UPGRADING THE ENVIRONMENTAL PROPERTIES OF KIRKUK KEROSENE USING GLACIAL ACETIC ACID

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ABSTRACT

Glacial acetic acid was used to improve Kirkuk kerosene samples and decrease their aromatics contents. Two sets of experimental processes were performed: the first set included more process steps (mixing by orbital shaker, heating, centrifugation, and stabilization over many days). This set of experiments showed its maximum improvement when 1 mL of glacial acetic acid was added to 10 mL of Kirkuk kerosene sample to get a 42% improvement in the aniline point and a 12.5% improvement in the smoke point. The smoke point test values gave confusing results when the stabilization was increased to 4 days; the reason may be the chemical cracking of single-ring aromatic components into polyromantic components like naphthalene, which reduced the quality of the kerosene samples. The second set of experiments included only mixing and leaving the processed kerosene sample with 2 mL mixtures of glacial acetic acid and distilled water to set for 5 minutes. The greatest improvement was obtained when 1.8 mL of water containing 0.2 mL of glacial acetic acid was mixed with 10 mL of kerosene samples, resulting in a 19% improvement in aniline point and a 45% improvement in smoke point. The total sulfur percent and flashpoint tests revealed that the second set also had an acceptable chemical effect on kerosene samples by reducing 4.8% for the total sulfur test and increasing 11.7% for the flashpoint test. As a number, the first set of experiments showed better improvements in comparison with the second set, but to scale up these experiments and apply them industrially will be very difficult and expensive, and some steps are difficult to apply like centrifugation because of its high cost and because the stabilization step consumes a lot of time. Therefore, the second set of results will be more acceptable from an engineering point of view.

KEYWORDS

Kirkuk kerosene, Aniline point, Smoke point, Aromatics content, and Glacial acetic acid.

PAPER INDEX

1.   INTRODUCTION

Kerosene, also known as kerosine, paraffin, or paraffin oil, varies in color depending on its quality. It is a light yellow or colorless oily flammable liquid. It has an odor and volatile in the range of gasoline and gasoline/diesel oil and distills between 125°C and 260°C (Speight, 2019). When burnt in a wide lamp, kerosene's flash point of around 25°C makes it acceptable for use as an illuminant. The heat of combustion of gasoline ranges between 11,000 and 11,500 calories per gram, whereas that of kerosene (and diesel fuel) is between 10,500 and 11,200 calories per gram. Finally, the heat of combustion for fuel oil ranges between 9500 and 11,200 calories per gram (El-Gendy and Speight, 2015).

Kerosene is primarily utilized as a fuel for residential water heaters and air conditioning systems equipped with kerosene engine heat pumps (KHPs), as well as it used as a heating oil (Fuse et al., 2004).

On the other hand, domestic combustion is a significant cause of indoor air pollution in poor nations, and has been highlighted as a significant health concern influencing hundreds of millions of people, particularly women, children, and the elderly. The smoke produced by household combustion instruments or devices has been linked to respiratory disorders such as chronic bronchitis, emphysema, expectorative coughing, and dyspnea. Exposure to unvented indoor cooking smoke may result in the development of cancer, most notably lung cancer (Kim Oanh et al., 2002).

To produce kerosene that burns cleanly, the aromatic content must be kept low. This quality is defined by the smoke point standard. The flash point is used to provide the front end of the distillation specification, whereas the freeze point is used to specify the back end (Holbrook, 1996).

In the petroleum industry and petroleum products, polycyclic aromatic hydrocarbons (PAHs) such as fluorene, anthracene, and fluoranthene are recognized to be harmful by-products of combustion that are hazardous to human health. PAHs are classified as persistent organic pollutants, which means they are able to stay in the environment for an extended period of time (POPs). These are organic pollutants that are resistant to degradation and can therefore persist in the environment for extended periods of time if not properly managed (Wild and Jones, 1995, Sankoda et al., 2013). Scientists have rarely questioned the concept that polycyclic aromatic hydrocarbons (PAHs) are inert substances even at high temperatures (Necula and Scott, 2000). PAHs are known to damage air, soil, and water resources at even low concentrations, and they have a high thermal stability and persistence in soil and groundwater, making them a significant threat to human health (Nelkenbaum et al., 2007).

