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## **Evaluation of Cetane Improver Additive in Alternative Jet Fuel Blends**

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U.S. Army Tank Automotive Research,  
Development, and Engineering Center  
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# **U.S. Army Tank Automotive Research, Development and Engineering Center**

Warren, Michigan 48397-5000

## **Evaluation of Cetane Improver Additive in Alternative Jet Fuel Blends**

**Jill M. Bramer**

**Joel Schmitgal**

**Force Projection Technology**

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## List of Symbols, Abbreviations and Acronyms

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%	Percent
°C	Degrees Centigrade
2-EHN	2-ethylhexyl nitrate
API	American Petroleum Institute
ASTM	ASTM International
ATJ	Alcohol-to-Jet
CI	Cetane Improver Additive
CVCC	Constant Volume Combustion Chamber
DCN	Derived Cetane Number
DLA	Defense Logistics Agency
DTL	Detail
EN	English
FAA	Federal Aviation Administration
FBP	Final Boiling Point
FT	Fischer–Tropsch
HEFA	Hydro-Processed Esters and Fatty Acids
Hg	mercury
IAW	in accordance with
IBP	Initial Boiling Point
IPK	Iso-Paraffinic Kerosene
IPN	isopropyl nitrate
JP-8	Jet Propellant 8
kg	Kilogram
L	Liter
MIL	Military
MJ	Megajoule
mm	micrometer
NATO	North Atlantic Treaty Organization
OEM	Original Equipment Manufacturer
ppm	Parts Per Million
s	seconds
SIP	Synthesized Iso-Paraffin
SPK	Synthetic Paraffinic Kerosene
TARDEC	Tank Automotive Research, Development and Engineering Center
TRL	Technology Readiness Level
Vol	Volume

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## Introduction

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ASTM International defines cetane number as a measure of the ignition performance of a diesel fuel oil obtained by comparing it to reference fuels in a standardized engine test (1). The cetane number has an inverse relationship with the fuels ignition delay, the time period between the start of injection and the first identifiable pressure increase during combustion of the fuel. A fuel's cetane number is a rating expressed on an arbitrary scale, ranging from zero (0), alpha-methylnaphthalene, to one hundred (100), cetane, obtained on a standard single cylinder engine. In the 1960s, heptamethylnonane replaced alpha-methylnaphthalene as it had better storage stability characteristics and was widely available.

Cetane number requirements are found in all diesel fuel specifications. In the United States, diesel fuel is procured to meet ASTM D975 and has a minimum cetane number requirement of 40 (2). EN 590, specification for automotive diesel sold in the European Union has a minimum cetane requirement of 51 (3). Higher cetane number fuels have shorter ignition delays thereby providing for more time for the fuel combustion process to be completed. Higher speed diesel engines operate more effectively with high cetane number fuels, with increased power, easier starting at low temperature, lower noise, and reduced smoke and emissions. The lower the cetane number of the fuel, the harder it becomes to start the engines, particularly at low temperatures.

Cetane number is not a specification requirement for aviation fuels, since turbine engines do not rely on compression ignition for operation. In the 1980s, the Department of Defense implemented the Single Fuel Forward policy, requiring all combat and tactical ground equipment to use JP-8, Turbine Fuel, Aviation, Kerosene Type, JP-8 (NATO F-34), NATO F-35, and JP-8+100 (NATO F-37) (MIL-DTL-83133). As alternative fuels began to enter the aviation fuel market, the U.S. Army was successful in adding a cetane requirement to JP-8 containing synthetic fuel components as found in the appendix of MIL-DTL-83133 (4). Two synthetic blending components, Fischer-Tropsch synthetic paraffinic kerosene (FT-SPK) and Hydro-processed Esters and Fatty Acids synthetic paraffinic kerosene (HEFA-SPK), have been approved and incorporated into MIL-DTL-83133J. On the commercial side, five synthetic hydrocarbon blending components have been approved and published in ASTM D7566-16, Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons (5). When the synthetic components are blended at the maximum approved ratio, with conventional aviation fuel, the fuel meets the performance requirements of ASTM D1655-15d<sup>e1</sup> Standard Specification for Aviation Turbine Fuels (6). The blending ratios are based on key fuel properties of the conventional aviation fuel; such as aromatic content and density. Fuel containing Iso-Paraffinic Kerosene (IPK) and Alcohol-to-Jet (ATJ), in particular, have been shown to be deficient in cetane quality.

Cetane improver additives are marketed to the commercial trucking industry to increase the cetane number of diesel fuel, with the desire to achieve an increase of 5 or 6 cetane numbers. Cetane improver additives can also be added at the refinery to fuel exhibiting a low cetane number. Alkyl nitrates, specifically 2-ethylhexyl nitrate (2-EHN) are the most common cetane improver additives. The goal of this evaluation is to determine if the use of additives at low

concentrations in fuels exhibiting poor cetane values is feasible. If successful, the use of cetane improver additives could give fuel users a tool to improve fuel quality at field locations.

Traditionally, cetane number has been tested in accordance with (IAW) ASTM D613, Standard Test Method for Cetane Number of Diesel Fuel Oil (7). The test method requires a large test engine and a highly skilled operator; which is not feasible for all testing laboratories. Laboratory-sized instruments have been designed to correlate to the cetane engine and provide a calculated result known as the derived cetane number (DCN). This project was conducted using two constant volume combustion chamber (CVCC) instruments.

- ASTM D6890, Standard Test Method for Determination of Ignition Delay and Derived Cetane Number (DCN) of Diesel Fuel Oils by Combustion in a Constant Volume Chamber (8).
- ASTM D7668, Standard Test Method for Determination of Derived Cetane Number (DCN) of Diesel Fuel Oils – Ignition Delay and Combustion Delay Using a Constant Volume Combustion Chamber Method (9).

