Comparison study of the properties of kerosene-naphthalene blends with turpentine A. Mushtaq^{1*}, R. Muhammad Khan¹, Z. Uddin Ali², A. R. Ali Khan¹, M. Mazhar-ul-Haque¹,

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Blending of kerosene with naphthalene to improve the properties of turpentine is the chief objective of this research. Through blending the cost of turpentine will be reduced by around 20 to 30% of its actual price. Kerosene and naphthalene are only used for blending whereas turpentine is used for comparison. The blending process was carried out using a hot plate magnetic stirrer. Distinct wt. % of naphthalene was measured and inserted into the calculated wt. % of kerosene. Different tests were performed for comparing the properties of blend and pure turpentine. Flash point of the blend exactly corresponds to that of turpentine whereas the boiling point is deflecting from the boiling point of turpentine. This blend cannot exactly replace turpentine but further research and delving can make it more comparable with turpentine.

Keywords: Blending; kerosene; naphthalene; turpentine; flashpoint; boiling point; fluorescent indication.

INTRODUCTION

Kerosene, turpentine and naphthalene are the materials required for preparing blends of kerosene and naphthalene. The properties of the blends were compared with the properties of turpentine. This research is a step towards synthetic turpentine, which will yield a cost-effective solution.

Paint is a viscous form of material that needs thinning for easy coating on the wall. Turpentine is one of the few means of thinning paint [1, 2].

Turpentine oil is made of the resin of certain pine trees, having 75-90 wt. % of resin and 10-25 wt. % of oil. Turpentine is a mixture of Turpen and essential oil which vary in wt. % based on geographical location, tree species and distillation process. It is also used in soap, cosmetics, and medicine (but it is unsafe when taken by mouth or used over a large area of skin). Recently, fragrant chemical compounds are synthesized, in which turpentine is used as a raw material. The expense of distilled turpentine is much higher than that of its alternates. Mineral spirits solvent or acetone is an inexpensive, petroleum-based replacement for turpentine [3, 4].

In this research, the blend between kerosene and naphthalene (mock ball) is to get the properties of turpentine most cheaply. As like dissolves like an expression used to show how solvents work on polarity.

Kerosene, like naphthalene, is non-polar. This means that naphthalene is dissolved in kerosene and their blend is possible. A magnetic stirrer was used to prepare the blend at room temperature. To measure the properties different testing equipment

were used (flash point, boiling point, fire point and others) of blends of different composition. However, this method of fabricating turpentine is timeconsuming. In industry, a different mixing system is used which is brisk and efficient. For example, a turn-key liquid mixing system consists of tanks, control, and top- or bottom-mounted mixers. These mixing modules are designed to blend, dissolve, hydrate, emulsify, and homogenize powders into liquids.

Turpentine

Turpentine is obtained by distillation of gum resin from pine trees, called oleoresin. The word turpentine derives from the Greek word terebinthine meaning 'feminine of resin'. Turpentine oil is used in medications, paints, perfumes, food additives, household cleaning agents and insecticides. It is also a cure of skin aging. Hippocrates used turpentine against lung diseases and other [5, 6]. Pine is having five species that make Turkey a dominating conifer area. Figure 1 shows tapping of exudates from pine trees.



Fig. 1. Tapping of exudates from pine trees

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Pine oleoresin is gained by bark tapping (chips obtained from pine trees) and the collection of exudates of forestry products. The structure of alphapinene is given in Figure 2. Acidic and neutral diturpentine together give a complicated mixture having volatile compounds. Turpentine collected from different forests was having different percentage of constituents [7, 8].



Fig. 2. Structure of alpha-pinene, a major component of turpentine.

Turpentine unit of active resins-dissolved semifluid substances associated with very volatile oil is separable by various distillation techniques into a volatile portion referred to as turpentine oil and a non-volatile portion called rosin. It is originally stated that complete oleo resin exudates change in a very extreme way the turpentine fraction (that has different uses in business and assortment of the ensuing exudates, and is a crucial biology product). Acidic and neutral di-turpentine in a mixture having volatile compounds (mono- and sesquiterpenes) compose the oleoresins [9, 10].

Steam distillation is employed to convert the mixture into gum turpentine (volatile compounds) and gum rosin (di-terpenes). Steam distillation is a special style of distillation (a separation process) for temperature-sensitive materials like natural aromatic compounds. It was a well-liked laboratory methodology for purification of organic compounds, which, although of diminished use, thanks to the proliferation of vacuum distillation and steam distillation, remains important in certain industrial sectors.

