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Transitions from Diesel Muds: Options, Properties, and a Proposal

Richard Baxter and Matt Offenbacher, AES Drilling Fluids; Didier Bedel and Philippe Lemaire, Total Fluides; Christopher Miano, Calumet Specialty Products, L.P.

Abstract

The most common drilling fluid system for land-based unconventional applications in the United States remains a diesel-based invert emulsion. While studies show this base fluid meets requirements for exposure to personnel, advances in refining technology offer an opportunity to improve conditions for personnel and the environment with a transition to new base oil alternatives.

This paper will discuss these advancements as well as recommendations for base oil properties that improve working conditions at the rigsite and lower the potential risks to the environment from exposure. With millions of dollars of diesel-based drilling fluid in inventory, an economic analysis reviews the timetable to convert this inventory over to new base oil systems. The authors will share experience with similar transitions.

Through a comprehensive review of the options discussed, the authors are seeking to initiate a conversation within the industry to generate consensus on the necessary properties and requirements that would result in a cost-effective transition if and when operators choose to enhance the health and safety profile of invert emulsion drilling fluid systems in the U.S. unconventional market.

Introduction

Diesel remains a common, low-cost option for non-aqueous drilling fluids and it is approved in many locations throughout the United States. While it remains an acceptable option, enhancements in refining continue to narrow the cost gap between diesel and mineral oils where lower toxicity options become more practical.

Demand for diesel alternatives grows as drilling operations expand near environmentally sensitive and/or residential areas, operators tighten internal policies regarding raw material consistency, and as they seek to enhance their profile as a greater steward of the environment. In the midst of requests for alternatives comes confusion defining the differences among a number of options. While the term “synthetic” is traditionally associated with “better”, it is important to focus on advantages relative to diesel and specifically identify and quantify key favorable properties inherent to diesel alternatives.

Overview and History

The history of alternative base oils for drilling fluids has its origins in the offshore market. In the early 1990’s onsite discharge of cuttings using oil-based muds was banned, requiring the transition to synthetic-based muds to avoid the cost of cuttings transport to onshore disposal sites. Requirements varied by jurisdiction; however, the primary driver focused on environmental impact, particularly discharge and seabed accumulation of cuttings. [1,2] Additional standards consider exposure to personnel, including enclosed areas such as pit rooms and the shakers[3].

In the United States, many land applications still allow the use of diesel. The cost and availability of diesel makes it the base fluid of choice, where permitted. Beyond local regulations, alternative base oils are used for their perceived health and safety benefits. Near populated areas, some operators have employed diesel alternatives to minimize odors. [4]

Base Oil Production

Base oils are manufactured through a variety of processes, ranging from crude oil refining to chemical synthesis. These processes vary in complexity and associated cost. Products may be blended or further modified to achieve key properties.

In many cases, nearly identical molecules are derived from different processes. Historically, refining technology was cheaper but left trace impurities not seen with chemical synthesis processes[2]. With the advent of stricter regulations for fuels, processing technology can now dramatically reduce or eliminate these trace impurities.

Definitions of mineral oils versus synthetics are inconsistent between regulatory bodies, creating significant confusion[5,6]. Diesel is universally considered an oil-based drilling fluid. Other categories include mineral oils, enhanced mineral oils and synthetics.

Generally speaking, the manufacturing process is a key factor in defining a base oil category; however, highly refined materials with treatment processes offer the same molecules with potential for trace impurities. Materials produced with purely synthetic processes generally cost more, but have nearly all impurities removed. Mineral oil and synthetic materials include paraffins, olefins, and esters. Molecular structure is noteworthy as it impacts various performance factors.

Distillation Products

Refining processes begin with crude oil, which varies in composition and yield. The source crude is separated into carbon fractions using a distillation unit (**Figure 1**). These fractions are further processed. Heavy carbon fractions can be reduced to lighter carbon fractions through conversion. Other refining processes remove impurities, such as sulfur.

Petroleum diesel is a fractional distillate of crude oil. It does not have a specific molecular structure and varies by refinery; however, ASTM D975 standards define properties such as cetane number for suitability in combustion engines and sulfur content.[7] Diesel properties vary beyond these standards but offer a more consistent profile than crude oil.

The EPA began regulating sulfur levels in diesel fuel in 1993. Phase-in of more stringent regulations began in 2006 to reduce sulfur content to 15 ppm[8]. Ultra low sulfur diesel regulations resulted in the upgrading of many refining facilities to meet stringent requirements[9]. These upgraded facilities now provide greater control of a variety of impurities, resulting in the availability of base oils containing far fewer toxins than their predecessors.

Refined Processes and Materials

Upgraded refineries feature both new and larger scale equipment and processes to achieve the required objectives. Fluid catalytic cracking (FCC) uses a catalyst to produce high yields of distillate material, including olefins. Catalysts utilized for FCC fail to perform in the presence of sulfur, requiring treatment before processing.

Hydrocracking is a process that uses hydrogen streams and a catalyst to further convert crude fractions. This process removes sulfur and dramatically reduces aromatics. Refineries with FCC units commonly feature a hydrocracker to process high aromatic and high sulfur streams before they enter an FCC process[10]. Ultra low sulfur diesel requirements, in combination with extensive sources of hydrogen from the unconventional market, has resulted in significant increases in hydrocracker capacity for a variety of refined products[11,12].