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## Approach

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### Fuel additive market survey

A market survey and internet search were conducted to determine the cetane improvers commercially available (10). The survey indicated there are 3 types of cetane improvers available: 2-ethylhexyl nitrate (2-EHN), di-tertiary butyl peroxide, and isopropyl nitrate (IPN), with 2-EHN being the most common. Initially, three, 2-EHN cetane improvers were selected for this evaluation:

- CI-0801 manufactured by Innospec Fuel Specialties
- Lubrizol 8090 manufactured by The Lubrizol Corporation
- HiTEC4103 manufactured by Afton Chemical Company

Upon completion of testing with 2 cetane improvers, it was decided to end the project due to the similar chemistries and results.

### Test Sample Matrix

To quantify the effect of the cetane improver additives a matrix of test samples with varying additive concentrations was developed. The test matrix consisted of a commercial, petroleum derived Jet A fuel conforming to ASTM D1655, and 50:50 blends of the Jet A fuel and synthetic blending components. The synthetic blending components included:

- Iso-Paraffinic Kerosene (IPK) from SASOL
- Hydro-Processed Esters and Fatty Acids (HEFA) from UOP
- Alcohol-to-Jet (ATJ) from Gevo
- Synthesized Iso-Paraffin (SIP) from Amyris

The Jet A fuel and blending stocks used in this study may not be representative of every batch of fuel or blending stock produced by the manufacturers. Their properties can vary batch-to-batch and the data reported here is intended to look at the trends not absolute numbers. Each test sample was doped with two, 2-EHN based cetane improver additives at levels provided in Table 1.

**Table 1. Test Sample Matrix additized with both the 2-ethylhexyl nitrate based additives.**

		Cetane Improver Additive Concentration				
		0 ppm	10 ppm	50 ppm	100 ppm	500 ppm
Test Sample	Jet A	X	X	X	X	X
	IPK	X	X	X	X	X
	HEFA	X	X	X	X	X
	ATJ	X	X	X	X	X
	SIP	X	X	X	X	X
	50:50 Jet A - IPK	X	X	X	X	X
	50:50 Jet A - HEFA	X	X	X	X	X
	50:50 Jet A - ATJ	X	X	X	X	X
	50:50 Jet A - SIP	X	X	X	X	X

### Fuel Properties

To quantify changes attributable to the cetane improvers, testing of select fuel properties was conducted on all of the test samples listed in Table 1. The fuel properties, in addition to DCN, were selected based on their inclusion in ASTM D4054; Standard Practice for Qualification and Approval of New Aviation Turbine Fuels and Fuel Additives (11). ASTM D4054 was developed by aircraft and engine original equipment manufacturers (OEM), the Federal Aviation Administration (FAA), and other government agencies to provide guidance on the testing required and OEM involvement to obtain approval for a fuel or additive in their respective engines and airframes. The standard includes property targets that are based on OEM experience with the impact of fuel or additives on the design and performance of gas turbine engines.

The Department of Defense previously broke out the ASTM D4054 framework into Technology Readiness Levels (TRLs) which are used to evaluate the maturity of evolving technologies (12). Table 2 provides a list of the selected TRL1-3 tests performed to evaluate the effect of the additive on the fuels in question.

Special attention was paid to fuel properties that could affect aircraft performance; such as freeze point, thermal stability, and low temperature viscosity as negative impacts to these fuel properties would hinder the use of cetane improver additives by the Army.



**Table 2. Select TRL 1-3 fuel property tests performed on test samples additized with both 2-ethylhexyl nitrate based additives**

Property	Measurement	ASTM D	TRL
Aromatics	vol %	1319	1
	mass %	5186	
Sulfur, Total	mass %	2622	2
Hydrogen	%	3343	2
Distillation	IBP, °C	86	2
	10% recovered, °C		
	20% recovered, °C		
	50% recovered, °C		
	90% recovered, °C		
	FBP, °C		
	Residue, vol %		
Loss, vol %			
Flash Point	°C	93	2
Density	API	4052	2
	kg/L at 15°C		
Freezing Point	°C	7153	2
Viscosity	@ -20°C, mm <sup>2</sup> /s	445	2
	@ 40°C, mm <sup>2</sup> /s		
Derived Cetane Number	IQT	6890	3
	CID	7668	3
Cetane Index	Equation 1	976	2
	Equation 2		
	4 Variable	4737	2
Thermal Stability	Change in press drop, mm Hg	3241	2
	Heater tube deposit, visual rating		
	Time to 25 mmHg (Minutes)		
Net Heat of Combustion	MJ/kg	3338	2
BOCLE	wear scar diameter, mm	5001	3

All DCN test results provided in this report are an average of three test runs; while all other tests (except thermal stability) are duplicate test runs. Because of the relatively large volume of fuel required and the 2.5 hour test time, only a single run was conducted for each thermal stability test.

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**Evaluation and Data Analysis**


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**Derived Cetane Number (DCN)**

DCN was tested IAW ASTM D6890 and ASTM D7668. The instruments measure the ignition delay of the fuel and calculate a derived cetane number. While the instruments cover a large cetane range, each method has a precision statement dictating the valid operating range. ASTM D6890 covers a DCN ranging from 33 to 64, outside of this range the precision may be affected. The precision statement for ASTM D7668 covers a DCN ranging from 39-67, the precision of any measurements outside of this range is unknown. Both instruments are able to obtain measurements and report DCN outside of this range, but the precision of the measurements is questionable. For research purposes this report contains data outside the valid precision ranges of the instruments. For discussion purposes, the closest precision value within the acceptable range will be applied to values outside the precision statement range.

Table 3 displays the DCN results for the base fuel (Jet A), each blending stock (ATJ, IPK, HEFA, SIP), and the 50:50 blended fuels without addition of cetane improver additives. From a combustion perspective, the Jet A, HEFA, HEFA/Jet A, SIP, and SIP/Jet A samples would not pose any problems for diesel engine powered combat and tactical ground equipment. Alternately, the ATJ, ATJ/Jet A, IPK, and IPK/Jet A samples could be problematic as fuels for Army ground equipment due to their low cetane values and are of particular interest in this study. The ATJ/Jet A and IPK/Jet A blends displayed increased DCN over the neat synthetic components due to the higher cetane of the Jet A component.

