud point of around -60°C.

Currently, the cetane number is determined in a test with a single cylinder cetane engine using ASTM D613. When a cetane engine is not readily available, an approximation of the cetane number can be made with the cetane index. The cetane index is calculated from bulk fuel properties via an empirical correlation developed for conventional petroleum diesel fuels. For conventional petroleum diesel fuels, the cetane index is a reasonable approximation of the cetane number (26). The applicability of the cetane index to F-T diesel fuels is not known at this time. However, because the properties of F-T fuels fall outside of the range for which the cetane index correlation was developed, it is unlikely that the correlation can provide an accurate estimate of cetane number for these fuels.

Aromatic Content

As various studies with conventional diesel fuel have observed, a decrease in fuel aromatic content could lead to a decrease in exhaust emissions. A literature review of the effect of aromatic content on exhaust emissions found lowering aromatic content from 30% to 10% produced up to a 5% reduction in NO_x emissions (17, 23). Aromatic compounds, and especially poly-aromatics, burn less readily in a diesel engine (23) and burn at a higher flame temperature, thus increasing NO_x emissions. By reducing the aromatic content of diesel fuel, the flame temperature can be lowered, leading to reduced NO_x emissions (12). Additionally, the fact that lower aromatic, higher H/C ratio fuels will produce lower O radical concentrations during combustion can also contribute to lower NO_x (17). The effect of fuel aromatic content on PM emissions is mixed, with different studies showing increases, decreases, and no change. The types and relative proportions of aromatics in the fuel may not be independent of other fuel properties, clouding the prediction of exhaust emission effects.

The F-T production process favors the formation of normal paraffins and 1-alkenes. The alkenes can be removed by very mild post-processing (22). The selectivity of the F-T reaction for aromatics is very low at low temperatures, however the selectivity increases as the reaction temperature increases. Low temperature F-T processes are more suited to producing diesel fuels (22). Mossgas’s F-T/COD diesel fuels contain levels of aromatic compounds in between the levels characteristic of F-T diesel fuel and those of conventional diesel fuels (i.e. Mossgas has an average aromatic content of 15% versus 30% for conventional diesel fuel). Small changes in aromatic content are not likely to result in a significant change in the exhaust emissions. Larger changes, in the range of 5% to 10% or more are very likely to change exhaust emissions.

The effect of poly-aromatic compounds on exhaust emissions has also been recently investigated. Reducing poly-aromatic compound levels in diesel fuel reduces the NO_x and HC emissions, with little effect on CO emissions (17). Particulate matter emissions from older engines are more sensitive to poly-aromatic compounds in the fuel; older engines have greater PM emission reductions due to reductions in fuel poly-aromatic content. Newer technology engines (mid to late 1990s model year) are relatively insensitive to decreases in poly-aromatic compounds in diesel fuel.

Reductions in poly-aromatic compounds should make a more significant contribution to a reduction in emissions than reductions in monoaromatic compounds (17). The emissions benefit from reducing poly-aromatic compounds stems from the reduction in the flame temperature due to an increase in the H/C ratio of the fuel. Analyses of several conventional diesel fuels show poly-aromatic content up to 10% (26).

Density

The effect of fuel density has recently been studied independently of other fuel properties (17). An important result of reducing density is the resultant loss of peak, or rated, engine power, regardless of the type of fuel involved. For example, in the same engine or vehicle, a less dense No. 2 diesel fuel will result in less power at rated power than a more conventional, denser No. 2 diesel fuel. Evaluation of the effect of density on exhaust emissions should therefore be done on a constant power basis. On this basis, older technology engines show greatly reduced PM emissions as fuel density is decreased. The PM emission reduction is less in newer technology engines (17). NO_x emissions may also benefit from a reduction in fuel density, but CO emissions are slightly increased. The effect of density is caused by complex interactions with fuel injection systems that can lead to changes in dynamic timing and mass injection flow rate.

Distillation Temperature

The effect of distillation temperature on heavy-duty exhaust emissions has been difficult to determine, with conflicting results presented in the literature (3, 12). A literature review found that high-end distillation temperature had a minimal influence on exhaust emissions (17). Fuels with heavier fractions, indicated by high T90 and T95 points, may be more difficult to combust due to the presence of high molecular weight compounds. If these high molecular weight compounds are poly-aromatics, a reduction in T90/T95 will likely result in a reduction in the NO_x emissions. However, the high molecular weight compounds may be heavy paraffin waxes with high cetane numbers. If the T90/T95 is reduced by reducing these waxes, an increase in the NO_x emissions may result due to the reduced cetane number.

Inclusion of Oxygenates

Irrespective of potential DOE designation of F-T diesel fuels under sec. 301(2), such fuels are classified by EPA as within the diesel fuel family for purposes of EPA’s registration requirements at 40 CFR Part 79. EPA has recently ruled that F-T diesel will be treated as equivalent to baseline diesel fuel; thus it is covered by baseline diesel fuel registrations unless the oxygen content exceeds 1%. For formulations with greater than 1% oxygen content, a separate registration in the non-baseline category will be required. This will entail “Tier 1” testing – an emissions characterization (speciation of specific exhaust compounds) and a literature search on any such compounds that are not found in baseline diesel exhaust. “Tier 2” testing – actual health effects testing by exposing laboratory animals to exhaust, may be required, as determined by evaluating Tier 1 data.

In general, adding oxygenates to diesel fuel can cause a significant reduction in PM emissions, however, oxygenates that cause a significant reduction in fuel cetane number or otherwise negatively impact important performance properties may not have PM emission benefits. For example, methanol blends are less suited for use in diesel engines because methanol is insoluble in diesel fuel and a surfactant is required to produce stable fuel mixtures. Also, methanol is slow to autoignite (cetane number near 0) and methanol emulsions can significantly diminish the cetane number of diesel fuel.

The exhaust emissions of neat biodiesel, an alternative diesel fuel containing about 10% oxygen, have been extensively reviewed in the literature (27). This oxygenate causes a significant reduction in PM and toxic compound emissions, but may cause a small increase in NO_x. Conversely, Natarajan identified several oxygenates that, when blended in diesel fuel, produced a significant increase in toxic emissions (28). As shown by Natarajan, not all oxygenates provide environmental benefit. Glycol ethers such as monoglyme and diglyme have been used to oxygenate diesel fuel in controlled engine tests (29). These ethers are effective at reducing ignition delay and PM emissions in diesel engines, however their teratogenic qualities (determined by oral dosing of mice) and the possibility of ground water contamination make monoglyme and diglyme unsuitable for use in diesel engines (30-34).

A wide array of oxygenates can be readily produced during the F-T process (22). Oxygenates produced during the F-T process are mainly alcohols, aldehydes, ketones, and carboxylic acids. Oxygen containing compounds can be removed by post-F-T synthesis processing, or their presence can be avoided by control of process conditions. In addition to the oxygenated compounds produced through the F-T process, other GTL processes can produce oxygenates. Examples of these GTL-derived oxygenates include the aforementioned glyme, diglyme, and methanol. When considering the environmental benefits of oxygenated compounds, exhaust emission reductions and overall health and environmental impacts, including toxicity, should be considered.

Emissions Performance of Fischer-Tropsch and Fischer-Tropsch Like Diesel Fuels

In determining whether fuels have acceptable emissions impacts under the Clean Air Act (section 211 (f)), EPA requires evidence of acceptable performance in four categories: instantaneous emissions, drivability, durability (with respect to emissions), and materials compatibility (with respect to emissions control systems). Furthermore, the standard of "substantial environmental benefit" under EPAct in the form of emissions reductions is clearly a higher standard than what is required under the Clean Air Act. The Clean Air Act only requires that a fuel not "cause or contribute to the failure of any emissions control device or system to attain the [emission standard for which the vehicle was certified].

In reviewing the publicly available data on the emissions performance of F-T diesel fuels, we have found a number of studies providing comparative emissions data with conventional fuels. Where possible, these data are assessed to determine the degree of statistical significance of any reported change in emissions using F-T diesel fuels. The data assessment seeks to determine if a significant difference was observed for the specific engine and vehicle platforms tested. In many instances, a highly significant improvement in emissions is observed when using F-T diesel fuels. For a change in emissions to be "substantial," it must first be significantly different from zero. Because what qualifies as a substantial environmental benefit is not defined by EPAct, we have not assessed whether any reported significant emissions benefits are substantial. This important point will need to be resolved as a part of DOE's rulemaking process.

The emission data available in the literature are for only a few engine and vehicle models and for only a few model years. Thus, the emissions testing data are not adequate to allow us to quantify the potential significance of any emissions reductions across the nation's diesel vehicle population as a whole. Existing knowledge, however, probably permits DOE to promulgate standards that apply to all producers based on fuel parameter limits that will assure the criteria are met.

While drivability is not considered to be a significant issue for diesel engine fuels, emissions durability and emission control system materials compatibility were not addressed in any of the publicly available studies or in any of the petitions.

Exhaust Emissions Effects on Current Technology Engines and Vehicles

Several studies have been performed to examine the emissions performance of Fischer-Tropsch diesel fuels relative to conventional petroleum-based diesel fuel. In general, results of the studies show emissions reductions with F-T diesel fuels in light- and heavy-duty diesels and in engine and chassis dynamometer testing. A review of the emission testing results is presented below.