Synthesis

Chemical synthesis relies on a variety of processes, many of which may be components of a refining process, combining base molecules, such as ethylene into more complex materials.

One means to produce suitable drilling fluid base oil is a gas-to-liquid conversion. The Fischer-Tropsch method uses a multi-step process to convert hydrogen and carbon monoxide into base oil molecules. Even this process, which excludes the use of crude oil for base material, requires a process to remove impurities, including sulfur, which compromises catalyst performance.

Esters are naturally occurring materials, commonly derived from plant or vegetable oils through the reaction of a fatty acid and an alcohol under temperature and pressure (**Figure 2**).

Base Oil Varieties

As mentioned, base oils may be produced through several means. In many cases, same molecule can be generated through combinations of distillation, hydrotreating, isodewaxing, and/or hydroisomerization of crude oil or through combination and manipulation of other feedstock, such as natural gas, or even vegetable oil.

Modifications to hydrocarbon chains alter properties both for health, safety and performance characteristics. In general terms, some toxicity increases with decreasing molecular weight (including inhalation or skin sensitivity) and viscosity decreases with decreasing molecular weight. Materials with the same molecular weight may feature branching or relocation of double carbon bonds. A linear configuration often exhibits higher pour point and lower toxicity than a branched structure[13]. Example structures are shown in **Figure 3**.

Olefins (also known as alkenes) contain at least one carbon-carbon double bond with a general chemical formulation C_XH_{2X}. Some of the first generation synthetic base fluids were poly-alpha olefins; however, linear alpha olefins are more common today.

Isomerization is a modification where a carbon double bond is relocated on the molecule, but the molecular weight remains the same. A linear alpha olefin features a double bond at the primary position of the molecule followed by a linear carbon chain. Internal olefins are produced by moving the double bond to a different position, lowering pour point and viscosity as the molecules cannot "pack" as tightly together[2].

Paraffins (also known as alkanes) with all single carbon-carbon bonds with a general chemical formulation C_XH_{2X+2}. The longest chain of linked carbon atoms is the backbone. The shape of the backbone denotes a linear, branched, or cyclic paraffin. Linear paraffins are produced through synthetic means or through hydrocracking and severe treatment[2].

Branched paraffins (also known as isoparaffins) include those produced by reacting natural gas with oxygen as part of the gas-to-liquid process.

Olefins are manufactured from pure ethylene and then distilled to the desired molecular weight based upon the total carbon number. Linear paraffins are manufactured through refining or synthetic means[2].

Esters are considered some of the most "friendly" products; however, they are also the most expensive and require precautions at higher temperatures as they can undergo hydrolysis, potentially solidifying.

Base Oil Properties

The authors recommend that a diesel alternative meet a realistic set of properties. These properties are achievable through both refining and chemical synthesis and provide practical boundaries for performance, health, and safety relative to diesel. Many of the properties recognize existing regulatory standards while others, such as viscosity, are important for performance.

Flash Point

Flash point testing provides an ignition source to material as it is heated. As vapors are released, the temperature of ignition is the flash point. Automated devices are available featuring either an open-cup or closed-cup configuration. The closed-cup method offers the most consistent results and is required to define flammable liquids per ASTM D4206[14]. A flash point below 170°F requires added markings and protocols for storing and transportation.

Transportation

Diesel fuel is considered hazardous by the OSHA Hazard Communication Standard[15], and placarded accordingly[16], whereas diesel alternatives bearing flash point ranges of 170°F and above are shown to meet sustained burning exemptions per ASTM D4206 results. These alternatives ship unplacarded. This means that for materials that would otherwise be placarded combustible, the HAZMAT requirements for materials that do not sustain combustion per the ASTM D4206 methodology permit these diesel alternatives to ship as nonhazardous per DOT. Lower flash point diesel alternatives flash points below 170°F and may be transported with appropriate precautions – just as diesel is shipped now.

Viscosity

The inherent viscosity of base oil has a dramatic effect on performance. Diesel viscosity can vary dramatically by refinery and production run, whereas diesel alternatives target specific controlled properties for consistent performance. Base oil providers regularly cite the kinematic viscosity of their products on technical data sheets in centistokes, with water having a kinematic viscosity of 1 centistoke at 20°C.

In critical wells, lower viscosity aids in reducing equivalent circulating density. In cold weather or offshore environments, low viscosity aids to prevent dramatic thickening. Higher viscosity also limits flow rates for hole cleaning. In some applications, it is possible to compensate for elevated viscosity by adjusting the oil content; however, there is added cost.

In some applications, base oil viscosity may not be a critical factor. In these cases, blends of two or more base fluids can be used to achieve the acceptable viscosity at the lowest cost. (**Figure 4**)

BTEX, PAH and Total Aromatics

BTEX is a group of aromatic chemicals known to have significant impact on human health. Benzene and ethylbenzene are known carcinogens and all of these chemicals impact skin, sensory and the central nervous system[17]. As early as 1948 the API stated "it is generally considered that the only absolutely safe concentration is zero"[18]. The EPA requires gas chromatography/mass spectrometry (GC/MS) to measure BTEX. Polycylic aromatic hydrocarbons (PAH) includes priority pollutants[18], such as benzo(a)pyrene, fluorene, naphthalene, phenanthrene, etc. along with alkylated benzenes and biphenyls[18]. Many PAHs are classified carcinogenic and present human health risk.