**Table 3. Derived Cetane Numbers (DCN) of base fuel, blending stocks and 50:50 blended fuels without addition of cetane improver.**

	Derived Cetane Number	
	ASTM D6890	ASTM D7668
Jet A	46.3	48.2
ATJ	16.0	14.9
ATJ - Jet A	35.6	33.3
IPK	31.0	25.0
IPK - Jet A	39.1	39.1
HEFA	56.2	57.6
HEFA - Jet A	50.4	51.4
SIP	56.1	59.5
SIP - Jet A	50.6	52.3

***Alcohol-to-Jet (ATJ)***

Table 4 provides the DCN results for the ATJ blending stocks and ATJ/Jet A blends with cetane improver additions. The ATJ blending stocks fall outside the operational range of the instrument and the ATJ/Jet A blends fall outside the range of the published precision statement. Overall,

ATJ/Jet A blends do not meet desired minimum cetane requirement of 40. Although both of the blends containing 500 ppm of CI did have a DCN of just 40 or higher (40.0 and 40.8) per the ASTM D6890 results, the DCN for these test samples was well under 40 per the ASTM D7668 results.

**Table 4. Derived Cetane Numbers (DCN) of Cetane Improver additized Alcohol-to-Jet (ATJ) samples.**

	Derived Cetane Number	
	ASTM D6890	ASTM D7668
ATJ	16.0	14.9
ATJ + 10 ppm CI #1	16.5	14.8
ATJ + 50 ppm CI #1	16.6	14.8
ATJ + 100 ppm CI #1	17.5	14.8
ATJ + 500 ppm CI #1	17.6	14.8
ATJ + 10 ppm CI #2	Samples NOT Run due to IQT Gasket Failures	14.9
ATJ + 50 ppm CI #2		14.8
ATJ + 100 ppm CI #2		14.8
ATJ + 500 ppm CI #2		14.8
ATJ - Jet A	35.6	33.3
ATJ/Jet A + 10 ppm CI #1	36.3	33.7
ATJ/Jet A + 50 ppm CI #1	37.1	33.8
ATJ/Jet A + 100 ppm CI #1	38.2	33.6
ATJ/Jet A + 500 ppm CI #1	40.0	33.8
ATJ/Jet A + 10 ppm CI #2	37.9	33.7
ATJ/Jet A + 50 ppm CI #2	38.2	33.8
ATJ/Jet A + 100 ppm CI #2	38.6	33.8
ATJ/Jet A + 500 ppm CI #2	40.8	34.0

**ATJ with Cetane Improver #1** – Measurements taken IAW ASTM D6890 increased 1.5 DCN at concentrations of 100 ppm and 500 ppm, but DCN remained well below the desired value of 40. Measurements taken IAW ASTM D7668 showed a minor decrease in DCN, the largest decrease was 0.11 DCN. This measured difference is within the repeatability of the test and the DCN was not affected by the addition of cetane improver. Additionally, the thermal stability test failed to meet the requirements for maximum pressure drop at concentrations of 100 ppm and 500 ppm.

**ATJ with Cetane Improver #2** – Measurements taken per ASTM D6890 were not able to be collected. When testing the ATJ blending stocks, the ignition delay caused an over-pressurization within the combustion chamber damaging the combustion chamber gasket (see Figure 1). The over-pressurization happened with all of the ATJ samples and was not specific to Cetane Improver #2. The instrument was repaired and the gasket replaced on three occasions. The DCN was too low and it was decided to discontinue testing any further samples as the

ultimate result would be another split gasket. Measurements taken IAW ASTM D7668 showed a minor decrease in DCN, the largest decrease was 0.11 DCN, similar to Cetane Improver #1. The difference was within the error of the test and the DCN was not affected by the addition of cetane improver. The thermal stability test requirements were met with concentrations of 100 ppm and 500 ppm cetane improver.



**Figure 1. Damaged combustion chamber gasket caused by over pressurization while testing ATJ samples.**

**ATJ/Jet A Blends with Cetane Improver #1** – Measurements taken IAW ASTM D6890 presented a positive change in DCN as the concentration of cetane improver was added. The blended fuel results were within the valid operating range of the instrument. The addition of 100 ppm cetane improver provided a 2 DCN increase over the unadditized ATJ/Jet A blend; while the 500 ppm cetane improver provided over a 4 DCN increase. Unfortunately, the increase in DCN was still below the desired cetane value of 40. Measurements taken with ASTM D7668 exhibited slightly increased DCN values. The 0.5 DCN increase was outside the valid operating range of the instrument and the increases in DCN could be attributable to the error within the method. The thermal stability test results at 100 ppm and 500 ppm failed to meet the maximum pressure drop requirement. Therefore, addition of cetane improver at these concentrations would affect aircraft operations.

**ATJ/Jet A Blends with Cetane Improver #2** – Measurements taken IAW ASTM D6890 presented an increase in DCN as the concentration of cetane improver was added. The blended fuel results were within the valid operating range of the instrument. The addition of 100 ppm cetane improver provided a 3 DCN increase over the unadditized ATJ/Jet A blend; while the 500 ppm cetane improver provided over a 5 DCN increase. Measurement taken with ASTM D7668 exhibited slightly increased DCN values. The largest increase was 0.6 DCN, but this increase was outside the precision statement range of the instrument. These increases in DCN could be attributable to the error within the method. Thermal stability testing showed that the blend with

100 ppm of cetane improver passed the test requirements, but the blend with 500 ppm failed to meet the tube rating requirement for the test.