For further information, particulate matter (PM), carbon monoxide (CO), and organic compounds are the primary contaminants in smoke from residential combustion instruments or devices. The latter is composed of a diverse array of components. Among the organic chemicals released, polycyclic organic matter (POM) and formaldehyde are of particular importance. POM is a chemical group composed

of at least two benzene rings. The polycyclic aromatic hydrocarbons are one class of POM that have been identified as carcinogens or mutagens. The majority of PAH found in the environment are a result of incomplete combustion of organic molecules. PAH undergo changes in the environment, and the resulting derivatives are often more hazardous than the original PAH, hence increasing the potential for adverse health impacts (Kim Oanh et al., 2002).

The smoke point of aviation turbine fuels and kerosenes is a property that shows a fuel's tendency to burn with a smoky flame. Increased aromatic content in a fuel results in a smoky flame and energy loss owing to thermal radiation. The smoke point (SP) of a fuel is the highest flame height at which it can be burned without smoking in a standard wick-fed lamp. It is measured in millimeters, and a high smoke point signifies a fuel with a low tendency for smoke production(Baird, 1981). The ASTM D 1322 technique are used to determine the smoke point (Riazi, 2005, Speight, 2015).

The term "aniline point" refers to the lowest temperature at which equal amounts of aniline and oil are totally miscible. The procedure for determining the aniline point of petroleum products is detailed in ASTM D 611. The aniline point reflects the fraction's degree of aromaticity. The aniline point is inversely proportional to the aromatic concentration. As a result, the aromatic concentration of kerosene and jet fuel can be estimated using the aniline point(Jenkins and Walsh, 1968).

$$\%A = 692.4 + 12.15(SG)(AP) - 794(SG) - 10.4(AP)$$

where % A denotes the aromatic content, SG denotes the specific gravity, and AP is the aniline point in degrees Celsius (Riazi, 2005).

In general, the purpose of this research is to determine how adding GAA affects the quality of kerosene samples by lowering the aromatic content. more specific, improving the burning properties of local kerosene to meet Iraqi quality control standards for kerosene oil used for heating by improving specifications such as the smoke point and aniline point using simple processes and low-cost and safe chemicals.

2. MATERIALS AND METHODS

This study used a local kerosene sample known commercially as Kirkuk kerosene in the local market, which was of low grade and was sold as low-quality kerosene for house heating purposes in the local market. In this study, two experimental sets of processing were dependent. Four standard ASTM tests were used in both sets of experiments, including the smoke point, aniline point, total sulfur content ratio, and flash point, to compare the effects of the treatments, as explained in the following section.

The first set of experiments consisted of the following steps:

1. Heidolph® Unimax 2010 orbital shaker was used to mix a 10-mL of the kerosene sample with different milliliters   of glacial acetic acid (0.5,0.75,1,2,3,4,5,and 6 mL) for 3 minutes.

2. By using a mental heater, heat the mixtures for 15 minutes at 35 degrees Celsius.

3. Centrifuging the mixtures at 2000 rpm for 15 minutes

4) The mixtures were allowed to stabilize for two time durations (2 days and 4 days).

The second set of experiments consisted of the following steps:

1. 2 mL of pure water with different amounts of glacial acetic acid (5, 10, 15, and 20%) were prepared.

2. The water with GAA mixtures manually were mixed with 10 mL of the kerosene sample.

3. The final mixtures were mixed with Heidolph® Unimax 2010 orbital shakers for 20 minutes.

4. The treated kerosene samples were left for 5 minutes before analysis.
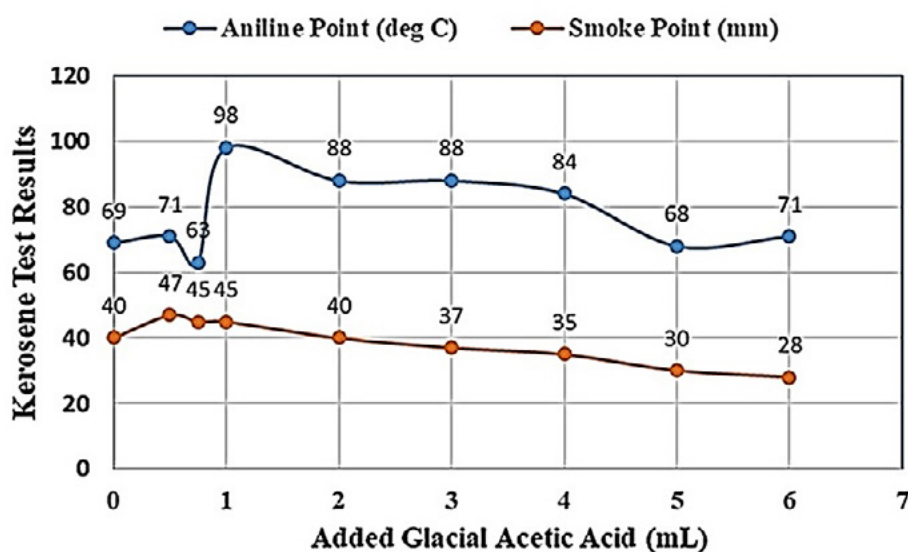
It is clear that the first set was more complicated than the second and consumed more time. The aniline point (ASTM-D611) and smoke point (ASTM-D1322) standard tests were used as main tests for both sets of experiments to compare the results of kerosene samples before and after acetic acid treatment to determine the effect of acetic acid treatment on the aromatic content of the kerosene samples. The total sulfur weight percentage (ASTM-D4294) and flash point (ASTM-D93-20) tests were used in the second set beside the main tests.