PAHs are detected with gas chromatography-mass spectrometry or liquid chromatography. Refining processes are able to achieve PAH levels below 10 ppm while synthetically manufactured materials exclude PAH completely.

Total aromatic content for ASTM D975 Type 1 and Type 2 Ultra Low Sulfur Diesel (ULSD) is limited to 35% volume[7]. Diesel alternatives are manufactured to intentionally limit total aromatic content to less than 1%.

In the United States, the State of California, Proposition 65, officially known as the Safe Drinking Water and Toxic Enforcement Act of 1986 ("Prop 65"), was enacted as a ballot initiative in November 1986. Its enforcement is intended to limit California citizens to exposure to chemicals suspected or shown cause cancer, birth defects or other reproductive harm in humans[21]. Diesel-based formulations frequently include warnings regarding potential exposure to Prop 65 substances due to the common presence of BTEX and other substances demonstrated by GC-MS to be present in diesel fuel.

Skin Sensitivity

Skin sensitivity testing to base oil alone fails to consider that a complete drilling fluid formulation includes other known skin irritants, such as many emulsifiers and the internal brine phase. Regardless of the type, most base oils will act as a solvent on the natural lipids and fats in the skin, resulting in a net loss that causes a drying effect. Irritation is generally associated with aromatics and C_8-C_{14} paraffins, which have limited or no presence in many diesel alternatives[22]. Most testing uses laboratory animals versus a control. OECD 404 recommends young adult albino rabbits[23].

Toxicity and Biodegradability

Many toxicity and biodegradability studies originated from the marine environment and focus on sea column and sediment dwelling organisms. Specific tests are established by various regulatory agencies. Occasionally, offshore regulations are adopted for land scenarios as they are more clearly defined. Overall, a reduction in aromatic content and other structures associated with toxicity results in more favorable results for most test methods[13]. While a number of methods and standards are available, it is difficult to specify comprehensive and representative testing applicable to the entire land market in the United States.

Toxicity and biodegradability are complex to evaluate, with numerous test methods sometimes yielding inconsistent results[13]. For example, In many areas, toxicity testing usually focuses on EPA Method 1007.0 using mysid shrimp as a baseline for toxicity[24]as it is the standard for offshore testing in the United States. More biodegradable materials appear more toxic in this test[13]. Other areas use the OSPAR commission requirements, which focus on the North Sea and North Atlantic.

Biodegradability is performed in aerobic and anaerobic environments, accounting for accumulation of materials that creates an oxygen-free environment, such as cuttings piles and burial. One procedure, OECD 301B determines readily biodegradable material by measuring CO_2 production or oxygen consumption over a minimum of 28 days in a liquid environment. OECD 306 uses seawater over 30 days and is more difficult to perform.

Under OECD, only readily biodegradable tests are allow for a classification as biodegradable. Inherently, biodegradation is only to show that a substance is not PBT (Persistent & Bioaccumulable & Toxic). The threshold value is 60% in 28 days for both tests (OECD 306 and 301B). For both readily biodegradation tests, a threshold value of 60% in 28 days should be passed to classify a substance biodegradable. It is important to take into account that the 60% value in itself has no meaning, it is just a threshold. A substance with, for instance, a biodegradation of 75% is not more biodegradable than a substance having only 62%. Many diesel alternatives exhibit some inherent to readily biodegradable properties, achieving 20% to over 60% biodegradation in the OECD 301B model.

Soil studies have attempted to further characterize the biodegradability of base oils through decomposition analysis, earthworm exposure, and plant exposure[25]. These trends may vary by base fluid and soil type.

Performance Claims of Diesel Alternatives

There are a wide variety of base oil options and with their introduction comes potential improvements to the drilling process. Some of these claims are speculative while others are supported by consistent data. It is a challenge to offer well-for-well comparisons as the drilling environment varies not only by formation but also the drilling fluid properties and practices required.

Another key factor in performance claims is the lack of data from subsequent wells. Field trials and new applications receive greater attention as the process change requires added steps to prepare personnel and equipment. Many field trials include technical experts and greater scrutiny from management, potentially yielding exceptional results not found when a new application becomes routine.

Over many years, diesel alternatives have been introduced with encouraging initial information suggesting any number of performance improvements, yet these products never became standards[26,27,28,29]. It is surmised that the benefits diminished over time and operators returned to the lowest cost option that meets regulatory requirements.

Elastomer Compatibility

Mineral oil and synthetic base oils generally feature a higher aniline point than crude oil or diesel. The aniline point is a worthwhile indicator of elastomer compatibility; however, it is unclear if elastomer failure from base oil is the first mechanism that requires replacement of these materials.

The aniline point is the lowest temperature at which equal volumes of aniline and the base oil are completely miscible. Low aniline points are generally tied to elastomer failure as they related to a higher aromatic concentration. API 13B-2 offers a method suited to test base oils[30]. The authors believe the aniline point is not a truly quantitative indicator of elastomer compatibility and that further work is necessary to quantify the potential significant benefits of using materials such as isoparaffins and paraffins to extend elastomer life.

Diesel features a relatively low aniline point; however, hundreds of wells are drilled every year without operators citing chronic elastomer failure as a key contributor to lost time. Additionally, the variability in diesel aniline point presents challenges for elastomer durability, batch to batch. **Table 1** presents a selection of aniline points of diesel and diesel alternatives.

