

ULSD COMPOSITION-2007

Michael Leister
Marathon Ashland Petroleum LLC

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DIESEL FUEL TIMELINES

6/1/2006 6/1/2007 6/1/2008 6/1/2009 6/1/2010

**HIGHWAY
RULE**

80% 15 PPM/20 % <500 PPM 100% 15 PPM →

**NON-ROAD
EPA'S
2 STEP ALT**

PART 89 <500 PPM 15 PPM →

RAILROAD <500 PPM

OR 15 PPM →

**HOME
HEATING
OIL**

HOME HEATING OIL >500 PPM →

WHAT WILL NEW CLEAN DIESEL LOOK LIKE?

- **MANY DIFFERENT TECHNOLOGIES/
REFINERY CONFIGURATIONS WILL
BE USED**
- **THERE WILL BE REGIONAL
DIFFERENCES**
- **CURRENT ULSD PRODUCTION MAY
NOT BE REPRESENTATIVE OF
FUTURE ULSD**

DIFFERENT TECHNOLOGY OPTIONS

- **HYDROTREATING – DHT**
 - REVAMP vs GRASSROOTS
 - OPERATING PRESSURES
 - HYDROGEN PURITY
 - CATALYST OPTIONS
 - UNDERCUTTING DISTILLATE FEED
- **HYDROCRACKING**
- **GAS OIL HYDROTREATING + DHT**

REGIONAL DIFFERENCES

- CALIFORNIA HAS DIFFERENT REFINERY CONFIGURATIONS
- NORTHERN REFINERIES WITH ACCESS TO CANADIAN CRUDE MAY CONSIDER GAS OIL HYDROTREATING
- GULF COAST REFINERIES WILL OPTIMIZE DESULFURIZATION w/CRUDE SLATE OPTIONS
- ULSD IMPORTS WILL BE A KEY FACTOR IN PADD 1

DIFFERENCES IN CURRENT vs FUTURE ULSD

- FEW REFINERIES MAKING ULSD FROM ENTIRE DISTILLATE POOL
 - FULL RANGE vs STRAIGHT RUN
 - BATCH vs CONTINUOUS OPERATION
- DIFFERENT DISTRIBUTION SYSTEM
- DIFFERENT QUALITY CONSTRAINTS

WHAT WILL NEW CLEAN DIESEL LOOK LIKE?

- **SULFUR CONTENT**
 - MANUFACTURED – 5-10 PPM SULFUR
 - DELIVERED – 15 PPM SULFUR
- **CETANE NUMBER – 1-2 NUMBER IMPROVEMENT**
- **AROMATIC CONTENT – SLIGHTLY LOWER**
- **ENERGY CONTENT – SLIGHTLY LOWER**
- **LUBRICITY – WILL MEET ASTM STANDARDS-MAY REQUIRE ADDITIVES**

2002 National Average Diesel Properties

(2002 Diesel Fuels Survey, includes California)

API Gravity	34.4
Sulfur, ppm	340
Flash Point, F	159
Viscosity, cs 40 C	2.73
Particulate Matter, mg/l	15 Max.
Cetane Index	45.8
Cetane Number	46.4
IBP, F	367
T10, F	424
T50, F	511
T90, F	605
EP, F	655
Aromatics, vol%	27.7

2007 EPA Diesel Certification Fuel

Specific Gravity, 60/60	0.840-0.865
API Gravity	32-37
Sulfur, ppm	7-15
Flash Point, F	130 Min.
Viscosity, cs 40 C	2.0 Min.
Particulate Matter, mg/l	15 Max.
Cetane Index	40-50
Cetane Number	40-50
IBP, F	340-400
T10, F	400-460
T50, F	470-540
T90, F	560-630
EP, F	610-690
Aromatics, vol%	27-32

BP15 Diesel Properties

API Gravity	37.5
Specific Gravity	0.8374
Sulfur, ppm	13.0
Flash Point, F	147
Viscosity, cs 40 C	2.5
Cetane Index	48.8
Cetane Number	49.7
IBP, F	330
T10, F	397
T50, F	501
T90, F	614
EP, F	654
Aromatics, vol%	29.0

BP inspection data 1/9/02 wolf lake.

WHAT DIESEL FUEL SHOULD ACES USE?