Table 3 illustrates the emissions reductions observed for the Sasol and Shell F-T diesel fuel relative to CARB diesel fuel for two different heavy-duty engines and relative to Certification diesel on a third engine. The Sasol fuel was produced using Sasol's proprietary Slurry Phase Distillate Process from natural gas. The Shell fuel was produced with Shell's Middle Distillate Synthesis Process from natural gas. The reported emissions are the average of at least three replicate hot-start, heavy-duty Federal Test Procedure (FTP) tests. For these engine-testing studies, using F-T diesel fuel produced large emissions reductions relative to the CARB and Certification fuels for all four regulated pollutants. In particular, PM reductions of 22% to 27% were observed for the DDC engines relative to CARB or 10% aromatic diesel. A much smaller PM reduction was reported for the Navistar engine. NO_x reductions ranged from 5% to 15%.

The values in Table 4 are from a study that only reported emissions as a percentage of those for the base fuel, a conventional No. 2 diesel. The "hot" emissions are the average of three replicate hot starts, while the "cold" are for a single cold start. For example, the CARB diesel on the 1999 Series 60 (S60) had hot start HC emissions that were 77% of the hot start HC emissions for the No.2 diesel fuel. Reported NO_x reductions are similar to those in Table 3 (i.e. 5% to 15%), but PM reductions are substantially higher—in the range of 35% to 45%.

Table 5 shows similar results for steady state testing. A 1993 Cummins B5.9 engine was tested under steady state conditions and emission reductions were observed for all regulated pollutants. The NO_x reduction obtained by using F-T diesel fuel was 10% and the PM reduction was nearly 30%—in good agreement with the results for transient testing. The emission benefits of Fischer-Tropsch diesel fuel are shown on a mode-by-mode basis for a 1994 Navistar T444E engine in Table 6. NO_x was significantly reduced in every mode while PM was reduced or unchanged.

Table 3. Heavy-duty engine dynamometer hot start FTP emission results for F-T diesel fuel compared to conventional diesel fuel.

		g/BHP-hr			
Fuel	**Engine**	**HC**	**CO**	**NO_x**	**PM**
CARB [4]	1991 DDC S60, 12.7L	0.16	2.86	4.44	0.207
Sasol [4,5]		0.07	1.92	3.79	0.163
Sasol [4]		0.08	1.88	3.82	0.160
CARB [6]	1994 Navistar T444E	0.274	1.091	4.893	0.109
Shell [6]		0.198	0.968	4.607	0.104
Cert. Diesel [15]	1991 DDC S60, 11.1L	0.020	4.914	4.773	0.247
10% Aro. [15]		0.029	4.980	4.478	0.231
Shell [15]		0.007	3.843	4.026	0.167

Table 4. Heavy-duty engine dynamometer FTP emission results for F-T diesel fuel relative to No.2 diesel fuel baseline. The values are percentages of the No.2 baseline emissions.

			% of No.2 baseline, g/BHP-hr			
Fuel	**Cycle**	**Engine**	**HC**	**CO**	**NO_x**	**PM**
CARB [11]	Hot	1999 DDC S60	77	94	93	93
Sasol [11]	Hot		63	63	83	63
CARB [11]	Cold		74	88	85	85
Sasol [11]	Cold		37	53	77	54

Table 5. Heavy-Duty engine dynamometer steady state emission results, composite of all modes.

		g/BHP-hr			
Fuel	**Engine**	**HC**	**CO**	**NO_x**	**PM**
2D [10]	1993 Cummins B5.9	0.110	0.776	3.998	0.044
Shell [10]		0.060	0.436	3.638	0.031

Table 6. Heavy-duty engine dynamometer steady-state emission results, mode-by-mode emissions.

		g/BHP-hr							
		F-T Unknown Source [7]				2D [7]			
Engine	Speed (rpm)/ Load (ft-lb)	HC	NO_x	CO	PM	HC	NO_x	CO	PM
1994 Navistar T444E	1300/100	0.092	4.132	0.812	0.040	0.155	5.798	1.507	0.056
	1300/WOT	0.013	3.128	9.089	0.104	0.010	3.689	10.552	0.141
	1500/200	0.027	3.661	0.279	0.013	0.039	4.572	0.369	0.015
	1500/400	0.012	3.450	1.470	0.034	0.011	4.174	1.793	0.048
	1500/WOT	0.010	3.204	3.127	0.069	0.009	3.769	3.948	0.103
	1900/200	0.021	3.105	0.288	0.015	0.034	4.144	0.415	0.021
	1900/400	0.010	3.003	0.130	0.012	0.010	3.642	0.157	0.019
	1900/WOT	0.009	3.573	0.138	0.012	0.010	4.170	0.172	0.019
	2200/150	0.027	3.210	0.387	0.025	0.037	4.485	0.653	0.035
	2200/300	0.013	2.950	0.175	0.011	0.020	3.837	0.197	0.020
	2200/WOT	0.011	3.189	0.151	0.016	0.011	3.716	0.157	0.025
	2600/WOT	0.012	2.613	0.222	0.032	0.014	3.387	0.229	0.049

Heavy-duty chassis dynamometer results using F-T diesel fuel in several heavy-duty vehicles are given in Table 7, representing the average of at least three replicate emission tests. The White-GMC trucks were tested on CARB diesel fuel and Shell F-T diesel fuel. In all cases, regulated emissions were decreased. The 40-foot transit buses were tested in one of two configurations, with older engines or with recently rebuilt engines and oxidation catalysts. The vehicles were tested with both CARB diesel fuel and Mossgas F-T/COD diesel fuel. In this table, it is important to compare emissions obtained from running different fuels on the same vehicle (i.e. vehicle number in the third column). Reductions in HC, NO_x, CO, and PM were observed when operating on F-T diesel fuel for all vehicles. For the 4-stroke Caterpillar engines, NO_x reductions ranged from 2% to 20% and PM reductions ranged from 1% to 40%. Engine deterioration in-use and the general state of maintenance and repair of the engine cause this much larger range relative to the engine lab test results, which underscores the importance of basing any conclusions on data sets that include a representative range of vehicle characteristics. A similar range of NO_x and PM reductions was observed for the 2-stroke 6V-92 engines.

Table 7. Heavy-duty chassis dynamometer emission test results.

				g/mi			
Fuel	**Vehicle/Engine**	**Vehicle**	**Cycle**	**HC**	**CO**	**NO_x**	**PM**
CARB [6]	White-GMC WG64T 1996 Caterpillar 3176B (dedicated diesel)	2011	5-mi route	0.66	2.77	14.6	0.37
Shell [6]		2011	5-mi route	0.41	2.55	11.3	0.35
CARB [6]		2016	5-mi route	0.89	4.26	12.8	0.59
Shell [6]		2016	5-mi route	0.50	3.21	11.2	0.48
CARB [6]	White-GMC WG64T 1996 Caterpillar 3176B (Dual-Fuel, diesel mode)	2019	5-mi route	0.61	3.97	12.0	0.47
Shell [6]		2019	5-mi route	0.36	3.45	10.7	0.33
CARB [6]		2012	5-mi route	0.52	4.96	14.0	0.50
Shell [6]		2012	5-mi route	0.33	3.87	13.7	0.30
2D [9]	Orion 40ft, 1991 DDC 6V92, rebuilt engine with catalytic converter	2025	CBD	0.75	1.96	34.51	1.23
Mossgas [9]		2025	CBD	0.44	1.02	31.37	1.01
2D [9]		2029	CBD	0.39	1.07	26.91	1.89
Mossgas [9]		2029	CBD	0.29	0.75	26.10	1.16
2D [9]		2048	CBD	0.75	2.11	29.71	1.12
Mossgas [9]		2048	CBD	0.49	0.82	26.53	0.76
2D [9]	Orion 40ft, 1991 DDC 6V92, as-is	2029	CBD	1.82	11.73	35.85	1.79
Mossgas [9]		2029	CBD	1.72	11.02	33.37	1.37
2D [9]		2030	CBD	2.11	6.65	34.88	1.18
Mossgas [9]		2030	CBD	1.75	5.73	32.92	1.16
2D [9]		2034	CBD	1.31	40.42	26.26	9.03
Mossgas [9]		2034	CBD	0.72	26.52	25.64	7.07

In the studies described above, emission reductions were reported for on-highway engines and vehicles. The NO_x benefits of F-T diesel fuel were also seen in off-highway engines (Table 8). The speed and load test points are not identical during the testing for the three fuels, but in general, NO_x emission reductions were observed for the F-T diesel fuel. Small increases in the HC emissions were also observed.

Table 8. Heavy-duty engine dynamometer steady state emission results, off-highway engine, mode-by-mode emissions.

		g/BHP-hr					
		F-T [8]		2D [8]		1D [8]	
Engine	**Speed (rpm)/ Load (ft-lb)**	**HC**	**NO_x**	**HC**	**NO_x**	**HC**	**NO_x**
1993 DDC 453T	1440/307	1.1	5.0				
	1448/301	1.1	5.0				
	1485/199	1.5	6.5				
	1485/303	1.2	5.0				
	1530/197	1.5	6.9				
	1528/195	1.5	7.4				
	1465/313			0.5	6.2		
	1507/202			0.6	8.3		
	1454/308					0.7	5.7
	1502/200					0.9	7.5

Table 9 illustrates the emissions benefit of F-T diesel fuel in three light-duty vehicles. The engines were tested at three different test facilities and the results combined in the table. The fuels in Table 9 are a conventional CARB diesel fuel, a low-sulfur highly hydrocracked fuel (LSHC, 1ppm fuel sulfur), and a F-T diesel fuel. NO_x and PM emissions benefits were observed in all three engines with the F-T diesel fuel, although the magnitude of the reductions was greatest in the DaimlerChrysler and the GM engines. Compared to the LSHC fuel, the F-T diesel fuel showed an emissions reduction for the Ford and GM engines with no EGR, and a reduction for all three engines at moderate EGR rates.