Rate of Penetration

Numerous publications cite elevated rate of penetration with the introduction of a new base fluid[26,27,28,29]. It remains unclear if this improved performance remains sustainable beyond the introduction of fresh drilling fluid with the new base oil. Throughout a search of literature, the authors are unable to find sustained claims of enhanced rate of penetration.

Reuse of fluid and required dilution introduces a set of acceptable but less pristine condition. Drilling fluid economics relies on the balance of acceptable properties while limiting aggressive dilution and it is believed that after extensive use any invert emulsion will exhibit rates of penetration similar to other base fluids.

Vapors

Exposure is difficult to quantify, particularly with individual case histories that do not account for chronic exposure. Multiple accounts cite appreciation for the elimination of a diesel odor both at the rigsite and in nearby populated areas[4,27].

A previous study[31] comparing vapor exposure at the rigsite indicate highest levels at the shakers and that vapor concentration decreased rapidly as sampling moved even several feet away from the surface of the drilling fluid. Measurements were 30% of those measured in the laboratory, further complicating measurement standards. Regardless of perceived and measured effects, elimination or reduction of vapors and the toxic aromatics associated with them benefits personnel.

Waste

Waste volumes and handling depends upon the regulatory environment of the location. There are potential savings if transportation or disposal costs are reduced using a diesel alternative. Cost efficiency depends upon equipment to treat drill cuttings to achieve required properties for onsite disposal. This eliminates offsite transportation and disposal costs, but in many areas costs may not justify this practice. In areas utilizing diesel alternatives, solids control efficiency receives more attention to retain a more expensive base oil. Additional processing equipment improves overall efficiency to reduce waste.

Education of regulatory bodies on the reduced toxicity of diesel alternatives could ultimately lead to reduced disposal costs as the impacts of various options become clear.

Recommended Properties

It is assumed that with regular use, all options will offer similar drilling performance. Properties are recommended as a practical medium to balance cost, availability, and sensitivity to people and the environment. It is believed that numerous products on the market meet these requirements.

Properties are cited in **Table 2**, limiting BTEX and total aromatics. Additional input from other experts may expand or modify the current recommendations.

The elimination of known carcinogens from potential water table and workplace exposures and the provision of acceptable land-based biodegradability, improved worker safety, and reduction in DOT compliance issues would provide drilling operations numerous benefits, which refiners could provide within a matter of months, sustaining supply across the United States.

Economics of a Transition

The greatest resistance to moving away from diesel is the perceived cost. As with the move to ultra-low sulfur diesel, costs are challenging to quantify as the primary benefit is not a direct economic driver. The value of improved environmental, health and safety conditions is difficult to estimate. The return extends beyond better working conditions to goodwill and the potential to limit more restrictive measures that offer less benefit.

A key consideration is how such a transition applies to a well, state, region, or the entire United States. There are thousands of barrels of diesel-based drilling fluid in use today with tremendous economic value. It's unreasonable to expect a transition to happen overnight. This is further complicated by the availability of qualified base oils. There is sufficient capacity, but increased demand can alter the economics. The energy information agency estimates that there is nearly 18,000,000 barrels per day capacity of hydrodesulfurization capacity[32], although this includes any application – including ultra low sulfur diesel processing (**Figure 5**).

Dilution Model

Given the current inventory of diesel-based drilling fluid, a transition to alternatives is impractical without a prolonged phase-in period. The authors have attempted to offer a set of calculations to estimate the time period required for the transition.

The model (**Figure 6**) proposed eliminates diesel additions for dilution and preparation of fresh drilling fluid. Instead, alternative oil is added until the diesel component of the drilling fluid is diluted to below 1% v/v. Whole drilling fluid is consumed through its adherence to cuttings, loss of circulation, left behind casing, or other means. The loss rate is exhibited in a ratio of volume lost to volume of hole drilled – a common benchmark. These estimates will vary by hole size and density, with the cited model using 8 ½” hole and 13.0 lbm/gal drilling fluid.

The diesel in the original drilling fluid composition will vary by density as oil:water ratio accounts only for the liquid component – not the solids present. Higher density fluids contain more solids and therefore less overall diesel.

Dilution volume addresses accumulation of fine solids and drilling fluid built onsite. This new fluid dilutes out the diesel component as fluid is consumed and new volume generated.

Statistical review of the author's data set provides typical volumes, loss rates, and dilution, with the caution that these ratios may vary dramatically by market. The model results in ultimate dilution to 1% diesel within 75,000 feet of hole drilled. The ultimate conversion time period is highly subject to conditions, particularly rig activity and intervals utilizing diesel muds. Nevertheless, the model offers a rough outline for conversation and a baseline for further refinement.

Considerations

There are many factors to consider with a transition beyond the base fluid composition. Any change requires care thought for a smooth transition. Because diesel alternatives are in use today, many of the change requirements are known quantities with known solutions or mitigations.

Drilling fluid additives require consideration both from a performance perspective and a composition perspective[33]. Solubility of emulsifier and wetting agent components may differ from diesel, requiring alterations. Lower viscosity oils may require greater attention to low-end rheological modifiers for fresh fluids.

Personnel Misconceptions

Previous experience has revealed significant health and safety misperceptions associated with diesel alternatives. This can lead to increased risk of exposure, particularly skin contact. The lack of odor or color of many products gives the impression that a “cleaner” solution is “safe”. This can result in lax hygiene practices. In some cases, rig personnel fail to wash clothing or skin after exposure, extending contact time.