- **ULSD TEST FUEL:**

- **MUST BE REPRESENTATIVE OF DIESEL DELIVERED TO VEHICLE TANKS**
 - **TYPICAL CONTAMINATION FROM JET, HEATING OIL, GASOLINE, ETC**
- **MUST REFLECT FULL RANGE DISTILLATE PRODUCTION FROM REFINERY UNITS**
 - **LCCO AND COKER DISTILLATE MUST BE PRESENT**
- **MUST REFLECT FULL CYCLE OF OPERATIONS**

OTHER ACES ULSD CONSIDERATIONS

- **AVERAGE vs 99TH PERCENTILE ULSD**
- **WHAT ARE THE DIESEL PROPERTIES OF CONCERN?**
- **WHAT ABOUT LIGHT DUTY VEHICLES? – WILL THEY USE A DIFFERENT ULSD?**
- **WHAT ABOUT LUBRICANT EFFECTS?**
- **HOW WILL ENGINE CHANGES AND EMISSION CONTROLS INTERACT WITH ULSD?**

HOW WILL FUTURE ULSD PROPERTIES EFFECT EMISSIONS?

- **SULFUR REDUCTION HAS BIGGEST IMPACT**
 - **REGENERATION SEVERITY AND FREQUENCY OF VARIOUS CATALYSTS IS STILL BEING DETERMINED**
- **ENGINE TECHNOLOGY IS LARGEST VARIABLE**
 - **EGR, HCCI, ACERT, etc.**
- **PM TRAPS, SCR, AND OXY CATALYSTS SHOULD HAVE LITTLE CHANGE IN PERFORMANCE**
- **NOX ADSORBER PERFORMANCE MAY BE IMPACTED**

Summary

- **ULSD USED IN ACES TESTING MUST BE REPRESENTATIVE OF VEHICLE TANK FUEL QUALITY**
- **EMISSIONS MUST BE FROM ENGINE/EMISSION CONTROL SYSTEMS THAT MEET THE NEW STANDARDS**
 - AGED CATALYST
 - CATALYST REGENERATION CYCLES
- **FUTURE LUBE OILS MUST BE REPRESENTED**
- **CURRENTLY MORE QUESTIONS THAN ANSWERS ABOUT BOTH ENGINES AND FUEL**

BACKGROUND SLIDES

Acronyms

- **ULSD = Ultra Low Sulfur Diesel**
- **HDS = Hydrodesulfurization**
- **DMDBT = DiMethylDiBenzoThiophene**
- **LCO = Life Cycle Oil**
- **CGO = Coker Gas Oil**
- **SHDMDBT = Sterically Hindered DiMethylDiBenzoThiophene**
- **LHSV = Liquid Hourly Space Velocity**
- **IFP = Institute Francais Du Petrole**
- **STARS = Super Type II Active Reaction Sites**
- **MAKFining = Mobil M.W. Kellogg Akzo Fina Technology**
- **UOP = Universal Oil Products**
- **HDN = Hydrodenitrogenation**
- **RVA = Relative Volume Activity**
- **EP = End Point**
- **LCGO = Light Coker Gas Oil**
- **HDA = HydrDeAromatization**
- **CARB = California Air Resources Board**
- **BDS = BioDesulfurization**
- **FCC = Fluid Catalytic Cracker**
- **MQD = Maximum Quality Diesel**

Diesel background and Challenges (continued)