Table 9. Light-duty steady state emission test results.

		Weighted total g/test			
		No EGR		Moderate EGR	
Fuel	**Engine**	**NO_x**	**PM**	**NO_x**	**PM**
CARB [13]	DaimlerChrysler 1.9L	19.82	0.834	7.41	0.720
FT Unknown Source [13]		18.14	0.409	5.80	0.470
LSHC		16.87	0.486	6.37	0.690
CARB [13]	Ford, 1.2L DIATA	39.66	0.091	12.31	0.115
FT Unknown Source [13]		38.97	0.090	10.92	0.210
LSHC		39.30	0.185	12.39	0.173
CARB [13]	GM 1.26L	28.07	0.532	9.73	0.400
FT Unknown Source [13]		20.81	0.351	8.21	0.299
LSHC		24.42	0.610	8.78	0.439

Emissions Reductions in Future Engines

The previous section shows emissions reductions compared to current diesel fuels and in current and past diesel engines. For heavy-duty diesel engines, new emissions standards will be effective in 2004 and 2007. Preceding the 2007 emissions standards, EPA will introduce mandated ultra-low sulfur diesel fuel in 2006.

For heavy-duty engines meeting the 2004 standards, an analysis by EEA, Inc. found that fuel properties such as cetane number and aromatic content had considerable impact on engine out emissions, (34) consistent with the trends described previously. Similar results were observed for light-duty vehicle emissions using advanced common rail and EGR systems (13). Extrapolating these results with the diesel fuel studies from the literature, F-T diesel fuels will continue to offer emissions benefits. Beyond the light-duty Tier 2 and heavy-duty 2004 standards, it is difficult to assess the benefits of Fischer-Tropsch diesel fuels, as data from these advanced engines is not yet available. Given the lower engine out emissions generally observed, and the benefits of F-T diesel fuel that may accrue when using diesel particle filters and NO_x adsorber catalysts, it seems likely that tailpipe emissions impacts will be much lower in absolute terms, even if the percentage reductions remain the same. As indicated above, however, impacts from lowering sulfur (e.g., below 15 ppm) on engine out emissions show diminishing returns.

Beyond the 2004 emissions standards, exhaust aftertreatment technologies for NO_x reduction will be required. One approach is selective catalytic reduction where NO_x is reacted with a reductant to produce nitrogen and to oxidize the reductant. The NO_x may be concentrated using an adsorbent. In many respects, the vehicle fuel is the most practical NO_x reductant, and hydrocarbon molecular structure can have a significant impact on selectivity and on the temperature of maximum NO_x reduction. Several studies (35, 36) find the following general trend for efficiency in NO_x reduction when fuel is injected directly into the exhaust:

Isoparaffins<aromatics<n-paraffins<olefins=alcohols

NO_x reduction efficiency of paraffins also increases with increasing molecular weight, but becomes nearly constant at 10-12 carbon atoms. Because F-T diesel fuels are rich in n-paraffins of C_{10} or higher, these fuels may be excellent reductants for NO_x relative to conventional diesel fuels. This expectation has been confirmed in one study that found lean NO_x catalyst conversion efficiency was higher with F-T relative to CARB diesel (14).

Because F-T diesel fuel has many premium properties relative to conventional diesel, like high cetane number and low sulfur and aromatic content, there is an opportunity to optimize engine designs to take advantage of these properties. In particular, the high cetane number and ultra-low sulfur content are important in this regard. A study examining this idea has recently been completed by the DOE and NREL. As part of this study, a 2000 Power Stroke diesel engine was tested and modified to take advantage of the unique properties of F-T diesel fuel. Table 10 gives the “as-is” and optimized engine emissions for both light- and heavy-duty test cycles. The optimized engine build includes cooled high pressure EGR, an optimized piston bowl, a $DeNO_x$ catalyst, and a catalyzed particulate filter. In both cases, the F-T diesel fuels yield emissions benefits compared to conventional diesel fuel. The high cetane number and low sulfur level of the F-T diesel fuels allowed the engine to be designed to handle very high EGR rates and enabled the use of the aftertreatment system. Table 11 illustrates the efficiency of the $DeNO_x$ catalyst with the three test fuels. Based on the limited data for this research engine, it appears the F-T diesel fuels allowed greater NO_x reductions with the catalyst than the 10% aromatic/19ppm sulfur diesel fuel.

Table 10. Light- and heavy-duty emission test results for as-is and optimized configuration for a Ford Power Stroke 7.3L diesel engine.

			g/mi	
Engine	**Fuel**	**Cycle**	**NO_x**	**PM**
2000 Power Stroke 7.3L V8	"F-TA" [14]	LD	4.582	0.122
	10% Aromatic [14]	LD	4.405	0.092
	"F-TA" [14]	Optimized LD	0.143	0.005
	"F-TB" [14]	Optimized LD	0.101	0.007
	10% Aromatic [14]	Optimized LD	0.221	0.002
			g/BHP-hr	
			NO_x	PM
	"F-TA" [14]	HD	3.667	0.055
	10% Aromatic [14]	HD	3.409	0.039
	"F-TA" [14]	Optimized HD	0.253	0.009
	"F-TB" [14]	Optimized HD	0.238	0.008
	10% Aromatic [14]	Optimized HD	0.283	0.004

Table 11. Engine out and catalyst out NO_x emissions for a $DeNO_x$ catalyst for a Ford 2000 Power Stroke 7.3L diesel engine.

		Engine Out NO_x			**Catalyst Out NO_x**		
Engine	**Speed (rpm)/ Load (ft-lb)**	**"F-TA" [14]**	**"F-TB" [14]**	**10% Aro. [14]**	**"F-TA"[14]**	**"F-TB"[14]**	**10% Aro. [14]**
2000 Power Stroke 7.3L / $DeNO_x$ catalyst	700/14.2	5.15	2.66	4.46	0.88	0.64	3.83
	1350/42.3	9.79	5.28	7.77	4.75	1.82	6.15
	1100/149.3	3.93	3.87	5.66	1.32	0.49	2.86
	1600/149.9	6.50	5.75	8.55	3.41	3.91	5.47
	1350/257.1	22.79	17.11	12.80	3.74	3.25	3.11
	2480/480.7	231.29	232.40	158.96	94.25	99.97	114.32
	2600/265.7	87.08	78.50	74.04	23.74	18.87	17.81
	2700/85.7	27.74	24.79	37.39	7.70	7.43	9.50

Statistical Significance of Reported Emissions Reductions

NREL has analyzed the literature data to determine the significance of the emission reductions with F-T diesel fuel compared to conventional diesel on a case-by-case basis (i.e. for each individual vehicle or engine tested). This procedure was used to determine the statistical significance of the data reported in the literature, and was not used to draw larger conclusions about the entire in-use vehicle population. The analysis employed a two-sample t-test comparing mean emissions based on three or more repeated tests on both fuels. The t-test tool in Microsoft Excel was used under the assumptions of equal variance, two tailed t-distribution, and a hypothesized mean difference of zero. (See Appendix B for additional discussion). Results are presented as a p-value, which provides an indication of the level of significance of any difference in mean emission values. A p-value of 0.01, for example, indicates that a difference between means is significant at the 99% confidence level.

Using the p-value avoids the need to define a threshold confidence level for significance. This is important because EPAct does not define in a statistical sense what qualifies as a "substantial environmental benefit" and thus it is not appropriate to do so here. Estimating probability ranges (i.e. error bars) requires the specification of a confidence level and consequently probability ranges are not provided. In cases where repeated tests were not performed or where individual test results were not reported, we could not determine the level of significance.

Only three of the studies described above and listed in Table 12 provide sufficient data to perform the t-test. In all cases, the NO_x reductions have a high degree of significance (a low p-value). PM emission reductions are significant in most cases. Several other studies claim statistical significance, but do not report details of the statistical analysis nor adequate information for it to be replicated. The fuel properties with the greatest contribution to reduced engine-out emissions are believed to be the very high cetane number and the very low aromatic content.

Table 12. P-value for emissions reductions reported in literature comparing F-T and GTL diesel fuels to conventional diesel fuel.