Continued hygiene practices and discipline must be emphasized upfront with any change to make to make sure rig crews understand that any improvement to health and safety from a diesel alternative does not mean completely safe.

Conclusions

The evolution of diesel alternatives continues with increased availability of cleaner materials relative to even several years ago.

- A number of base oils can meet reasonably stringent properties for health, safety, and drilling performance, regardless of their nominal designation (mineral oil, synthetic, etc.)
- Consensus on a set of practically achievable and economically reasonable properties aids to better define the benefits of diesel alternatives and identify the most beneficial material
- The authors propose that a working group pursue consensus on key properties to eliminate confusion Agreement will aid to inform regulatory bodies and offer practical solutions when new restrictions are proposed

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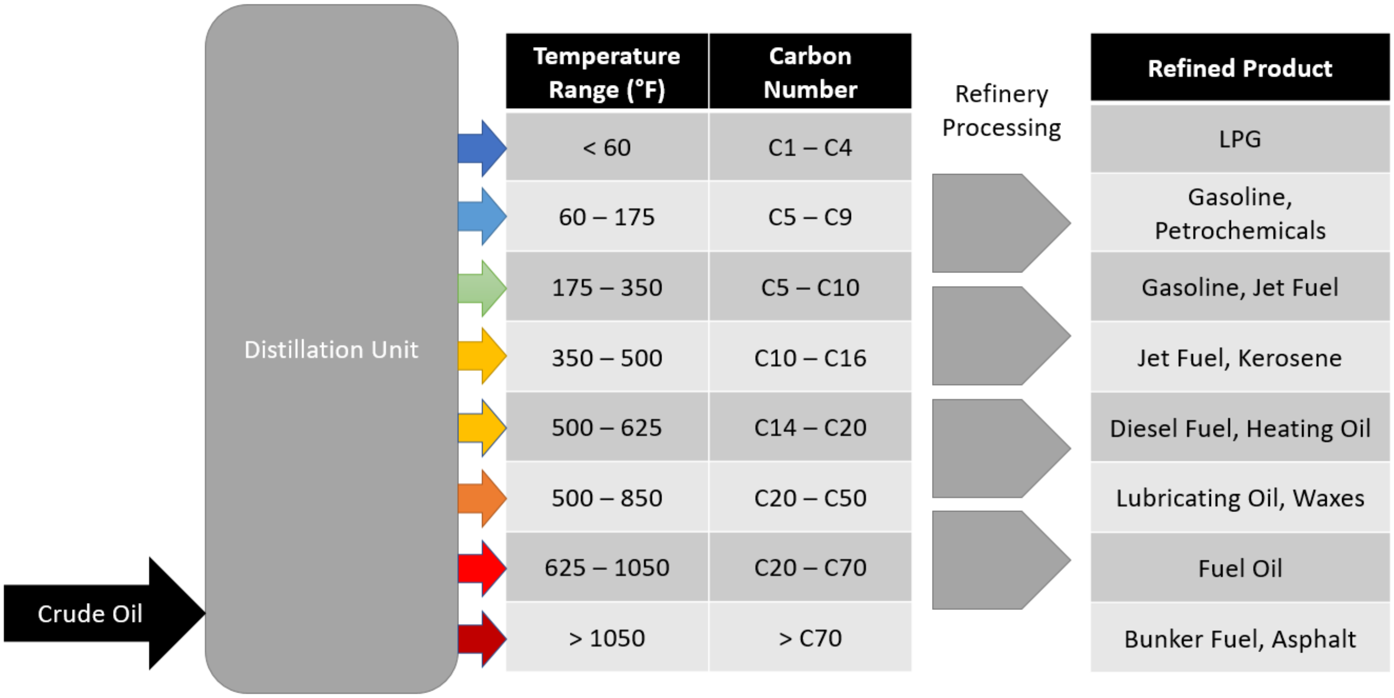

Temperature Range (°F)	Carbon Number	Refined Product
< 60	C1 – C4	LPG
60 – 175	C5 – C9	Gasoline, Petrochemicals
175 – 350	C5 – C10	Gasoline, Jet Fuel
350 – 500	C10 – C16	Jet Fuel, Kerosene
500 – 625	C14 – C20	Diesel Fuel, Heating Oil
500 – 850	C20 – C50	Lubricating Oil, Waxes
625 – 1050	C20 – C70	Fuel Oil
> 1050	> C70	Bunker Fuel, Asphalt

Figure 1: Crude oil products from fractional distillation

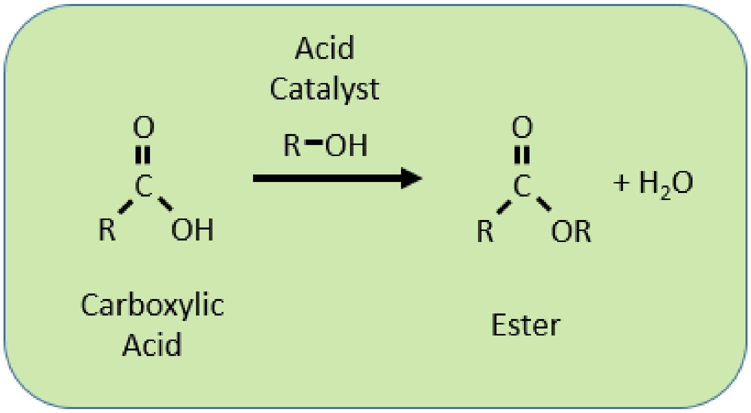

Figure 2: Example of esterification: Carboxylic acid reacted with alcohol to make an ester