3. RESULTS AND DISCUSSION

The increasing aniline point (aniline mixing temperature in oC) and smoke point (height of smokeless fire in millimeters) directly indicate a decrease in the aromatic content of treated or processed kerosene samples. Table (1) and Figure (1) show confusing results for the first set at most points. This unstable data may be due to the existence of multiple steps as chemical influencers on the kerosene samples (high centrifugation power, long stabilization time, and heating), in addition to the existence of GAA. The maximum improvement of the first set was satisfied when 1mL added in GAA was added to the kerosene samples with (29 oC of aniline point, (42%) of improvement and in the smoke point, 5 mm (12.5%)). Adding more GAA affected the results negatively for both 2 and 4 days duration of stabilization.
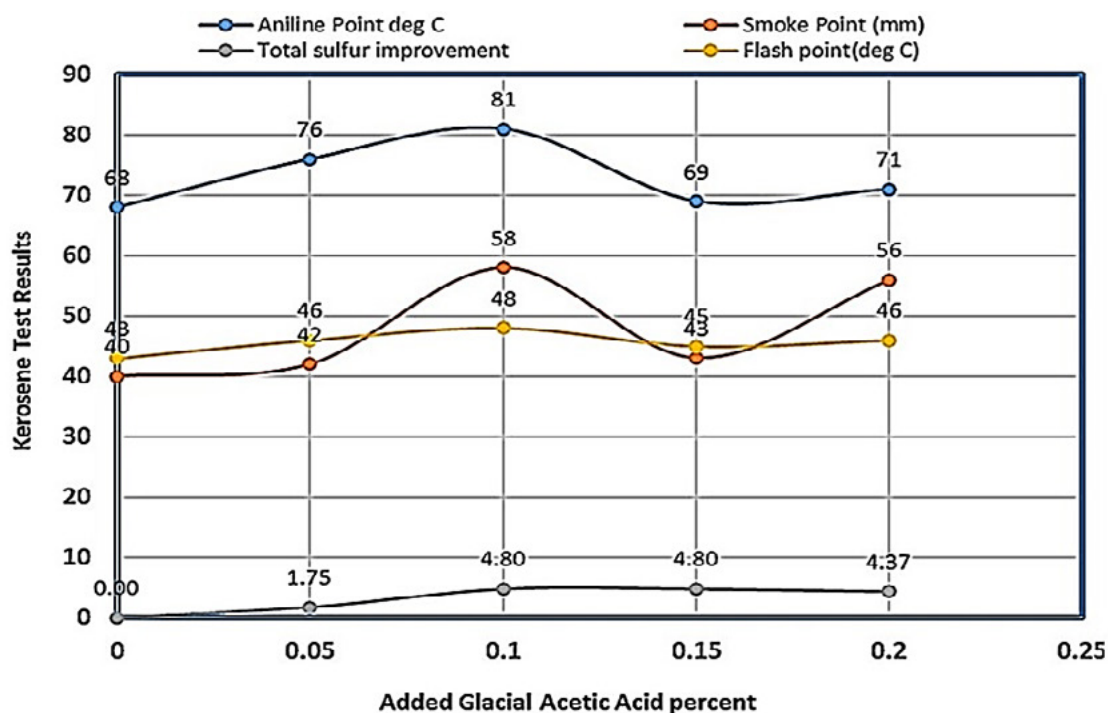
Table 1. First set of experiments results