Table	Fuel	Conventional Diesel Fuel	p-value			
			HC	**NO_x**	**CO**	**PM**
3	Sasol [4,5]	CARB [4]	0.134	<0.01	<0.01	<0.01
3	Sasol [4]	CARB [4]	0.013	<0.01	<0.01	<0.01
3	Shell [6]	CARB [6]	0.041	0.088	0.026	0.393
3	Shell [15]	Cert. Diesel [15]	0.008	<0.01	<0.01	<0.01
	Shell [15]	10% Aro. [15]	0.002	<0.01	<0.01	<0.01
4	Sasol [11]	CARB [11]	Inadequate data available			
5	Shell [6] (dedicated diesel)	CARB [6]	Inadequate data available			
5	Shell [6] (dual fuel, diesel mode)	CARB [6]	Inadequate data available			
5	Mossgas [9] (recently rebuilt engines w/ oxidation catalyst)	2 D [9]	Inadequate data available			
5	Mossgas [9] (older engines)	2 D [9]	Inadequate data available			
6	Shell [10]	2 D [10]	Inadequate data available			
7	Unknown Source [7]	2 D [7]	Inadequate data available			
8	Syntroleum [7]		Inadequate data available			
9	Unknown Source [13] (DaimlerChrysler – No EGR)	CARB [13]	N/A	Yes [a]	N/A	Yes [a]
9	Unknown Source [13] (Ford – No EGR)	CARB [13]	N/A	No [a]	N/A	No [a]
9	Unknown Source [13] (GM – Moderate EGR)	CARB [13]	N/A	Yes [a]	N/A	Yes [a]
9	Unknown Source [13] (DaimlerChrysler– Moderate EGR)	CARB [13]	N/A	Yes [a]	N/A	Yes [a]
9	Unknown Source [13] (Ford – Moderate EGR)	CARB [13]	N/A	Yes [a]	N/A	Yes [a]
9	Unknown Source [13] (GM – No EGR)	CARB [13]	N/A	Yes [a]	N/A	Yes [a]
10	"F-TA" [14]	10% Aro. [14]	Inadequate data available			
10	"F-TB" [14]	10% Aro. [14]	Inadequate data available			
11	"F-TA" [14]	10% Aro. [14]	Inadequate data available			
11	"F-TB" [14]	10% Aro. [14]	Inadequate data available			

[a]: Statistical significance claimed but details of analysis not reported in paper.

Yes = reduction in emission is significant, as reported in the literature.
No = reduction in emission is not significant, as reported in the literature.
N/A = not applicable

Overall Statistical Significance of the Literature Data

For ordinal data such as we have here, an appropriate non-parametric test allows us to determine whether emissions for F-T diesel fuel are greater than, less than, or equal to those for conventional diesel fuel and what the level of significance is for this directional difference. This analysis can be done using a Wilcoxon Signed-Rank Test (37). This test uses paired data to determine the statistical significance of directional differences between paired observations. These differences are ranked and a critical value is computed. The statistical significance is dependent on the magnitude of the critical value. The Wilcoxon procedure has been used to examine the entire F-T emission data set as an aggregate, rather than the test-by-test analysis shown above. The critical value and statistical significance for all regulated emissions are shown in Table 13. A detailed example of this procedure is presented in Appendix B.

Table 13. Critical Value and Statistical Significance of Emission Reduction with F-T Diesel Fuel Compared to Conventional Diesel Fuel, All Reported Literature Values.

Emission	Critical Value	Probability Emission Reduction with F-T is Significant
HC	4.87	Significant reduction at greater than 99% with F-T diesel fuel, compared to conventional diesel fuel
CO	5.93	Significant reduction at greater than 99% with F-T diesel fuel, compared to conventional diesel fuel
NO_x	6.80	Significant reduction at greater than 99% with F-T diesel fuel, compared to conventional diesel fuel
PM	6.96	Significant reduction at greater than 99% with F-T diesel fuel, compared to conventional diesel fuel

The critical values given in Table 13 are generated from the literature data, where F-T and conventional diesel fuel were compared. The statistical analysis includes engine and vehicle data, transient and steady state emissions. The NO_x and PM emissions were reduced for almost all cases and this directional change was very highly significant (greater than 99%). Reductions in the HC and CO emissions were also highly significant (greater than 99%) for the reported data. The average NO_x and PM emission reductions were 13% and 11%, respectively. The HC and CO emission reductions were 22% and 28%, respectively.

The analysis includes all types of F-T diesel fuel, indicating that the generic properties of the fuel (ultra-low sulfur, low aromatic content, and high cetane number) almost always reduce the NO_x and PM emissions from diesel engines, at least for the vehicle and engine models that have been tested.

Durability/Materials Compatibility

Little work has been done on the effect of Fischer-Tropsch diesel fuels on elastomers within diesel engines. Sasol performed immersion tests using their Fischer-Tropsch diesel fuel on new elastomeric materials (5). The mass, thickness, and tensile strength of the elastomers were compared to unexposed elastomers. In general, no notable changes were detected.

Sasol also investigated the corrosivity of Fischer-Tropsch diesel fuel compared to conventional diesel fuel (5). Several metals and metal alloys were exposed to conventional diesel fuel and the Sasol Fischer-Tropsch diesel fuel and examined for corrosion. The rates of corrosion of the metals and metal alloys were insignificant with both the conventional diesel fuel and the Fischer-Tropsch diesel fuel.

Emissions Durability/Engine Durability

The published technical literature does not contain information concerning long-term durability of diesel engines or of engine emissions when operating on F-T diesel fuels.

Fuel Economy

Fischer-Tropsch diesel fuels have mass specific heating values of about 47 MJ/kg, compared to roughly 45-46 MJ/kg for conventional diesels (see Table 1). This difference is probably not significant. However, F-T diesel fuels have a lower density than conventional fuels (i.e. 0.78 g/ml versus 0.84 g/ml), so that a gallon of F-T diesel fuel contains about 7% less mass than conventional diesel fuel. This implies that, if all other factors are held constant, a gallon of F-T fuel contains roughly 7% less energy than a gallon of conventional diesel. Thus volumetric fuel economy (miles per gallon) could theoretically decline by up to 7%.

A number of other factors will impact the actual fuel economy obtained in real-world operation of diesel vehicles, including how the F-T diesel fuel impacts drivability. LeTavec and coworkers presented a more accurate accounting of the real world effects of reduced density diesel fuels (38). Five Class 8 trucks were operated on conventional CARB diesel fuel and five trucks were operated on ULSD fuel over a period of 12 months. The heat of combustion for the ULSD was very similar to a typical F-T diesel fuel (26). Over the 12-month test period, the trucks fueled with ULSD had 2% to 3% lower fuel economy, and this slight fuel economy penalty was attributed to the lower energy density of the fuel. Clearly, further investigations need to be made into the real world fuel economy of vehicles operating on F-T diesel fuel. Public input is needed to determine if F-T diesel fuel impacts fuel economy and the effect of a change in fuel economy.

FUEL PROPERTY REQUIREMENTS TO ENSURE ENVIRONMENTAL BENEFITS

Clearly, the previous discussion indicates that fuel properties can have significant effects on exhaust emissions and that the generic properties of high cetane number, low aromatic content, and ultra-low sulfur content of F-T diesel fuels lead generally to lower emissions of PM and NO_x. DOE may wish to consider some minimum fuel property requirements in order to ensure environmental benefits from the use of the fuel. Table 14 lists the most important properties from an environmental benefit standpoint. Fuel properties have complex interactions and are difficult to isolate. Although the fuel properties in Table 14 are listed individually, they may have a confounding effect on the exhaust emissions. Many of the properties listed in Table 14 are also part of the ASTM D975 fuel property specification. F-T diesel fuels should also likely meet, at a minimum, the properties outlined in Table 1 (ASTM D975), which are required for conventional diesel.

Table 14. Important fuel properties for F-T diesel fuels.

Property	Reasoning
Sulfur	Fuel sulfur contributes to the sulfate emission. Ultra-low sulfur fuels can enable exhaust aftertreatment devices. Ultra-low sulfur fuels may reduce the risk of corrosion in EGR systems.
Cetane number	High cetane fuels may reduce exhaust emissions of NO_x and PM.
Paraffin content	Paraffins readily combust in diesel engines, and normal paraffins are responsible for the high cetane number of F-T fuels.
Normal paraffin content	The higher the normal paraffin content, the higher the cetane number of the fuel.
Branched paraffin content	Branched paraffins combust less readily (have a lower cetane number), but are responsible for improving the cold flow properties of Fischer-Tropsch diesel fuels.
Aromatic content	Aromatic compounds in diesel fuel do not combust as readily as paraffin compounds, leading to increased exhaust emissions of NO_x and PM.
Oxygen content	Oxygenates may lead to reduced PM emissions, but in some cases may also result in increased health effect and ecotoxicological concerns.
ASTM D975	Standard specification to ensure operability of diesel fuels

In 2006, the EPA 15 ppm sulfur requirements will begin to take effect, becoming fully effective in 2007. Thus a 15 ppm maximum sulfur limit will apply after 2006-7 for F-T diesel fuels, including any fuels DOE might designate under sec. 301(2), unless such a designation includes a lower sulfur limit. Note that EPA may revise this sulfur specification based on technology reviews over the coming years. The discussions of the effect of fuel properties on exhaust emissions shows that reducing sulfur content below 15 ppm has little benefit on engine out emissions, but is beneficial for aftertreatment devices. For example, a measurable decline in NO_x adsorber performance was noted when fuel sulfur was increased from 1ppm to 15ppm (20). Public input is needed to determine an appropriate specification for F-T diesel fuel sulfur level to ensure environmental benefits of the fuel.

The high natural cetane number of most F-T diesel fuels is partly responsible for the emissions benefits. Therefore, in order to ensure that this environmental benefit is realized in the event that F-T based diesel fuels were to be designated under sec. 301(2), it seems prudent to have a cetane number specification. Public input should be sought as to the exact specification level, however it should be well above the range of typical on-road fuels today. High levels of normal paraffins are responsible for the high cetane number. Thus, an alternative to a cetane number specification might be a minimum normal paraffin content specification.

Paraffin and aromatic content are related, as one goes up the other typically goes down, as long as olefin content is low. The low aromatic content of F-T diesel fuels is another important factor responsible for the observed emissions benefits, and specifying a maximum aromatic content is probably necessary to ensure environmental benefits. Public input as to the appropriate maximum aromatic level should be sought.