On average, DCN for CI #2 additized samples were 1 DCN higher than samples additized with CI #1 when measured IAW ASTM D6890. Measurements taken per ASTM D7668 did not show much variation between the different concentrations of cetane improver.

***Iso-Paraffinic Kerosene (IPK)***

Table 5 displays the DCN results for the IPK fuels and IPK/Jet A blends with cetane improver additions. The IPK fuels fall outside the operational range of the instruments to provide valid precision data but the IPK/Jet A blends fall within the range of the published precision statement.

**Table 5. Derived Cetane Numbers (DCN) of Cetane Improver additized Iso-Paraffinic Kerosene (IPK) samples.**

	Derived Cetane Number	
	ASTM D6890	ASTM D7668
IPK	31.0	25.0
IPK + 10 ppm CI #1	32.1	25.2
IPK + 50 ppm CI #1	33.8	25.1
IPK + 100 ppm CI #1	33.9	25.0
IPK + 500 ppm CI #1	35.1	24.6
IPK + 10 ppm CI #2	32.0	25.2
IPK + 50 ppm CI #2	33.1	25.1
IPK + 100 ppm CI #2	34.3	24.9
IPK + 500 ppm CI #2	36.3	24.5
IPK - Jet A	39.1	39.1
IPK/Jet A + 10 ppm CI #1	40.4	39.3
IPK/Jet A + 50 ppm CI #1	42.0	39.6
IPK/Jet A + 100 ppm CI #1	43.0	39.9
IPK/Jet A + 500 ppm CI #1	44.9	40.1
IPK/Jet A + 10 ppm CI #2	40.9	39.4
IPK/Jet A + 50 ppm CI #2	42.2	39.7
IPK/Jet A + 100 ppm CI #2	42.8	39.8
IPK/Jet A + 500 ppm CI #2	44.8	40.4

**IPK with Cetane Improver #1** – Measurements taken IAW ASTM D6890 show that the cetane improver additive increased the DCN of the fuel. IPK with 500 ppm exhibited an increase of 4 DCN over the neat fuel. Even with the increase in cetane value, the blending stocks do not meet the desired cetane value of 40. Measurements taken IAW ASTM D7668 were consistently lower than those taken IAW ASTM D6890. The DCN obtained via ASTM D7668 were within the

repeatability of the instrumentation at all concentration levels. The fuels did meet the thermal stability requirements for tube rating and maximum change in pressure drop at all cetane improver additive concentration levels. The use of this neat fuel in Army ground equipment would be problematic due to its low cetane value.

**IPK with Cetane Improver #2** – Measurements taken IAW ASTM D6890 showed that the cetane improver increased the DCN of the fuel. IPK with 500 ppm exhibited an increase of 5 over the neat fuel. Even with the increase in cetane value, the fuels do not meet the desired cetane value of 40. Measurements taken IAW ASTM D7668 were consistently lower than those taken IAW ASTM D6890. The DCN were the same or less when cetane improver was added. Even though the values are outside the valid operating range of the instrument, variation in DCN could be attributed to the repeatability of the test method. The fuels did meet the thermal stability requirements for tube rating and maximum change in pressure drop.

**IPK/Jet A with Cetane Improver #1** – Measurements taken IAW ASTM D6890 showed the cetane improver increased the DCN of the fuel blends and were within the valid operating range of the instrument. The IPK/Jet A blend with 500 ppm provided a DCN of 44.94 which was a 5 DCN increase over the unadditized blend. This increase helps the fuel exceed the minimum desired cetane value of 40. Measurements taken IAW ASTM D7668 were within the valid operating range of the instrument but were lower than those taken IAW ASTM D6890. The instrument running ASTM D7668 may be less sensitive to the addition of cetane improver. The IPK/Jet A blend with 500 ppm of cetane improver exhibited a DCN of 40.04, only 1 DCN increase over the unadditized fuel. The thermal stability test concluded that the 100 ppm and 500 ppm failed to meet the test requirements and could be detrimental to aircraft performance.

**IPK/Jet A with Cetane Improver #2** – Measurements taken IAW ASTM D6890 showed the cetane improver increased the DCN of the fuel blends and were within the valid operating range of the instrument. The IPK/Jet A blend with 500 ppm provided a DCN of 44.94 which was a 5 DCN increase over the unadditized blend, surpassing the minimum cetane value of 40. Measurements taken IAW ASTM D7668 were within the valid operating range of the instrument but were again lower than those taken IAW ASTM D6890. The instrument running ASTM D7668 may be less sensitive to the addition of cetane improver. The IPK/Jet A Blend with 500 ppm of cetane improver exhibited a DCN of 40.44, only 1 DCN increase over the unadditized fuel. The thermal stability test concluded that the 100 ppm and 500 ppm met the test requirements for change in pressure drop, but the tube rating for the 100 ppm concentration was a 3 and the 500 ppm concentration had a >4. These tube ratings could be detrimental to aircraft performance.

With respect to ASTM D6890, the response from both cetane improvers was very similar, both providing a 5 DCN increase. As with the ATJ fuel, the neat IPK fuels measurements taken IAW ASTM D7668 did not exhibit change from the baseline fuels with increasing levels of additives.

### ***Jet A***

Table 6 displays the DCN results for the Jet A fuel with cetane improver additions. The Jet A fuels fall within the operational range and published precision statement of both instruments.

The desired minimum cetane of 40 was met with the unadditized jet fuel and the cetane improver was able to improve the cetane quality by 4 DCN. Unlike data in Tables 4 and 5, the measurements taken IAW ASTM D7668 were, on average, higher than measurements taken IAW ASTM D6890. Additionally, the response from Cetane Improver #1 and Cetane Improver #2 were very similar.