Test no.	GAA mixing volume (mL)	Smoke point (mm)	Aniline point (°C)	Stand for time(days)
0	Zero	40	69	0
1	0.5	47	71	2
2	0.75	45	63	2
3	1	45	98	4
4	2	40	88	4
5	3	37	88	4
6	4	35	84	4
7	5	30	68	4
8	6	28	71	4

Figure 1. First set of experiments results

The results of the second set are more reasonable (Table (2) and Figure (2)). Although the heating, centrifugation, and stabilization time factors were canceled. The results of both the aniline point and the smoke point were improved in this set of experiments. These improvements will support our opinion that the long stabilization time is a reason for the confusing results of the first set of experiments. Here, the second test point (2 mL) of used water mixed with 0.2 mL of GAA increased the aniline point temperature by 13 oC (19% improvement), the smoke point by 10 mm (45% improvement), the flash point by 5 mm (11.6% improvement), and the total sulfur by 110 ppm (4.8% improvement). In addition to that, these experiments were performed at ambient conditions for temperature and pressure and mixed for only 20 minutes. It is expected that the polarity of water played an important role in these improvements, at least as an absorbing agent or washing agent for kerosene sample impurities.

Table 2. Second set of experiments results

Test no.	GAA volume ratio in 2 mL of pure water (mL)	Aniline point (°C)	Smoke point (mm)	Total Sulphur ratio w/w %	Flash point (°C)
0	Original sample	68	40	0.229	43
1	5%	76	42	0.225	46
2	10%	81	58	0.218	48
3	15%	69	43	0.218	45
4	20%	71	56	0.219	46

Figure 2. Second set of experiments results

The first study used a high temperature and pressure range hydrotreating lab unit (275-350 oC and 32-62 kPa), a catalyst (Ni w/-Al2O3), and a high purity hydrogen gas source (H2/HC ratios of 200-500). All of these improved the kerosene's aromatic content by only 1 to 12.8%(Hussein et al., 2018).

Another study worked on removing the aromatics components from hydrotreated kerosene from the Al-Dura refinery by using an organic solvent with a high mixing volume (solvent/fuel = 1). The solvents were methanol, glycerol, and sodium thiosulfate as surfactants. According to the study, the maximum aromatics percent satisfaction was around 47%. The problem with this study is that it is not cost-effective; they isolated 47% of aromatics from kerosene samples that contained 21% aromatics using organic solvents that are difficult to separate again to recover their value. In addition, these isolated aromatics caused a volume loss of about 10% for kerosene samples (Algawi et al., 2018).

The present study used acetic acid and water at ambient operating conditions. For both sets of experiments, the maximum ratio of used GAA to kerosene was 0.1 for the first set to increase 42% of the aniline point and 0.02 for the second set with a 19% improvement in the aniline point by using the mixing for 20 minutes. Comparing the present study results and the simplicity of the experimental processing with other studies, which worked on Iraqi hydrotreated kerosene (Al-Dura refinery), demonstrates the preference for the present study and the quality of its results.

Finally, it is clear that the processing of the Kirkuk kerosene samples did not have a big impact on the sulfur and paraffinic components because of the greater stability that these components possess in comparison to the aromatic components. When taking into account the relatively low amounts of glacial acetic acid that were used, these relatively minor shifts in total sulfur weight percent and flash points are still regarded as significant improvements. Increasing the flash point can regarded as a guide that the cracked aromatics converted chemically to saturated and long straight paraffins by more specified lab analyzers.

4. CONCLUSIONS

1. Even with a low mixed volume ratio, GAA showed a good effect on aromatics content of Kirkuk kerosene samples. The water supported the chemical effect of the GAA, and it supported the process economically because it is free.

2. The positive effect of using water with GAA encouraged us to use commercial-grade glacial acetic acid instead of an analytical grade in the future, which means lowering the final cost of processing more and more.

3. Aniline point test results were more reliable than smoke point test results because the latter had manual steps that made errors more likely in comparison to the aniline point test.

4. All of the reviewed references ensured that the smoke point is generally related to the aromatics content of kerosene, but this does not prevent the fact that the high existence of PAH effects the smoke point values negatively..

5. Reducing the quantity of aromatics is not the end of the story. To get a better smokeless fire, the quality of aromatics will also be affected. Less PAH means the best quality of fire and the best smoke point value.

6. The second set of tests   is easier to apply industrially and with low cost scale-up plant.

7. Other tests (total sulfur percent, flash point), even though they had a slight effect, can be used as make-up processing for kerosene samples that need a slight improvement to be salable commercially.

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