Fuel oxygenates can significantly reduce PM emissions. However it is not possible to predict in advance the toxic emissions from oxygenates or the ecotoxicity of the oxygenates themselves. Significant oxygen content is not necessary in order to obtain the environmental benefits of F-T diesel fuels. Because of this, and the uncertainty regarding toxic exhaust emissions and fuel toxicity, public input is needed to determine if F-T diesel fuels with some de minimus level of oxygen should be considered or if certain types of oxygenates should be restricted to properly determine the environmental impacts of oxygenated diesel fuels.

While not listed in Table 14, many F-T diesel fuels have poor lubricity. Fuel lubricity is not presently a part of the ASTM D975 specification for diesel fuels, and is not directly related to environmental benefits. However, lubricity is related to engine durability and emissions performance durability. Because of the low lubricity of F-T diesel fuels, DOE may want to consider a minimum lubricity specification for F-T diesel fuels, as this has potential implications on emissions deterioration over time. Public input as to the appropriate testing methods for lubricity and the appropriate minimum specification should be sought.

APPENDIX A - DISCUSSION OF F-T AND F-T/COD DIESEL PETITIONS

NREL has been asked by the U.S. Department of Energy (DOE) to evaluate emissions of criteria pollutants of diesel fuels produced from natural gas through variations of the F-T process. DOE expects to initiate a rulemaking to determine if such fuels should be designated as alternative fuels under sec. 301(2) of the Energy Policy Act of 1992, which requires among other findings, a finding that the fuels provide "substantial environmental benefits." Tailpipe emissions of criteria pollutants are a key determinant of overall environmental impacts. It has been suggested that reductions of such tailpipe emissions could be a basis for a finding that the natural gas derived diesel fuels offer substantial environmental benefits.

DOE's rulemaking is in response to three petitions received by DOE, one from a producer of natural gas based diesel fuels (Mossgas Pty. Ltd.), and two from developers of technologies related to potential production of such fuels (Rentech, Inc. and Syntroleum Corp.). The two petitions received from the technology developers relate specifically to processes that produce the diesel fuel streams directly from the reaction of the synthesis gas (produced from natural gas by reforming), and maximize diesel fuel within the product stream. Well-established refining processes are used to separate the diesel fuel from other hydrocarbon products and assure diesel fuel quality. The product of these processes is referred to herein as Fischer-Tropsch diesel (F-T). The Mossgas petition is for fuel from Mossgas's existing plant, which produces a broader slate of hydrocarbons from the F-T synthesis. Distillate produced directly from the Mossgas F-T reactor accounts for only about 28%-32% of the total Mossgas diesel. Some 60%-68% of the Mossgas diesel fuel is produced from oligomerization of lighter olefinic hydrocarbons produced by the F-T synthesis into diesel-like distillate paraffinic and aromatic hydrocarbons

The main body of this document reviewed the properties of F-T diesel fuels, how these properties are expected to impact air pollutant emissions, and the published literature on emissions produced by F-T diesel fuels. This review included the data provided in the three petitions. Considering the minimal levels of emission data provided in the individual petitions, DOE suggested NREL consider other data sources that might provide a basis for a possible rulemaking that would designate some diesel fuels made from natural gas with F-T processes as alternative fuels under sec. 301(2) of the Energy Policy Act of 1992. As illustrated in Table 2, F-T diesel fuels inherently share some key characteristics such as very low sulfur, high cetane number, and low aromatics levels that might be found to assure emissions reductions. The Mossgas F-T/COD fuels are also inherently low in sulfur, with aromatic content between those of F-T and conventional diesel fuel.

Both Rentech's and Syntroleum's petitions suggested that EPAct designations be made specific to their proprietary fuels and processes. Neither Syntroleum nor Rentech provided a rigorous description of the fuel production process and resultant fuel. Rentech subsequently clarified that it intended for DOE's designation to be made in terms of generic fuel parameter specifications. Syntroleum requests designation for a paraffin diesel fuel with properties similar to "S-2" and produced through the Syntroleum process. The properties of F-T diesel reactor output may or may not be related to proprietary catalysts, but they seem to be more related to plant-specific factors such as plant configurations, operating conditions (particularly temperature), and desired co-products. Ultimate fuel quality is primarily determined by the post-synthesis processing, which involves well-established refining processes such as distillation, isomerization, cracking, and hydrocracking.

Therefore, even if the petitions had included more comprehensive emission data so as to enable statistically significant estimation of emissions reductions, it is not clear that an analytical basis would exist for EPAct designations based on individual processes.

NREL examined whether the known fuel parameters associated with the natural gas based diesel fuels might provide a basis for designation. The generic properties of high cetane number, low aromatic content, and ultra-low sulfur content of F-T diesel fuels lead generally to lower emissions of PM and NO_x. Based on the data and analysis presented in the main body of this document, a basis does exist for claiming emission benefits from F-T fuels based on fuel properties generic to these fuels. A determination as to whether these emission benefits are substantial will be made through the DOE rulemaking process.

Syntroleum Petition

Syntroleum submitted a petition requesting EPAct qualification for “S-2,” a distillate product for use in compression ignition engines. Typical “S-2” product specifications are given in Table 15.

Syntroleum states the cetane number of its F-T diesel fuel may vary by +/- 3. The cetane number variations are a result of a different hydrocarbon makeup of the fuel. The changes between a cetane number of 77 and 74 will result in an insignificant change in ignition delay and thus will not significantly alter the overall emissions benefits from Syntroleum’s F-T diesel fuel. Even at the lowest value, the cetane number of the F-T diesel fuel is still significantly greater than conventional diesel fuels.

The API Gravity variations reported by Syntroleum for the F-T diesel fuel may result in approximately a 2% change in the fuel density. As discussed above, the emission changes due to changing fuel density may be confounded by related changes in other fuel properties. A change in fuel density of 2% will not increase the emissions from the Syntroleum diesel fuel significantly, and exhaust emissions will remain lower than conventional diesel fuel.

The typical fuel property specification submitted by Syntroleum in the petition is for a highly paraffinic, high cetane number, ultra-low sulfur diesel fuel. Individually, these fuel properties have been shown to produce reduced exhaust emissions (see above discussion). The high paraffin content, which is related to the high cetane number, suggests regulated emissions reductions would be observed with the Syntroleum fuel.

Table 15. Typical “S-2” fuel properties, provided by Syntroleum in petition to DOE.

Property	**Test Method**	**Value**
Specific gravity	ASTM D1298	0.771
API gravity, °API	ASTM D1298	52.0
RVP, psi	ASTM D323	0.5
Flash Point, °C	ASTM D93	64
Cloud Point, °C	ASTM D2500	< -17
Color, Inspection	ASTM D1500	<0.5
Sulfur, wt%	ASTM D2622	[a]
Viscosity, cSt @ 40°C	ASTM D445	2.1
Carbon Residue, wt%	ASTM D524	< 0.05
Copper Strip Corrosion	ASTM D130	1A
Aromatics, vol%	ASTM D1319	[a]
Olefins, vol%	ASTM D1319	[a]
Saturates, vol%	ASTM D1319	> 99
Cetane number	ASTM D613	> 74
Oxidation Stability, mg/100ml	ASTM D2274	0.0
Distillation	ASTM D86	
IBP, °C		160
T10, °C		199
T50, °C		266
T90, °C		316
FBP, °C		350
Lubricity, mm	ASTM D6079	< 0.37
Ash, wt%	ASTM D482	< 0.001

[a]: below detection limits

Table 16 shows the Federal Test Procedure (FTP – heavy-duty engine and light-duty chassis) results for the Syntroleum supplied test fuel compared to the standards in place for the various vehicle platforms. The limited test data submitted by Syntroleum showed that their F-T diesel test fuel produced emissions well below the engine certification standards. Tables 17-19 shows the dynamometer test results of the Syntroleum supplied diesel fuel compared to No.2 diesel, CARB diesel, and Swedish City 1 diesel fuel. The Syntroleum test fuel produces emissions well below the emissions of the other diesel fuels tested, with percentage reductions in line with what has been reported in the literature. The results presented in the petition have been published as part of an SAE paper (39).

Toxic (benzene, 1,3-butadiene, formaldehyde, and acetaldehyde) and nitrous oxide (N_2O) emissions were also compared for the Syntroleum Fischer-Tropsch diesel fuel under light- and heavy-duty test conditions. Results are presented in Table 20. The total toxic and nitrous oxide emissions were reduced with the Syntroleum test fuel compared to the No.2 diesel, CARB diesel, and Swedish City diesel.

The Syntroleum data is not representative of the in-use vehicle fleet. The statistical significance of the test data can be determined only for the specific test engine and vehicles employed. More general statistical conclusions applied to the nation's in-use fleet are not possible.

Table 16. Results of light- and heavy-duty FTP testing with S-2 compared to current emissions standards.

		Emissions in g/BHP-hr				
		HC	**CO**	**NO_x**	**PM**	
1999 5.9L Cummins B	EPA On-Highway Heavy-Duty 1998	1.3	15.5	4.0	0.10	
	Syntroleum Fischer-Tropsch diesel fuel	0.1	0.8	3.1	0.06	
		Emissions in g/mi				
		THC	**NMHC**	**CO**	**NO_x**	**PM**
2000 Dodge Ram 2500 HD with Cummins B	Tier 1 Standards [a]	NS	0.39	5.0	NS	NS
	Syntroleum Fischer-Tropsch diesel fuel	0.26	0.26	0.7	7.0	0.04
1999 Volkswagen Golf GL TDI	EPA Federal Light-Duty Tier 1	0.41	0.25	3.40	1.00	0.08
	Syntroleum Fischer-Tropsch diesel fuel	0.03	0.02	0.10	0.78	0.03

a: For comparative purposes, applicable certification standards are based on engine dynamometer test

NS = No standard in place

Table 17. Results of engine dynamometer FTP testing on 1999 Cummins 5.9L B engine.