**Table 6. Derived Cetane Numbers (DCN) of Cetane Improver additized petroleum based Jet A fuel samples.**

	Derived Cetane Number	
	ASTM D6890	ASTM D7668
Jet A	46.3	48.2
Jet A + 10 ppm CI #1	47.3	49.9
Jet A + 50 ppm CI #1	48.4	50.7
Jet A + 100 ppm CI #1	49.7	51.3
Jet A + 500 ppm CI #1	52.2	52.7
Jet A + 10 ppm CI #2	47.2	49.7
Jet A + 50 ppm CI #2	48.7	50.3
Jet A + 100 ppm CI #2	50.8	50.7
Jet A + 500 ppm CI #2	53.5	52.8

**Jet A with Cetane Improver #1** – Measurements taken IAW ASTM D6890 showed the cetane improver increased the DCN of the fuel. There was a 1 DCN increase with 10 ppm concentration of cetane improver. The 50 ppm concentration provided a 2 DCN increase, the 100 ppm concentration provided a 3 DCN, and the 500 ppm concentration provided a 5 DCN improvement over the neat Jet A. Measurements taken IAW ASTM D7668 also provided an increase in DCN. ASTM D7668 provided a higher DCN values than ASTM D6890 except at the 500 ppm concentration, contrary to what was seen with the ATJ and IPK fuels. The samples with 100 ppm and 500 ppm concentrations did not meet the thermal stability specification requirements failing to meet the maximum pressure drop. These concentrations would prove to be problematic for aircraft systems.

**Jet A with Cetane Improver #2** – Measurements taken IAW ASTM D6890 and ASTM D7668 were very similar to the data for Cetane Improver #1. These samples failed the thermal stability specification requirements also at 100 ppm and 500 ppm concentrations but by heater tube visual rating rather than by exceeding maximum pressure drop.

#### ***Hydro-Processed Esters and Fatty Acids (HEFA)***

Table 7 provides the DCN for the HEFA samples, which were at the upper end of the valid operating ranges of both instruments. The HEFA blending stocks have DCN higher than the petroleum base Jet A fuel they were blended with for this evaluation. No statistical differences were perceived between the CI #1 and CI #2 with either method.

**HEFA with Cetane Improver #1** – Measurements taken IAW ASTM D6890 showed the cetane improver increased the DCN of the test sample. The 50 ppm concentration provided a 4 DCN increase, the 100 ppm concentration provided a 5 DCN increase, and the 500 ppm concentration provided an 8.5 DCN improvement over the neat HEFA. Measurements taken IAW ASTM D7668 also provided an increase in DCN. ASTM D7668 exhibited approximately a 1 DCN higher value across the 4 different concentrations. The samples with 100 ppm and 500 ppm concentrations still met the thermal stability test requirements.

**Table 7. Derived Cetane Numbers (DCN) of Cetane Improver additized HEFA samples.**

	Derived Cetane Number	
	ASTM D6890	ASTM D7668
HEFA	56.2	57.6
HEFA + 10 ppm CI #1	58.3	59.7
HEFA + 50 ppm CI #1	60.3	61.3
HEFA + 100 ppm CI #1	61.3	62.3
HEFA + 500 ppm CI #1	64.7	65.9
HEFA + 10 ppm CI #2	59.1	60.0
HEFA + 50 ppm CI #2	61.2	61.6
HEFA + 100 ppm CI #2	61.8	63.0
HEFA + 500 ppm CI #2	65.2	66.5
HEFA - Jet A	50.4	51.4
HEFA/Jet A + 10 ppm CI #1	51.9	53.6
HEFA/Jet A + 50 ppm CI #1	53.8	54.6
HEFA/Jet A + 100 ppm CI #1	55.1	55.7
HEFA/Jet A + 500 ppm CI #1	58.1	58.2
HEFA/Jet A + 10 ppm CI #2	52.0	54.1
HEFA/Jet A + 50 ppm CI #2	54.3	54.8
HEFA/Jet A + 100 ppm CI #2	55.3	55.6
HEFA/Jet A + 500 ppm CI #2	58.5	58.4

**HEFA with Cetane Improver #2** – Measurements taken IAW ASTM D6890 and ASTM D7668 were very similar to the data for Cetane Improver #1. The 50 ppm concentration provided a 5 DCN increase, the 100 ppm concentration provided a 5.6 DCN increase, and the 500 ppm concentration provided a 9 DCN improvement over the neat HEFA. Measurements taken IAW ASTM D7668 also showed an increase in DCN. ASTM D7668 provided approximately a 1 DCN higher value across the 4 different concentrations. The samples with 100 ppm and 500 ppm concentrations also met the thermal stability test requirements.

**HEFA/Jet A Blend with Cetane Improver #1** - Measurements taken IAW ASTM D6890 showed the cetane improver increased the DCN of the fuel. The 50 ppm concentration provided a 3 DCN increase, the 100 ppm concentration provided an increase of 5 DCN, and the 500 ppm concentration provided an 8 DCN improvement over the neat HEFA/Jet A blend. Measurements taken IAW ASTM D7668 also provided an increase in DCN. ASTM D7668 provided a higher, by approximately 1 DCN value, except at the 100 and 500 ppm concentrations the DCN values



were nearly identical between instruments. The HEFA/Jet A with 100 ppm passed the thermal stability requirements, but the 500 ppm concentration did not meet the maximum pressure drop or tube rating.

**HEFA/Jet A Blend with Cetane Improver #2** - Measurements taken IAW ASTM D6890 showed the cetane improver increased the DCN of the fuel. The 50 ppm concentration provided a 4 DCN increase, the 100 ppm concentration increased the DCN by 5, and the 500 ppm concentration provided an 8 DCN improvement over the neat HEFA/Jet A blend. Measurements taken per ASTM D7668 also provided an increase in DCN. ASTM D7668 provided DCN values nearly identical to ASTM D6890. The HEFA/Jet A with 100 ppm passed the thermal stability requirements, but the 500 ppm concentration did not meet the tube rating requirement.