Many organic compounds tend to decompose at high sustained temperatures. Separation by distillation at the traditional (1 atmosphere) boiling points isn't a possibility. The little amounts of the volatile compounds are conveyed by vapor to the condensation flask, wherever the condensed-liquid part separates and permits fluent collection. This method effectively allows distillation at lower temperatures, reducing the deterioration of the specified product. If the substances to be distilled are sensitive to heat, steam distillation is also applied under reduced pressure, thereby reducing the operative temperature.

After the distillation the vapors are condensed. Normally, the instant product is also a two-phase system of water and organic liquid, permitting discriminating of the parts by decantation, portioning or appropriate alternative ways. The bottom-most is cheaper. But the maximum use of turpentine oil is at present in the chemical industry, as a raw material in the manufacturing of resins, insecticides, oil additives, synthetic pine oil and camphor. Turpentine oil is also used as a rubber solvent in the synthesis of plastic products [11, 12].

Turpentine is also being used by experimentation for the handling of MS and sexual dysfunctions. It is also being studied for its actions to prevent drug activity and inhibition of bone cell activity. Turpentine is used in scientifically experimented models of inflammation to induce general inflammation that is not capable of being affected in animals.

Naphthalene

Naphthalene $(C_{10}H_8)$ is made from coal tar or crude oil. Naphthalene is a white solid polycyclic hydrocarbon. It is produced by burning of cigarettes, car smoke and also during forest fires. It is used as an insecticide pest repellant, first registered as a pest repellent in the USA in 1948. Naphthalene is obtained by distillation from either coal tar or petroleum. It is used to manufacture phthalic anhydride and is also used in moth repellents as shown in Figure 3. It is a white crystalline volatile solid which sublimes at room temperature. Naphthalene is water-insoluble and is soluble in C_6H_6 , hydro-naphthalene, absolute EtOH, CCl_4 , CS_2 and in fixed volatile oils. It is a component of naturally produced crude oil and is also produced by natural uncontrolled combustion. It is non-polar [3, 13].



Fig. 3. Commercial grade of naphthalene (mothballs)

The molecular structure shows a fused pair of benzene structures, as shown in Figure 4. By and large, naphthalene is used as a controller of the clothes moth. In this usage, the naphthalene vapor fills the airtight container and kills the insects. Naphthalene is metabolically actuated by the body. Different tissues produce different metabolites, which is ultimately leading to specific site toxicity. Naphthalene is a non-polar solute. Hence, it dissolves in kerosene which is a non-polar solvent. Naphthalene doesn't dissolve in water which is a polar solvent.



Fig. 4. Structure of naphthalene.

Kerosene

Kerosene is a flammable liquid used in industries for light and fuel heat/ power. Kerosene is used for making wax and other viscous and non-viscous substances. It is also called paraffin or kerosene derived from the Greek word Keros meaning 'wax'. It was first discovered by the Persian scholar Raazi. Kerosene is obtained by fractional distillation from the crude oil giving a thin oil which is roughly 0.81 g/cm³. It is extracted at a temperature between 150-275 °C. It has a non-polar nature. Consumption of crude around the world is 12 million barrels per day; 1 barrel is 45 gallons or 205 liters [14, 15].

Kerosene is obtained by crude oil distillation and it is heavier than naphtha. It may also be obtained by catalytic cracking or hydrocracking but is usually less stable than that obtained by the atmospheric distillation process because of the presence of olefinic constituents. It is a colorless liquid that does not stop flowing until temperature drops below -30°C, due to this reason kerosene is blended with diesel to increase the efficiency of vehicle mobility in cold regions. In old days it was used as a lamp fuel but now it is used as a jet fuel after adjusting its freezing point and burning quality and is classified as JP1, JP2, JP3 and JP4. It is also used as a cleaning agent and is used in many industries for removing lubricants before re-lubrication [16, 17].