Test Fuel	**Emissions, g/BHP-hr**			
	HC	**CO**	**NO_x**	**PM**
EPA No.2 Diesel	0.12	1.2	4.0	0.10
CARB Diesel	0.09	1.1	3.7	0.08
Swedish City 1 Diesel	0.09	1.2	3.6	0.08
Syntroleum Fischer-Tropsch diesel fuel	0.07	0.8	3.2	0.06

Table 18. Light heavy-duty test results for a 2000 Dodge Ram 2500HD with a Cummins B engine.

Test Cycle	Test Fuel	Emissions, g/mi				
		THC	NMHC	CO	NO_x	PM
Light Duty FTP	EPA No.2 Diesel	0.38	0.38	1.4	9.13	0.058
	CARB Diesel	0.34	0.34	1.2	8.10	0.051
	Swedish City 1 Diesel	0.33	0.32	1.2	7.83	0.042
	Syntroleum Fischer-Tropsch diesel fuel	0.26	0.26	0.7	7.05	0.035
Light Heavy Duty HFET	EPA No.2 Diesel	0.19	0.19	0.5	5.10	0.034
	CARB Diesel	0.16	0.16	0.5	4.48	0.030
	Swedish City 1 Diesel	0.16	0.16	0.4	4.26	0.023
	Syntroleum Fischer-Tropsch diesel fuel	0.14	0.14	0.3	4.07	0.020
US06	EPA No.2 Diesel	0.19	0.19	0.7	4.24	0.105
	CARB Diesel	0.17	0.17	0.6	4.86	0.060
	Swedish City 1 Diesel	0.18	0.17	0.6	4.65	0.086
	Syntroleum Fischer-Tropsch diesel fuel	0.16	0.15	0.5	4.50	0.059

Table 19. Light-duty test results for a 1999 Volkswagen Golf GL TDI.

Test Cycle	Test Fuel	Emissions, g/mi				
		THC	NMHC	CO	NO_x	PM
FTP	EPA No.2 Diesel	0.04	0.03	0.00	0.70	0.04
	CARB Diesel	0.06	0.05	0.10	0.79	0.03
	Swedish City 1 Diesel	0.02	0.02	0.00	0.46	0.03
	Syntroleum Fischer-Tropsch diesel fuel	0.03	0.02	0.10	0.78	0.03
HFET	EPA No.2 Diesel	0.01	0.01	0.00	0.47	0.07
	CARB Diesel	0.03	0.02	0.00	0.48	0.04
	Swedish City 1 Diesel	0.01	0.01	0.00	0.46	0.03
	Syntroleum Fischer-Tropsch diesel fuel	0.01	0.01	0.00	0.49	0.02
US06	EPA No.2 Diesel	0.02	0.01	0.00	1.72	0.42
	CARB Diesel	0.04	0.04	0.10	1.83	0.22
	Swedish City 1 Diesel	0.01	0.01	0.00	1.71	0.11
	Syntroleum Fischer-Tropsch diesel fuel	0.01	0.01	0.00	1.75	0.05

Table 20. Comparison of Syntroleum test fuel with conventional diesel fuel for toxic and N_2O emissions.

Heavy Duty FTP Emissions in mg/BHP-hr (Cummins B)						
	Benzene	**1,3 Butadiene**	**Form-aldehyde**	**Acet-aldehyde**	**Total**	**N_2O**
No.2 Diesel	1.2	1.5	15.2	5.9	23.8	7.1
CARB Diesel	1.2	1.0	11.2	4.5	17.9	5.9
Swedish City 1 Diesel	1.3	1.1	13.6	5.5	21.5	5.4
Syntroleum Fischer-Tropsch diesel fuel	0.8	1.2	9.7	3.9	15.6	5.0
Heavy Light Duty FTP Emissions in mg/mi (Dodge Ram)						
	Benzene	**1,3 Butadiene**	**Form-aldehyde**	**Acet-aldehyde**	**Total**	**N_2O**
No.2 Diesel	1.4	0.8	18.3	8.9	29.4	6.5
CARB Diesel	1.4	0.3	17.7	7.8	27.2	5.5
Swedish City 1 Diesel	1.3	0.8	16.1	9.6	27.9	5.5
Syntroleum Fischer-Tropsch diesel fuel	0.9	0.6	12.9	5.5	19.9	5.0
Light Duty FTP Emissions, mg/mi (Volkswagen Golf)						
	Benzene	**1,3 Butadiene**	**Form-aldehyde**	**Acet-aldehyde**	**Total**	**N_2O**
No.2 Diesel	0.2	Trace	3.0	2.7	5.9	8.7
CARB Diesel	0.2	0.0	3.1	2.7	6.0	8.7
Swedish City 1 Diesel	0.1	0.0	2.0	2.6	4.7	5.4
Syntroleum Fischer-Tropsch diesel fuel	0.1	0.0	1.5	2.3	3.9	5.4

NREL analyzed the statistical significance of the emission results provided by Syntroleum (Table 21). The p-values were calculated using the two-tailed t-test (see Appendix B). Additionally, the Syntroleum test fuel was compared to both the CARB diesel fuel and the Swedish City 1 diesel fuel for regulated pollutants. We found that NO_x and PM emissions were lower with a high degree of significance relative to No. 2 diesel fuel in almost all cases. In some cases, NO_x or PM did not change significantly relative to CARB or Swedish City 1 diesel fuel. Insufficient data was provided to generate the p-values for the air toxic emissions presented in Table 20.

Table 21. P-values for Syntroleum supplied diesel fuel compared to CARB diesel, No.2 diesel, and Swedish City 1 diesel fuel.

Engine	Comparison Fuel	Cycle	p-value			
			HC	CO	NOx	PM
Cummins 5.9B	CARB	Heavy-Duty FTP	0.413	0.033	0.006	0.001
	No.2		0.137	0.015	0.002	0.0002
	Swedish City 1 Diesel		0.111	0.026	0.010	0.003
VW Golf	CARB	Light-Duty FTP	0.178	0.637	0.539	0.0003
	No.2		0.434	0.587	0.084	0.052
	Swedish City 1 Diesel		0.178	0.653	0.127	0.333
	CARB	Light-Duty US06	0.044	0.069	0.017	0.046
	No.2		0.306	0.651	0.086	0.0007
	Swedish City 1 Diesel		0.598	0.494	0.225	0.015
	CARB	Light-Duty HFET	0.023	0.277	0.820	0.005
	No.2		0.644	1.00	0.077	0.0002
	Swedish City 1 Diesel		1.00	0.592	0.143	0.008
Dodge Ram	CARB	Light Heavy-Duty FTP	0.001	0.004	0.045	0.029
	No.2		0.270	0.003	0.019	0.046
	Swedish City		0.006	0.010	0.003	0.038
	CARB	Light Heavy-Duty US06	0.055	0.032	0.014	0.930
	No.2		0.061	0.013	0.250	0.230
	Swedish City 1 Diesel		0.061	0.055	0.163	0.408
	CARB	Light Heavy-Duty HFET	0.040	0.007	0.010	0.479
	No.2		0.020	0.002	0.025	0.484
	Swedish City 1 Diesel		0.049	0.021	0.052	0.432

Mossgas Petition

Mossgas has submitted a petition requesting EPAct qualification for three diesel fuels produced at its existing plant through its F-T/COD process with blending variations. Table 22 lists the Fischer-Tropsch, GTL, and conventional diesel fuel proportions in each of the three fuels. Typical fuel properties for these fuels are listed in Table 23.

Table 22. Composition of Mossgas RFD1, RFD2, and RFD3 fuels.

Composition	Fuel		
	RFD1	RFD2	RFD3
COD Syndiesel (GTL)	63	68	60
SLO Syndiesel (Fischer-Tropsch)	30	32	28
Condensate Diesel	7	0	7
Mosstanol 120	0	0	5
Total	100	100	100

COD = Conversion of Olefins to Distillate
SLO = Synthetic Light Oil

Table 23. Typical fuel properties for Mossgas RFD1, RFD2, and RFD3 fuels, provided by Mossgas in petition to DOE.