***Synthesized Iso-Paraffin (SIP)***

Table 8 provides the DCN for the SIP test samples, which similarly to the HEFA test samples are at the upper end of the valid operating ranges of both instruments. Regardless of the instrument, the SIP blending stock test samples contained DCN higher than the petroleum base Jet A fuel they were blended with for this evaluation. No statistical differences were perceived between the CI #1 and CI #2 with either method.

**Table 8. Derived Cetane Numbers (DCN) of Cetane Improver additized SIP samples.**

	Derived Cetane Number	
	ASTM D6890	ASTM D7668
SIP	56.1	59.5
SIP + 10 ppm CI #1	58.5	60.8
SIP + 50 ppm CI #1	59.5	61.4
SIP + 100 ppm CI #1	60.5	62.3
SIP + 500 ppm CI #1	64.0	66.1
SIP + 10 ppm CI #2	58.6	61.2
SIP + 50 ppm CI #2	60.0	62.1
SIP + 100 ppm CI #2	61.1	63.2
SIP + 500 ppm CI #2	63.9	66.3
SIP - Jet A	50.6	52.3
SIP/Jet A + 10 ppm CI #1	52.3	53.6
SIP/Jet A + 50 ppm CI #1	53.7	54.7
SIP/Jet A + 100 ppm CI #1	55.6	55.5
SIP/Jet A + 500 ppm CI #1	57.3	57.8
SIP/Jet A + 10 ppm CI #2	52.2	53.8
SIP/Jet A + 50 ppm CI #2	54.5	55.3
SIP/Jet A + 100 ppm CI #2	55.5	55.6

**SIP with Cetane Improver #1** – Measurements taken IAW ASTM D6890 exhibited an increase in DCN as additive levels were increased in the test sample. The 50 ppm concentration provided a 3 DCN increase, the 100 ppm concentration provided a 4 DCN increase, and the 500 ppm concentration provided an 8 DCN improvement over the neat SIP. Measurements taken IAW

ASTM D7668 also displayed an increase in DCN. The increase in values are approximately two (2) DCN higher than the ASTM D6890 measurements across the 4 different concentrations. The sample with 500 ppm concentration failed to meet the tube rating requirement for the thermal stability test.

**SIP with Cetane Improver #2** – Measurements taken IAW ASTM D6890 and ASTM D7668 were very similar to the data for Cetane Improver #1. The response to the thermal stability test was also similar, failing the visual tube rating at 500 ppm.

**SIP/Jet A Blend with Cetane Improver #1** - Measurements taken IAW ASTM D6890 showed the cetane improver increased the DCN of the fuel. The 50 ppm concentration provided a 3 DCN increase, the 100 ppm concentration provided a 5 DCN increase, and the 500 ppm concentration provided an 8 DCN improvement over the neat SIP/Jet A blend. Measurements taken IAW ASTM D7668 also provided an increase in derived cetane number. ASTM D7668 provided a higher, roughly by 1 DCN, except at the 500 ppm concentration level, the DCN values were nearly identical. The SIP/Jet A with 100 ppm failed the maximum pressure drop requirement of the thermal stability requirements and the 500 ppm concentration failed the tube rating. These concentrations would prove to be problematic for aircraft systems.

**SIP/Jet A Blend with Cetane Improver #2** - Measurements taken per ASTM D6890 showed the cetane improver increased the DCN of the fuel. The 50 ppm concentration provided a 4 DCN increase, the 100 ppm concentration increase the DCN by a value of 5, and the 500 ppm concentration provided an 8 DCN improvement over the neat SIP/Jet A blend. Measurements taken IAW ASTM D7668 also exhibited an increase in derived cetane number commensurate with those seen with ASTM D6890. The HEFA/Jet A with 100 ppm passed the thermal stability requirements, but the 500 ppm concentration did not meet the tube rating requirement.

### **Effect of Additive on Other Fuel Properties**

The appendices contain all of the data collected in this research report. Based on this research, the addition of cetane improvers did not impact the following fuel properties:

- Aromatics
- Sulfur, Total
- Hydrogen Content
- Distillation
- Flash Point
- Density
- Freezing Point
- Viscosity, -20°C and 40°C
- Net Heat of Combustion

### **Calculated Cetane Index**

The calculated cetane index was measured IAW with ASTM D976, Standard Test Method for Calculated Cetane Index of Distillate Fuels (13), and ASTM D4737, Standard Test Method for Calculated Cetane Index by Four Variable Equation (14). Both formulas were shown to provide inaccurate values for the synthetic blending stocks, finding agreement with previous TARDEC

research (15). The cetane index improver additives did not have an effect on the calculated cetane indexes as expected since the calculations are not applicable to fuels containing additives for raising cetane number. The calculations are completed using density/API Gravity and distillation temperatures and since these properties were unaffected; the addition of cetane improver would not be characterized.

### **Thermal Stability**

To save time and supplies, the thermal stability test was only conducted on the 100 ppm and 500 ppm samples. Cetane improver #1 and #2 induced several failures of thermal stability. However, the data suggests that cetane improver #2 was more thermally stable at the 100 ppm concentration, as no failures were observed. There was a degradation of thermal stability of the overall fuels, as the change in pressure drop and tube ratings were higher than the unadditized samples. As discussed above, the thermal stability failures were widespread and would affect aircraft operations.

The impact of cetane improvers on thermal stability negates their use during fuel refining, blending, and allowance into distribution systems. Thermal stability is not a concern within compression ignition engines. Cetane improvers could be blended in as an additive near point of use, but great care would be required to ensure that the additive is regulated to compression ignition engines only and not allowed within turbine engines. Care would also need to be taken to segregate additized fuel when performing defueling operations.