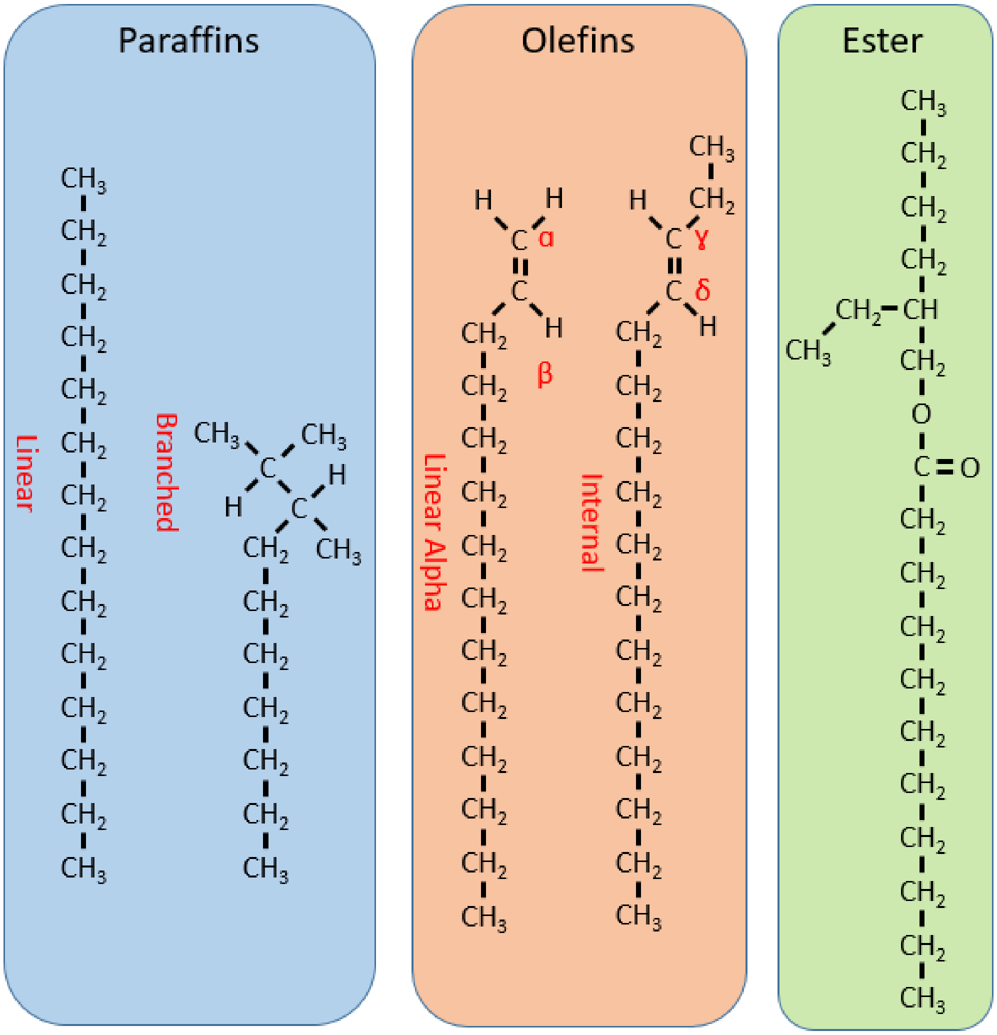

Figure 3: Structural comparison of select base oil molecules

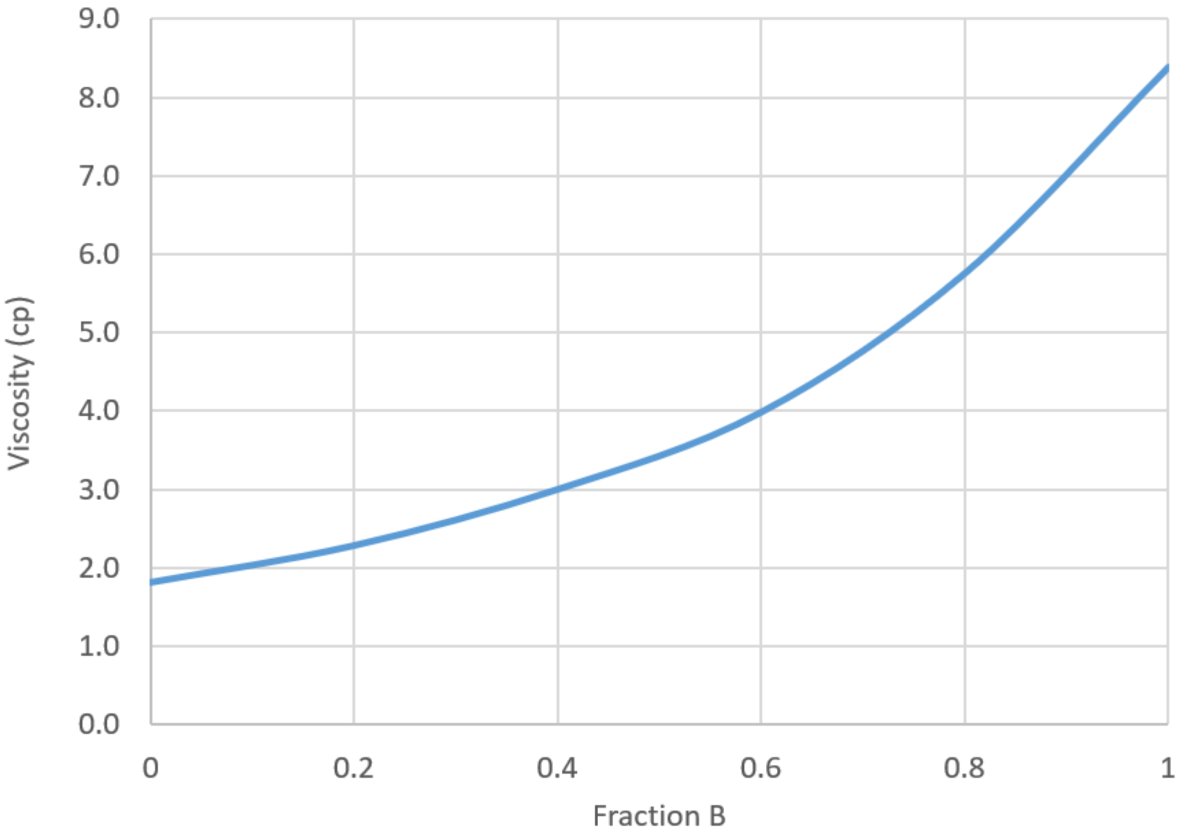

Figure 4: Example of blending to achieve properties. In this example, two