Property	Test Method	RFD1	RFD2	RFD3
Color	ASTM D1500	L1.5	L1.5	L1.5
Appearance	Visual	Clear and bright	Clear and bright	Clear and bright
Density @ 20°C, kg/l	ASTM D4052	0.8088	0.8066	0.8065
Distillation, °C	ASTM D86			
IBP		221.7	225.8	81.3
10%		236.6	235.8	238.5
50%		254.9	255.3	250.8
90%		322.5	324.0	317.5
FP		360.4	362.6	363.3
Flash Point, °C	ASTM D93	100.5	102.5	20.0
Viscosity @40°C, cSt	ASTM D445	2.784	2.781	2.175
CFPP, °C	IP 309	-25	-23	-24
Ash, %mass	ASTM D82	< 0.01	< 0.01	< 0.01
Sediment by extraction, %mass	ASTM D473	< 0.01	< 0.01	< 0.01
Water content, %vol	ASTM D1744	0.006	0.006	0.006
Carbon Residue, %mass	ASTM D4530	< 0.01	< 0.01	< 0.01
Copper corrosion	ASTM D130	1A	1A	1A
Strong acid number, mgKOH/g	ASTM D974	Nil	Nil	Nil
Acid Number, mgKOH/g	ASTM D974	0.001	0.001	0.001
Sulfur, %mass	ASTM D2622	< 0.001	< 0.001	< 0.001
Cetane number	ASTM D613	53.0	49.4	49.3
Aromatic content, %vol	IP391	16.4	15.6	15.9
PNA content, %vol	IP391	< 0.1	< 0.1	< 0.1
Calorific value, MJ/kg	IP12	46.7	47.5	46.1
Lubricity @ 60°C, μ	HFRR	< 400	< 400	< 400
Oxidation stability, mg/100ml	ASTM D2274	0.1	0.1	0.1

Because the three Mossgas fuels contain roughly 30% F-T diesel fuel and 70% gas to liquid products, all of the emissions benefits noted in the literature review for 100% F-T diesel fuels will not necessarily be realized. In particular, these fuels contain about 15% aromatics and have cetane numbers of about 50. These levels of aromatics and cetane numbers represent premium fuel properties relative to conventional (49 state) No.2 diesel, but would only be expected to produce a fraction of the emissions benefits of a very high cetane number and near zero aromatic diesel fuel. Although the aromatic content of the Mossgas fuels are around 15%, less than 0.1% of the total is poly-aromatic compounds. The very low levels of poly-aromatics may provide some emission benefits compared to conventional diesel fuels with poly-aromatic contents up to 10%. Additionally, Table 23 indicates that RFD3 has a flashpoint of 20°C. This is well below the 52°C minimum required by ASTM D975 and puts this fuel in the same fire safety category as gasoline. Conventional diesel fuel storage tanks, vehicle tanks, and fueling systems are not designed to handle this fuel safely and thus its market is likely to be severely limited.

Engine and chassis dynamometer testing of Mossgas fuels showed emissions reductions for CO, CO_2, NO_x, and PM. Hydrocarbon emissions were not universally reduced, but were very low in any case. Table 24 shows the emissions reductions from engine tests. Each line in the table is the average of three replicate emissions tests. A roughly 10% NO_x reduction is observed for the 1998 engine (using RFD1 or RFD3), but less than a 2% NO_x reduction was reported for the 1992 engine (using RFD1). PM reductions of 15% to 20% are reported for both fuels.

Vehicle emissions results are illustrated in Table 25. Each line in the table is the average of three replicate emissions tests. NO_x emissions benefits are much smaller on a percentage basis compared to engine tests shown in Table 24, but PM emission benefits for RFD1 are in the 10%-15% range. The data in Table 25 suggest an added PM benefit for RFD3 with the Mosstanol 120 oxygenate additive.

Table 24. Heavy-duty engine dynamometer FTP emissions using Mossgas F-T and GTL fuels.

Engine	Fuel	Emissions in g/BHP-hr				
		HC	CO	CO_2	NO_x	PM
1998 Navistar T444E	No.2 Diesel	0.183	1.091	669.81	3.848	0.112
	RFD1	0.169	0.890	647.37	3.459	0.096
	RFD3	0.327	1.016	643.38	3.339	0.096
1992 DDC 6V-92TA	No.2 Diesel	0.67	1.58	726.38	5.00	0.24
	RFD1	0.59	1.32	699.95	4.93	0.20

Table 25. Chassis dynamometer emissions on transit buses fueled with Mossgas fuel.

Vehicle	Test Cycle	Fuel	Emissions in g/mi				
			HC	CO	CO_2	NO_x	PM
Unmodified Bus #1 - PA	CBD	No.2 Diesel	1.02	39.4	5059	27.5	10.0
	CBD	RFD1	0.90	32.5	4908	26.5	8.86
	CBD	RFD3 (5% Mosstanol 120)	0.96	21.8	5034	26.9	7.45
	CBD	No2. Diesel	1.33	39.9	4896	26.3	8.93
	CBD	RFD1	1.07	33.2	4771	24.8	8.56
Catalytic Converter Equipped Bus #2 - PA	CBD	No.2 Diesel	0.43	1.72	4356	26.8	1.69
	CBD	RFD1	0.40	1.72	4356	26.8	1.69
	CBD	RFD3	0.42	0.27	4369	26.6	0.97
	CBD	No.2 Diesel	0.35	1.07	4458	26.9	1.89
New York City Transit Bus	CBD	No.2 Diesel	0.05	2.09	2869	36.7	0.150
	CBD	COD	0.05	1.03	2816	32.2	0.085
	NYBus	No.2 Diesel	0.12	15.50	7639	85.7	0.730
		COD	0.15	6.55	7272	0.370	1.27
	Route 22	No.2 Diesel	0.10	2.60	2506	32.9	0.130
		COD	0.15	1.96	2386	26.9	0.097

CBD: Central Business District Cycle
NYBus: New York City Bus Cycle
Route 22: Ad hoc cycle developed from trip data for buses operating in New York City
COD: Mossgas Conversion of Distillate Fuel

While the emissions data provided by Mossgas show consistent emissions reductions for RFD1, RFD3, and COD, the data were acquired for a very small sample of engines and vehicles and are therefore not representative for predicting emissions benefits for the U.S. in-use diesel fleet in general. No data was presented for light-duty emissions. Statistical analysis can only be performed for the specific test vehicles in the data provided, with no extrapolation to the larger fleet.

The emissions effects reported by Mossgas are consistent with the previous discussion of fuel properties and the review of fuel property effects on emissions provided in this document. The statistical significance of the emission data is shown in Table 26. The p-values were calculated using the procedure outlined in Appendix B. For the engine data, the Mossgas fuel was compared to No.2 diesel fuel. Insufficient data were provided from the chassis dynamometer testing to assess statistical significance. The results indicate highly significant reductions in PM in all cases, and highly significant reductions in NO_x for two out of three cases.

Table 26. Statistical significance of emissions reductions for Mossgas fuels (p-value), compared to conventional No.2 diesel fuel for engine testing only.

Vehicle/Engine	Fuel	Cycle	p-value			
			CO	NOx	HC	PM
Navistar T444E	RFD1	FTP	0.0008	<0.001	0.442	0.001
	RFD3	FTP	0.031	<0.001	<0.001	<0.001
DDC 6V-92TA	RFD1	FTP	0.013	0.216	0.978	0.003

Although test data was not provided for the RFD2 fuel, emission test results should be similar to the results provided for RFD1. The RFD2 fuel is highly similar to the RFD1 fuel (see Tables 22 and 23). The RFD2 fuel is a 100% GTL and F-T product, without the small amount of conventional diesel fuel in the RFD1. It is reasonable to assume that the emissions from the RFD2 would be highly similar to the RFD1 results presented above. The additional 7% of GTL and F-T products in the RFD2 may even produce an additional emission benefit compared to the RFD1 fuel.

The RFD1 and RFD2 fuels do not contain oxygen. The RFD3 fuel contains 1.18 mass% oxygen. The oxygen is in the form of mixed alcohols, added as Mosstanol 120 at 5 vol% to the fuel. Per the above discussion on oxygenate effects on diesel emissions, the composition of the Mosstanol 120 should be provided. Some alcohols were identified by Natarajan et. al. (28) as being potentially toxic. The composition of the Mosstanol 120 oxygenate is not known at this time. Therefore, based on the data available, the effect of combustion of some oxygenates is not well understood. The oxygenates in the Mosstanol 120 and their relative proportions are necessary to determine the environmental benefits of the RFD3 fuel. Public input is needed to assess the environmental benefits of oxygenated diesel fuels.

Rentech Petition

Rentech Inc. submitted a petition for EPAct qualification of a F-T diesel fuel with typical fuel properties shown in Table 27. Also included in Table 27 is a Rentech proposed fuel specification for F-T diesel fuels. The test methods, with the exception of the lubricity method, were not given. The ash, viscosity, distillation, carbon residue, and flash point proposed specifications are identical to those in the current ASTM D975 standard (see Table 1). The sulfur, aromatic, and copper strip corrosion specifications are stricter than those laid out in ASTM D975. A cetane index specification is also proposed, but given that the cetane index correlation was developed specifically for petroleum derived diesel fuels, cetane index is probably not an appropriate parameter for F-T diesel fuels.

Table 27. Typical Rentech product analysis and recommended Fischer-Tropsch diesel fuel standards, provided by Rentech in petition to DOE.

Property	Test Method	Typical Analysis	Rentech Proposed Specification
Cetane Index		67	> 60
Sulfur, ppm		<0.001[a]	< 5 ppm
Aromatic, wt%		<0.001[a]	< 0.05
Copper Strip Corrosion		1A	1A
Distillation, T90, °C		299	317-338
Viscosity, cSt @ 40°C		1.96	1.9-4.1
Carbon Residue, 10% Bottoms, wt%		< 0.001[a]	< 0.35
Ash, wt%		<0.001[a]	< 0.001
Heat of Combustion, MJ/kg		47.85	> 41.8
Flash Point, °C		74	> 52
Carbon Content		Not given	
Oxygen Content, %		Not given	< 1
Lubricity	ASTM D6079	Not given	< 675

[a]: below detection limits

Rentech provides some evidence of a reduction of criteria pollutants from diesel vehicles. Studies using the Rentech fuel are between 10 and 20 years old, on two vehicles and one engine from that period. Results are shown in Table 28. NO_x emission benefits for this fuel are relatively small—on the order of 1% to 5% for 4-stroke engines. Large PM reductions in the range of 20% to 50% are shown. The No.2 diesel fuel that was standard during the period when the Rentech tests were conducted was not the same as the low sulfur fuel currently in use. The conventional diesel fuel available at the time the Rentech tests were performed was high sulfur (3,000 ppm cap), and particulate matter reductions with the use of Fischer-Tropsch diesel fuel will be magnified due to the high sulfur level of the base fuel.