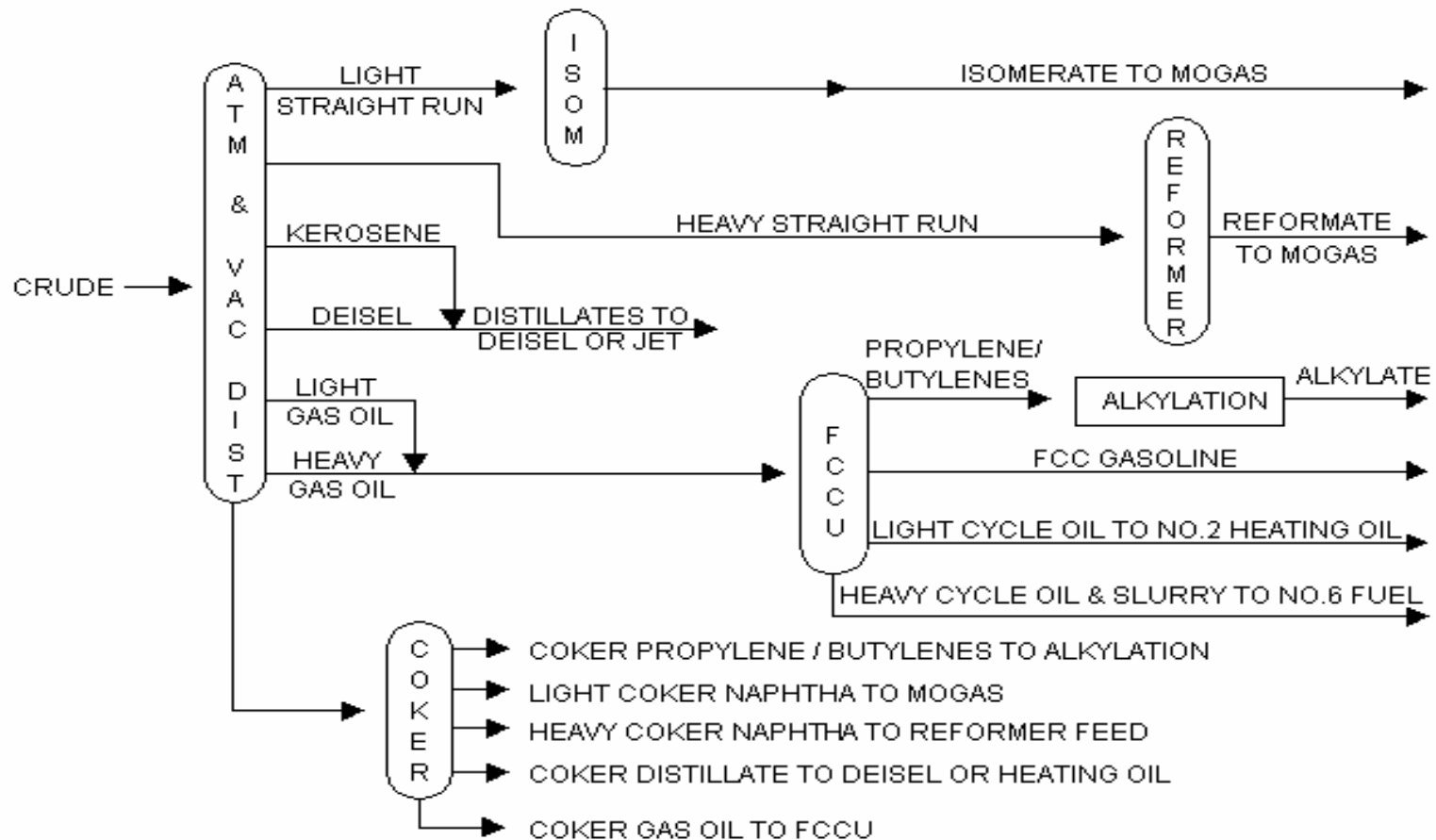
- **ULSD production involves DMDBT chemistry**
- **When the alkyl groups are in the 4, 6 position adjacent to the sulfur atom, they are known as SHDMDBT (sterically hindered)**
- **Two reaction pathways for sulfur removal – direct extraction and hydrogenation**
- **Hydrogenation pathway is the key for ULSD production**
- **To complicate matters, a “floor” exists for sulfur removal, at which further increase in temperature has no effect on sulfur reduction**
- **If “floor” is too high, no option other than reducing end point or space velocity or increasing pressure**
- **LCO is the most difficult to treat and may have to be undercut**
- **Quality of fractionation is important for separation precision**
- **Typically, the impact of reducing sulfur from 500 ppm to 15 ppm is a threefold increase in catalyst volume – all operating conditions, feedstock, activity, cycle length are unchanged.**

World Wide Fuel Charter Category 4 Diesel

Specific Gravity, 60/60	0.82-0.84
Sulfur,ppm	5 -10
Flash Point, F	122 Min.
Viscosity, cs 40 C	2.0-4.0
Particulate Matter, mg/l	24 Max.
Cetane Index	52.0 Min.
Cetane Number	55.0 Min.
T90, F	608 Max.
T95, F	644 Max.
EP, F	662 Max.
Aromatics, wt%	15 Max.
Lubricity, HFRR scar <u>dia.@60 C</u>, micron	400 Max.

Refinery Process Scheme

FIGURE 1
REFINERY PROCESS SCHEME



Impact of diesel sulfur species

Sulfur Species	Relative reaction rate	Boilint Point, F
Thiophene	100	185
Benzothiophene	30	430
Dibenzothiophene	30	590
Methyl dibenzothiophene	5	600-620
Dimethyl dibenzothiophene	1	630-650
Trimethyl dibenzothiophene	1	660-680