**Table 9. Addition of cetane improver additives on Thermal Stability measured IAW ASTM D3241**

	Thermal Stability		
	Change in press drop, mm Hg	Heater tube deposit, visual rating	Time to 25 mmHg (Minutes)
	D3241		
ATJ	0.00	<1	n/a
ATJ + 100 ppm CI #1	100.18	<1	83
ATJ + 500 ppm CI #1	100.11	<1	54
ATJ + 100 ppm CI #2	0.01	<2	n/a
ATJ + 500 ppm CI #2	3.53	<2	n/a
ATJ - Jet A	0.00	<1	n/a
ATJ/Jet A + 100 ppm CI #1	100.16	<1	116
ATJ/Jet A + 500 ppm CI #1	100.04	4A	75
ATJ/Jet A + 100 ppm CI #2	2.00	<2	n/a
ATJ/Jet A + 500 ppm CI #2	5.24	<4	n/a
IPK	0.12	2	n/a
IPK + 100 ppm CI #1	0.39	<1	n/a
IPK + 500 ppm CI #1	0.69	<1	n/a
IPK + 100 ppm CI #2	0.41	<1	n/a
IPK + 500 ppm CI #2	0.06	1	n/a
IPK - Jet A	0.00	1	n/a
IPK/Jet A + 100 ppm CI #1	25.13	<1	150
IPK/Jet A + 500 ppm CI #1	100.04	>4	36
IPK/Jet A + 100 ppm CI #2	3.12	3	n/a
IPK/Jet A + 500 ppm CI #2	0.44	>4	n/a
HEFA	0.05	<2	n/a
HEFA + 100 ppm CI #1	0.03	1	n/a
HEFA + 500 ppm CI #1	0.00	<1	n/a
HEFA + 100 ppm CI #2	0.00	<1	n/a
HEFA + 500 ppm CI #2	0.00	1	n/a
HEFA - Jet A	0.00	<1	n/a
HEFA/Jet A + 100 ppm CI #1	2.73	<1	n/a
HEFA/Jet A + 500 ppm CI #1	100.05	<4	35
HEFA/Jet A + 100 ppm CI #2	0.94	<2	n/a
HEFA/Jet A + 500 ppm CI #2	0.22	4	n/a
SIP	0.13	<1	n/a
SIP + 100 ppm CI #1	0.00	<1	n/a
SIP + 500 ppm CI #1	11.14	4	n/a
SIP + 100 ppm CI #2	0.00	<1	n/a
SIP + 500 ppm CI #2	0.00	<4	n/a
SIP - Jet A	0.00	<1	n/a
SIP/Jet A + 100 ppm CI #1	100.01	1	89
SIP/Jet A + 500 ppm CI #1	0.00	>4A	n/a
SIP/Jet A + 100 ppm CI #2	0.00	1	n/a
SIP/Jet A + 500 ppm CI #2	0.00	>4	n/a
Jet A	0.66	<1	n/a
Jet A + 100 ppm CI #1	100.23	<1	105
Jet A + 500 ppm CI #1	100.09	>4P	112
Jet A + 100 ppm CI #2	1.55	3	n/a
Jet A + 500 ppm CI #2	100.19	4	126

**Lubricity**

Two of the market survey responses indicated that cetane improver additives potentially have a negative effect on lubricity. A negative impact would result in larger wear scar diameters. Therefore, lubricity was added to the testing matrix and tested IAW ASTM D5001, Standard Test Method for Measurement of Lubricity of Aviation Turbine Fuels by the Ball-on-Cylinder Lubricity Evaluator (16). The average wear scar diameters were not negatively impacted by either cetane improver. In the case of Jet A and ATJ, the wear scars showed a decrease in average wear scar diameter.

**Table 10. Effect of Cetane Improver on Fuel Lubricity**

	BOCLE
	wear scar diameter, mm
	D5001
ATJ	0.69
ATJ + 500 ppm CI #1	0.60
ATJ + 500 ppm CI #2	0.59
IPK	0.55
IPK + 500 ppm CI #1	0.55
IPK + 500 ppm CI #2	0.55
HEFA	0.54
HEFA + 500 ppm CI #1	0.54
HEFA + 500 ppm CI #2	0.54
SIP	0.59
SIP + 500 ppm CI #1	0.57
SIP + 500 ppm CI #2	0.56
Jet A	0.62
Jet A + 500 ppm CI #1	0.57
Jet A + 500 ppm CI #2	0.55

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**Conclusions and Recommendations**

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The intention of this test project was to examine the use of low concentrations of cetane improvers in aviation fuel for use in ground applications. Two cetane improvers, with the same chemistry, 2-EHN, were evaluated using two instruments providing a derived cetane number. Below is a list of the conclusions based on the data from this research:

- The ATJ test samples experienced over-pressurization and caused instrument failure when tested IAW ASTM D6890.

- Measurements taken IAW ASTM D7668 should strictly adhere to the valid operating range of the method. Fuels with a DCN of 40 or lower have poor results and the lack of additive effect may be an indication of the method rather than the additive effects.
- Measurements taken in the valid operating range of each instrument were consistently within 1 DCN of each other.
- Changes to the DCN values for the 10 and 50 ppm concentrations tended to more within the error of the instrument and do not prove to be useful for ground vehicles.
- Thermal stability requirements were not met for the 100 ppm and 500 ppm sample concentrations.
- Cetane Improvers did not negatively impact lubricity at 500 ppm concentration levels. However, further testing of additive concentrations over 500 ppm should be performed prior to use.

The negative impact of cetane improvers on thermal stability negates their use during fuel refining, blending and allowance into distribution systems. Since thermal stability of the fuel is not a concern for compression ignition engines, there is a potential benefit for the Army ground equipment. However, great care would be required to ensure that the additive is regulated to compression ignition engines only and not allowed within turbine engines.

While the use of cetane improver additives does increase some of the DCN values of the test samples, the feasibility of field use is unlikely at this time. However, if cetane improver additives are considered, additional research should be performed to ensure that proper lubricity requirements are still maintained when using higher cetane improver additive concentrations. Care would also need to be taken to segregate additized fuel when performing defueling operations, as the fuel could not be used in aircraft operations.