Blends

Blending is a unit operation in which two or more components in an unmixed or partially mixed form are treated in such a way that the components lie as nearly as possible in contact with each other. Blending may aim a change in the physical state of components and properties of the materials are shown in Table 1. Jet fuels are made by blending of naphtha, gasoline, or kerosene to meet specific military or commercial specifications. JP-4 is a blend of kerosene with lower boiling distillates. JP-7 is a blend of kerosene distillates with a maximum of 5% aromatics by volume and a maximum total weight of 0.1% sulfur. In case of dissolving a solid in a solvent the process is too slow and for fastening a process agitator is used. In this research, as turpentine is an expensive material and not easily available but used on a large scale in paint and many industries, a blend of naphthalene and kerosene was studied to achieve properties of turpentine which will reduce the cost of the raw material. It was calculated to make a blend of different compositions of 5wt. %, 10wt. %, 15wt. %, 20wt. %, 25wt. %, and 30wt. % of naphthalene in kerosene. By comparing the properties of different refined products, naphthalene and kerosene were found to be closer to turpentine. Both kerosene and naphthalene are nonpolar and miscible with turpentine [3, 18-20]. Turpentine is used as a paint thinner for reducing the viscosity of the paint. However, turpentine is very expensive and not easily available while this blend will be of low cost owing to the ease in availability of raw material and ease in the process. Therefore, it will be highly effective for the paint industry and it will reduce around 2/3 of the cost of turpentine [21, 22].

Properties	Kerosene	Naphthalene	Turpentine
Molecular weight (g/mol)	185	128.16	136
Boiling point, °C	175 to 325	217.9	150 to 180
Melting point, °C	-48 to -26	80	-55
Flash point, °C	40-65	88	38
Density, g/cm ³	0.77 to 0.81	1.16	0.86 to 0.9
Autoignition temperature, °C	220	540	300-330
Molecular formula	C_9 to C_{16} hydrocarbons	$C_{10}H_{8}$	$C_{10}H_{16}$

Table 1. Properties of the materials

METHODOLOGY

Chemical blending is a process in which different chemicals may be liquid or powder, inorganic, or organic blended. Blended substances have various chemical and physical properties to achieve blends of combined or mixed constituents so the constituents are indistinguishable. By blending a product is changed to meet a specification, dilute contamination to insignificance and make a new product. There are two main classes of components in a blend – blend stocks and additives.

Blend stocks

Major components are referred to as blend stocks. They make up a significant part of the blend, generally measured in percentage terms -e.g. 1 wt. %, 10 wt. %, 20 wt. %, 50 wt. %. In this research kerosene and naphthalene were used as the blend stock. The percentage of naphthalene was 5 wt. %, 10 wt. %, 15 wt. %, 17.5 wt. %, 20 wt. %, 25 wt. %, and 30 wt. %. This percentage assigns the main characteristics to the blend. Naphthalene may be introduced as a blend stock into kerosene to affect the properties of turpentine. Blend stocks must produce the required specification in the mixture across a variety of parameters of quality. They must be an economical choice for the production of the required product. So in this project the achieved property of turpentine is the cost of 200 Pkr/L whereas, turpentine can be bought at the rate of 1000 Pkr/L. They must be compatible, so that the mixture is stable, in this research 10 wt. % of naphthalene can be dissolved in kerosene so it must be stable at 10% solubility.

Additives

Additives are substances that can be added to a blend to modify its performance. They are generally used in very small amounts, often measured in parts per million. In this research there are no additives, only a blend stock is used. In experience there are four main classes of problems that arise in making petroleum blends as compatibility and stability issues. Blend design does not perform as mathematically predicted blends not being properly mixed and there is lack of quality reserve.

Blending processes

The research to improve the properties of kerosene by naphthalene or synthesis of turpentine by making a blend between kerosene and naphthalene powder involved four separate tasks. The apparatus used for the blending procedure included beaker, conical flask, hand chopper, Duran bottle, funnel and magnetic stirrer. This blend is consisting of kerosene and naphthalene powder. Make powder of mock ball by a hand chopper for perfect mixing. Weigh naphthalene powder (mock ball powder) according to the calculation. According to requirement there is 5 wt.%, 10 wt.%, 15 wt.%, 17.5 wt.%, 20 wt.%, 25 wt.%, 30 wt.% of naphthalene in 100 ml of solution. The 17.5 wt.% in 100 ml solution is the volume of solute 17.5 ml, the density of solute 1.14 g/ml, the mass of solute 19.95 g, the volume of solvent 82.5 ml and 19.95 g of naphthalene added into 82.5 ml of solution for making this blend. Put naphthalene powder into the Duran bottle using a spatula. Convert the volume of kerosene into mass by density. Weigh mass of kerosene according to the calculation and mix with naphthalene powder into the Duran bottle using a magnetic stirrer. Provide electricity and activate the apparatus for the test. Without any heat mix the kerosene and naphthalene up to six hours at room temperature. Remove the blend from the magnetic stirrer. Detach the magnetic beat from the bottle with the help of a forceps. Filter through filter paper in order to remove undissolved naphthalene from the liquid. Figure 5 shows the blend ready for further testing.