base oils, A and B, are blended to achieve a target kinematic viscosity at 20°C

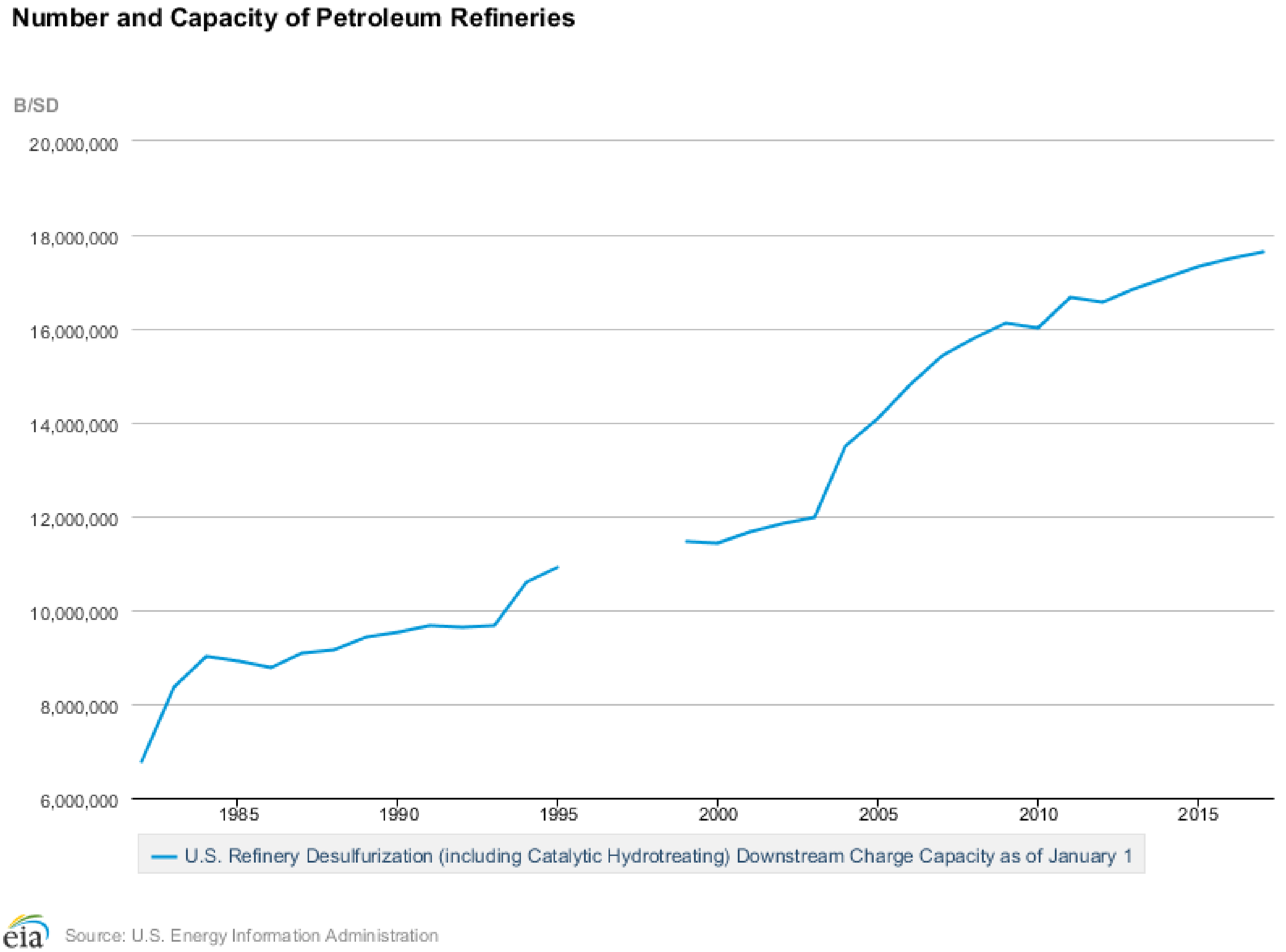

Figure 5: EIA estimate of catalytic hydrotreating capacity (barrels per stream day)