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	Aromatics		Sulfur, Tot	Hydrogen	Distillation								Flash Point	Density		Freezing	Viscosity		Derived Cetane Number		Cetane Index			Thermal Stability			Net Heat	BOCLE
	vol %	mass %	mass %	%	IBP, °C	10% recovered, °C	20% recovered, °C	50% recovered, °C	90% recovered, °C	FBP, °C	Residue, vol %	Loss, vol %	°C	API	kg/L at 15°C	°C	@ -20°C, mm <sup>2</sup> /s	@ 40°C, mm <sup>2</sup> /s	IQT	CID	Equation 1	Equation 2	4 Variable	Change in press drop, mm Hg	Heater tube deposit, visual rating	Time to 25 mmHg (Minutes)	MJ/kg	wear scar diameter, mm
	D1319	D5186	D2622	D3343	D86								D93	D4052		D7153	D445		D6890	D7668	D976			D4737	D3241			D3338
SIP	1.1	0.1	0.000	15.1	236.2	244.0	244.2	244.6	245.2	252.5	1.3	0.6	108.5	51.3	0.7741	<-100	14.090	2.350	56.1	59.5	72.7	70.8	82.9	0.13	<1	n/a	44.022	0.59
SIP + 10 ppm CI #1	1.3	0.1	0.000	15.1	235.7	243.7	243.9	244.1	244.8	253.8	1.3	0.7	108.5	51.3	0.7742	<-100	14.090	2.352	58.5	60.8	72.5	70.6	82.6				44.016	
SIP + 50 ppm CI #1	1.3	0.2	0.000	15.1	238.0	243.8	244.0	244.2	244.9	254.5	1.3	0.6	108.5	51.3	0.7742	<-100	14.090	2.355	59.5	61.4	72.5	70.6	82.7				44.016	
SIP + 100 ppm CI #1	1.0	0.2	0.000	15.1	238.0	244.1	244.3	244.5	245.2	253.8	1.4	0.3	108.5	51.3	0.7741	<-100	14.080	2.352	60.5	62.3	72.6	70.8	82.9	0.00	<1	n/a	44.022	
SIP + 500 ppm CI #1	1.0	0.2	0.000	15.1	236.9	243.6	243.9	244.1	244.8	252.3	1.4	0.5	108.5	51.3	0.7743	<-100	14.150	2.351	64.0	66.1	72.5	70.6	82.6	11.14	4	n/a	44.018	0.57
SIP + 10 ppm CI #2	1.1	0.2	0.000	15.1	238.5	244.2	244.4	244.5	245.3	255.4	1.5	1.0	109.5	51.3	0.7742	<-100	14.110	2.351	58.6	61.2	72.6	70.8	82.9				44.021	
SIP + 50 ppm CI #2	1.1	0.1	0.000	15.1	238.1	244.1	244.3	244.5	245.2	255.5	1.5	0.9	109.5	51.3	0.7742	<-100	14.110	2.352	60.0	62.1	72.6	70.7	82.8				44.019	
SIP + 100 ppm CI #2	1.0	0.2	0.000	15.1	236.9	244.1	244.3	244.5	245.3	254.7	1.3	1.0	109.5	51.3	0.7742	<-100	14.110	2.352	61.1	63.2	72.6	70.7	82.8	0.00	<1	n/a	44.022	
SIP + 500 ppm CI #2	1.1	0.1	0.000	15.1	237.8	244.1	244.4	244.6	245.3	254.7	1.4	0.9	108.5	51.3	0.7743	<-100	14.090	2.351	63.9	66.3	72.6	70.7	82.8	0.00	<4	n/a	44.019	0.56
SIP - Jet A	8.5	9.5	0.050	14.6	183.7	205.6	213.9	231.3	244.5	252.1	1.5	0.8	68.5	48.9	0.7844	-56.2	7.420	1.733	50.6	52.3	63.5	62.4	67.2	0.00	<1	n/a	43.700	
SIP/Jet A + 10 ppm CI #1	8.4	9.6	0.051	14.6	182.2	204.3	212.3	230.4	244.0	251.3	1.4	0.3	68.5	48.9	0.7845	-55.8	7.408	1.726	52.3	53.6	63.2	62.1	66.7				43.708	
SIP/Jet A + 50 ppm CI #1	8.3	9.6	0.051	14.6	181.1	204.6	212.4	230.4	224.1	252.0	1.4	0.6	68.5	48.9	0.7845	-56.1	7.414	1.723	53.7	54.7	63.2	62.1	66.7				43.699	
SIP/Jet A + 100 ppm CI #1	8.6	9.6	0.051	14.6	185.3	205.5	213.4	231.0	244.4	251.6	1.4	0.5	69.0	48.9	0.7845	-56.1	7.420	1.728	55.6	55.5	63.4	62.3	67.0	100.01	1	89	43.697	
SIP/Jet A + 500 ppm CI #1	8.4	9.5	0.050	14.6	185.3	204.3	212.9	230.5	244.0	251.1	1.5	0.4	68.5	48.9	0.7846	-56.2	7.433	1.727	57.3	57.8	63.2	62.1	66.7	0.00	>4A	n/a	43.695	
SIP/Jet A + 10 ppm CI #2	7.9	9.5	0.050	14.6	185.6	205.4	213.7	231.3	244.6	254.0	1.5	1.1	69.5	48.9	0.7844	-56.3	7.450	1.726	52.2	53.8	63.5	62.4	67.1				43.708	
SIP/Jet A + 50 ppm CI #2	8.0	9.5	0.051	14.6	185.1	205.5	213.5	231.1	244.4	252.3	1.5	0.6	69.5	48.9	0.7845	-56.2	7.446	1.727	54.5	55.3	63.5	62.3	67.1				43.706	

Table A5. Synthesized Iso-Paraffin (SIP) and SIP/Jet A data