Fig. 5. Blend of kerosene and naphthalene.

Characterization testing

After filtration the sample is ready for testing the properties of the blend. The following results show many comparable properties of the blend with turpentine.

Flash point test. Flash point is the lowest temperature at which the material emits sufficient to form a combustible mixture with air. There are two approaches to doing the flash point test. An open cup flash point test is conducted in an open environment with complete access to air to interact with the sample. It is the most practical phenomenon because most of the substances are being stored in an open environment where the air has clear access to contact with the substance stored. A closed cup flash point test is conducted in a closed vessel which is not open to the environment. In the present research the sample was tested in the Pensky-Martens flash point

test apparatus with ASTM D-56 in a closed cup flash point test apparatus.

Boiling point test. The boiling point is the most basal physical property of an organic compound. There are several methods for estimating the boiling point of a chemical compound, such as distillation method, reflux method, Thiele tube method. In this research, all the samples were tested by the Thiele tube method.

Pour point test. Pour point is the temperature below which the liquid loses its flow characteristics. In this study, all pour tests were performed by inserting the sample into a cooling bath according to ASTM D-97. No results were found even at -40°C which is clear evidence that the pour point must be beyond -40°C.

Density. Density is the ratio between the mass of the sample and the volume. In this study, density was measured using an RD-bottle which has a constant volume of 100 ml. Insert the sample of 100 ml blend and measure the weight of the sample. By dividing both of them density can be determined.

Aniline test. Aniline point is the temperature at which aniline $(C_6H_5NH_2)$ and the sample are miscible and form a single phase. This value tells the number of aromatic compounds present in the sample because aniline itself is an aromatic compound. The higher the aniline point, the lower is the amount of aromatics present in the sample. In this study, the sample was tested according to ASTM D-611. For aromatic oil with 75% aromatic content,

the aniline point would be around 50. In this research, the aniline point of the blend was 51.5 which means 75% aromatic content present in the sample.

Fluorescence indicator test. This test was performed to check the amount of paraffin, olefin and aromatic compounds present in the sample. Different colors were observed at different levels of the tube by which the amounts of paraffins, olefins and aromatics can be calculated through a formula.

pH Test. pH is the measure of hydrogen ions present in the solution. It is a figure indicating the nature of the sample either acidic or alkaline. Low values are acidic and high values are alkaline. Pure water has a pH of exact 7.

RESULTS AND DISCUSSION

Flash point, boiling point, pour point, density, aniline, fluorescence indicator and pH testing results show the comparable properties of the blends with turpentine.

Flash point

The flash points of kerosene and turpentine (52 and 44 °C, respectively) are shown in Figure 6. All samples made were then tested for flash point at 5, 10, 15, 20, 25, 30 wt.% and showed that the required results were obtained at 17.5 and 15 wt. %. Samples in wt. % were compared with the properties of turpentine as shown in Figure 7.



Fig. 6. Comparison of flash points of pure kerosene, turpentine and blends



Fig. 7. Graphical representation of flash points of kerosene, turpentine and blends

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Fig. 8. Comparison of densities of kerosene, turpentine and blends.

From the above results it was concluded that the flash point of a sample changes as the amount of naphthalene changes in the blend because there is a change in blend composition. After all, flash point depends on the molecule structure. As naphthalene is added in kerosene the molecular mass of the blend decreases and this causes an increase in vapor pressure. Vapor pressure indicates the substance volatility and it shows the strength of interaction forces between the molecules. So, when the temperature increases there is an increase in vapor pressure and this causes a decrease in the flash point [13, 18].

Density

Figure 8 shows the density test of the samples. The density of kerosene is 0.782 g/ml and that of turpentine is 0.767 g/ml. Densities of the samples were determined at 5, 10, 15, 20, 25, 30 wt. % of naphthalene and showed that the required results were obtained at 17.5 and 15 wt. %. The trend of the densities was plotted against different wt. % of naphthalene blended.