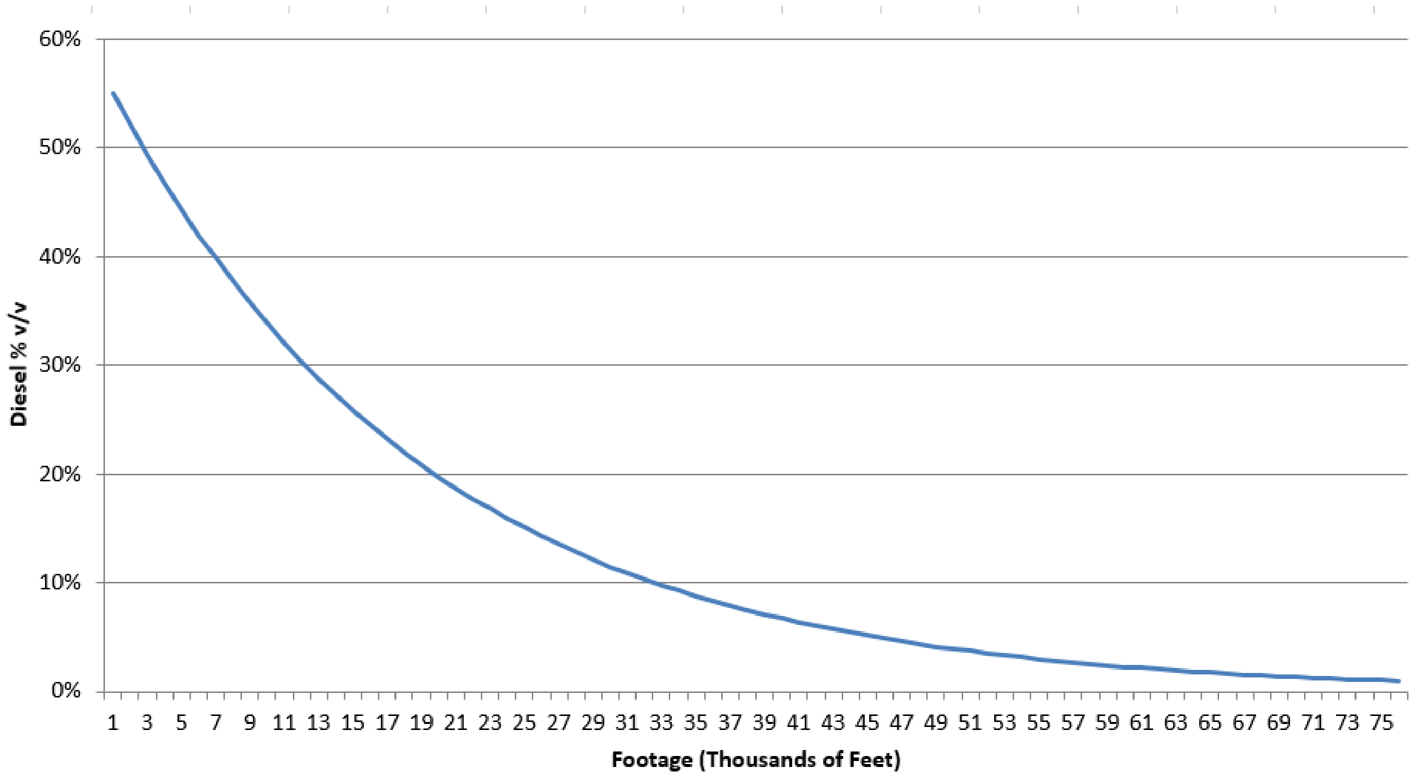

Figure 6: Diesel in invert system by footage drilled

Table 1: Aniline Point of Various Diesel Alternatives

Aniline Point Comparison	
Sample Identification	**Aniline Point (ASTM D611)**
Diesel Sample 1	190°F
Diesel Sample 2	138°F
Diesel Alternative A	160°F
Diesel Alternative B	165°F
Diesel Alternative C	160°F
Diesel Alternative D	170°F
Diesel Alternative E	165°F
Diesel Alternative F	174°F
Diesel Alternative G	153°F
Diesel Alternative H	165°F
Diesel Alternative I	172°F
Diesel Alternative J	174°F
Diesel Alternative K	185°F

Table 2: Recommended Properties

Properties	**UOM**	**Test Methods**	**Min**	**Max**
BTEX		EPA 8260B		
Benzene	*mg/kg*		Non-Detect	
Ethylbenzene	*mg/kg*		Non-Detect	
Toulene	*mg/kg*		Non-Detect	
Xylene (total, m-, p-, o-)	*mg/kg*		Non-Detect	
Total Aromatics	wt%	UV	0	0.5<
Flash Point	°F	ASTM D 93	> 140	
Viscosity*, Kinematic at 40°C	cSt	ASTM D 445	1.3	4.5
Aniline Point	°F	ASTM D611	> 150	

**Viscosity is a performance component, but not a requirement to meet health, safety, and environmental goals. This value may vary by density and well complexity.*