Table 28. Emissions Reductions with Rentech Diesel Fuel.

Engine or Vehicle	Emissions Reductions			
	HC	CO	NO_x	PM
1983 VW Quantum Turbo Diesel	53%	41%	1%	35%
1984 GMC Sierra 1500 Series, 6.2L Diesel Engine	25%	30%	6%	55%
1989 DDC 8V-92TA	15%	14%	-6%	18%

In the petition, it is not clear if the VW results reported in Table 28 represent multiple emission test runs, or a single run with the Rentech diesel fuel. The GMC results are for a single test and repeatability cannot be determined from the information provided. No determination of statistical significance can be made using a single data point. Additional data is needed to determine the significance. The DDC results do show repeatability over a single test series, but Rentech provided insufficient emission data to determine the statistical significance of the test data. Because the fuel was not tested on a representative sample of in-use vehicles, no extrapolation can be made to the nation's in-use fleet.

The fuel properties listed in the Rentech petition have many of the properties that are conducive to reduced exhaust emissions, such as ultra-low sulfur content and low aromatic content. The cetane number of this fuel is also likely to be high, although cetane number was not reported.

Conclusions

Each of the petitioners included some emission test data with their petitions. Mossgas's test data was based on F-T/COD fuel actually produced at the Mossgas plant. Syntroleum's test fuel was produced during a pilot run of some aspects of the Syntroleum process. Rentech's test fuel was also produced during a pilot run of the Rentech process.

Only Syntroleum presented test data comparing an F-T diesel test fuel to a fuel meeting EPA 2006 ultra low sulfur diesel (ULSD) standards.[1] These tests showed somewhat lower emissions for the F-T diesel test fuel, but the difference was not statistically significant. While a typical fuel property analysis was given in the petition, the exact composition of the test fuel was not. Syntroleum published the petition data in an SAE paper (39), where the fuel properties were presented. It is reasonable to assume the fuel properties presented in the technical literature are the same fuel properties that were used for the tests presented in the petition.

The petition data shows overall emissions reductions relative to No. 2 diesel in the range of 20% for PM, and 10% for NO_x, although one of Rentech's tests showed a 6% NO_x increase, compared to No.1 diesel fuel. The data also showed overall smaller emissions reductions for CO and HC, although one Mossgas test showed a substantial HC increase.

None of the data for individual petitions included a broad range of vehicles representative of the overall U.S. diesel population. To be considered representative, the data would have to include a variety of makes, model years, engine and emissions system types, ages and levels of mileage accumulation, and possibly other characteristics. Moreover, the volume of data included in the individual petitions was clearly insufficient to make estimates of overall emission reductions that would achieve any meaningful level of statistical significance.

NREL augmented the petition data with other published studies on emissions of Fischer-Tropsch diesel fuels. This aggregated data set showed reductions in regulated emissions in nearly every case. However, even the aggregated data does not include a sufficient variety and quantity of data to estimate emissions reductions for the current and future in-use diesel vehicle fleet.

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[1] EPA's Final Rule establishing the 2007 diesel fuel standards had not yet been promulgated at the time the petitions were submitted to DOE. EPA's proposed rule had been pending for some time, however, and the likely sulfur standards was well known to petitioners as they undertook the test programs for their petitions.

APPEDNIX B – DISCUSSION OF STATISTICAL ANALYSIS TECHNIQUES

Two Sample t-test Analysis-Approach

The two sample t-test was used to determine the effect of Fischer-Tropsch diesel fuel on exhaust emissions for small sets of sample data (i.e. for an individual engine or vehicle). The t-test compares the average emission of each sample by pooling the variance and generating a p-value. The p-value provides an indication of significance of the data.

Usefulness of the Two Sample t-test

The two sample t-test can be used for small sets of sample data. The t-test is applicable if no information is known about the larger population. For emission testing, the t-test almost always applies due to the large number of engine/vehicle combinations that represent the in-use population. Due to the small size of the samples used in the t-test, the results cannot be applied to the population as a whole.

Assumptions of the Two Sample t-test

The t-test assumes that the two samples being tested are independent and random. For engine and vehicle testing this assumption is valid. For example, an engine is tested on conventional No.2 diesel fuel and F-T diesel fuel—three tests on one fuel and three tests on the other fuel. For this type of test, which is typical for engine and vehicle testing, the results from each fuel are independent. The emissions from first fuel will have no influence on the emissions from the second fuel, thus the samples are independent.

The assumption of randomness of the emissions is less intuitive. The variation of the emission results is assumed to be due to indeterminate error of the test equipment. By definition, indeterminate errors are random. The variation comes from differences between tests due to the test equipment, rather than differences in the fuel. This assumption is widely used in analyzing the statistical significance of engine and vehicle test results.

The variance of the samples is assumed to be equal. The variances are equal because the samples are randomly selected from a population. The population is assumed to be normal, and thus the standard deviations of any samples taken from the population are equal. The result of this assumption is that the standard deviation of the two samples can be pooled. This pooled standard deviation is a better estimate of the population standard deviation.

Example of Two Sample t-test

The procedure for the two sample t-test is not shown here, as the test is readily available in many current spreadsheet programs, eliminating the need for manual calculations. For an example of the t-test, see Reference 40.

Wilcoxon Signed-Rank Test

Approach

The Wilcoxon Signed-Rank test (30) is used to determine the statistical significance of paired data. An example is given below using the NO_x data in Table 3. In the Wilcoxon test, average NO_x emissions are paired such that for a given test series on a given engine, the NO_x is paired for the F-T diesel fuel and the conventional diesel fuel. Once the data is paired, the difference of the data is determined. The absolute differences of the pairs are ranked from low to high. Data pairs where no difference exists are omitted from the ranking. Identical differences are assigned as a 'tie', with equal ranking for each occurrence. The ranked pairs are then reassigned as positive or negative, based on the original difference. For example, an original negative difference is assigned a negative rank. The signed ranks are used to determine the critical value. The critical value is used to determine the statistical significance of the data.

Usefulness of Wilcoxon Signed-Rank Test

The Wilcoxon test allows for many types of emission data to be aggregated. This aggregated data increases the sample size and broader statistical conclusions can be drawn. For exhaust emissions, the Wilcoxon test incorporates both engine and vehicle emission data. Because the test uses differences in paired data, no corrections need to be made if data is in different units (i.e. g/BHP-hr and g/mi). Additionally, the Wilcoxon test can incorporate steady state and transient data into the same determination.

Example of Wilcoxon Signed-Rank Test

Using the NO_x emission data from Table 3, the following table can be produced. Each data point in Table 29 corresponds to an average NO_x emission from Table 3. Note that where a single conventional diesel fuel was compared to multiple Fischer-Tropsch diesel fuels, the NO_x emission for the conventional diesel fuel was entered into the table twice.

Table 29. Paired NO_x data from Table 3 for demonstration of Wilcoxon Signed-Rank Test.

x_A	x_B	**Explanation of Terms**
3.79	4.44	NO_x emissions for Sasol[3] and CARB[3] diesel for a 1991 DDC S60 engine
3.82	4.44	NO_x emissions for Sasol[3,4] and CARB[3] diesel for a 1991 DDC S60 engine
4.607	4.893	NO_x emissions for Shell[5] and CARB[5] diesel for a 1994 Navistar T444E engine
4.026	4.478	NO_x emissions for Shell[14] and 10% aromatic[14] diesel for a 1991 DDC S60 engine
4.026	4.773	NO_x emissions for Shell[14] and CARB[14] diesel for a 1991 DDC S60 engine

The difference and absolute difference of x_A and x_B is calculated in Table 30.

Table 30. Calculation of the difference of the paired NO_x data and the absolute value of the difference for the Wilcoxon Signed-Rank Test.

x_A	x_B	$x_A - x_B$	$\lvert x_A - x_B \rvert$
3.79	4.44	-0.65	0.65
3.82	4.44	-0.62	0.62
4.607	4.893	-0.286	0.286
4.026	4.478	-0.747	0.747
4.026	4.478	-0.452	0.452

The absolute value of the difference of the pairs are ranked from low value to high value (Table 31). The ranked differences are reassigned the appropriate sign from the original difference between observations. The signed differences are averaged to compute W. The total number of non-zero observations is also calculated. The sample standard deviation, σ_w, is computed using (1). From W and σw, the critical value, Z, can be calculated using (2).

Table 31. Rank and signed rank of the difference of the NO_x data taken from Table 3.

$\lvert x_A - x_B \rvert$	Rank	Signed Rank
0.286	1	-1
0.452	2	-2
0.62	3	-3
0.65	4	-4
0.747	5	-5
	W	**-15**
	N	**5**
	σ_w	**7.4**
	Z	**-2.09**

$$\sigma_w = \sqrt{\frac{N(N+1)(2N+1)}{6}} \tag{1}$$

$$Z = \frac{W - 0.5}{\sigma_w} \tag{2}$$

For this example, the critical value is –2.09. Using a non-directional test, the significance table provided in (40), the NO_x reduction with Fischer-Tropsch diesel fuel compared to conventional diesel fuel is significant at the 95% confidence level. This procedure was followed to compute the critical values in Table 13.

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