From the above results it was concluded that as naphthalene quantity in kerosene increases, the density increases. As the density of the material is affected by one factor, namely, how atoms are arranged in a certain volume or the concentration of atoms in a volume, this indicates the molecule structure of a material. As the density of naphthalene is high as compared to kerosene because naphthalene is a solid, the molecules are tightly packed to each other and there is no space between the molecules in a given volume while the density of kerosene is lower because it is a liquid, which means that there is a space between molecules which are not tightly packed and have less intermolecular forces. It shows that the molecular structure also affects density [8, 21].

pH

Initially, the pH of the pure samples of kerosene and turpentine was calculated, which showed kerosene as a basic product and turpentine with acidic nature. Figure 9 shows the 17.5 and 15 wt. %

naphthalene samples tested along with the pure samples of kerosene and turpentine. The sample with 17.5 wt. % was found neutral and that with 15 wt. % acidic. As an aromatic hydrocarbon, naphthalene's structure consists of a combined pair of benzene rings. In that way, naphthalene is named a benzenoid polycyclic aromatic hydrocarbon. The eight carbons that are not shared by the two rings convey one hydrogen atom each. The particle is planar, similar to benzene. In contrast to benzene, the carboncarbon bonds in naphthalene are not of a similar length. In electrophilic aromatic substitution responses, naphthalene responds more promptly than benzene. The selectivity for alpha over beta substitution can be explained as far as the resonance structures of the moderate: for the alpha substitution intermediate, seven resonance structures can be drawn, of which four protect an aromatic ring. For beta substitution, the moderate has six resonance structures, and just two of these are aromatic. Protonated cations of naphthalene $(C_{10}H_{+9})$ are a part of the range of the Unidentified Infrared Emissions (UIRs). Protonated naphthalene differs from impartial naphthalene in that it has an extra hydrogen atom [16, 18].

Boiling point

Figure 10 shows that the boiling point of the sample is increasing concerning the increment of wt. % of naphthalene in the blend. The boiling point of a substance gives the strength of intermolecular forces and to break these strong intermolecular forces it is required to increase the kinetic energy which can only be done by the increase of its temperature. The boiling point is affected by molecule size, presence of a functional group, number of carbon atoms and degree of branching and types of intermolecular bonding. As the amount of naphthalene in kerosene increases, the boiling point increases because the molecule size increases as there are more nuclei and electrons in the large molecule that create intermolecular force and this causes an increase in density and an increase in boiling point [5, 8].

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Fig. 9. Comparison of pH values of kerosene, turpentine and blends



Fig. 10. Comparison of boiling points of kerosene, turpentine and blends

Property	Minimum length, mm	Maximum length, mm	Length, mm	Total length, mm	Length/Total length, %		
For turpentine							
1st reading							
Olefins (blue) %	365	415	50	65	76.92		
Saturated (yellow) %	415	430	15		23.07		
2nd reading							
Olefins (blue) %	470	520	50	69	72.46		
Saturated (yellow) %	525	544	19		27.53		
For 15 wt.% blend							
1st reading							
Aromatic (red) %	651	664	13	84	15.4		
Olefins (blue) %	664	714	50		59.5		
Saturated (yellow) %	714	735	21		25		
2nd reading							
Aromatic (red) %	730	745	15	85	17.6		
Olefins (blue) %	745	797	52		61.2		
Saturated (yellow) %	797	815	18		21.2		
For 17.5 wt.% blend							
Aromatic (red) %	642	660	18	86	20.93		
Olefins (blue) %	660	715	55		63.95		
Saturated (yellow) %	715	728	13		15.11		

Table 2. Results of fluorescent indicators for turpentine and blends

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Fig. 11. Percentage of aromatics in turpentine, kerosene and blend



Fig. 12. Percentage of olefins in turpentine, kerosene and blend



Fig. 13. Percentage of saturated hydrocarbons in turpentine, kerosene and blend

Fluorescent indicator

Cyclic terpenes are another significant wellspring of inexhaustible phenols. Even though not as rich as lignin, normally happening terpenoids, including pcymene, α -and β -pinene, are promptly accessible as turpentine. Naphthalene was inspected as a fueladded substance to liquor during a whirl combustor to get conservative consuming and ultra-low outflow exploitation entirely unexpected warming value powers. Naphthalene is a poly-fragrant compound frequently viewed as a waste fuel that outcomes in large amounts of contamination outflow. The viability of a hydrocarbon as a fuel-added substance to liquor on NO and CO discharges and soundness was harmless [3, 5, 8, 13, 18]. The above experiment shows the amounts of aromatic hydrocarbons, olefins and saturated hydrocarbons present in the blends. It shows that naphthalene is a polycyclic hydrocarbon (having double benzene rings) and it contains more aromatic hydrocarbons and olefins as compared to kerosene in which saturated hydrocarbons are present in high quantity followed by olefins. As naphthalene amount in kerosene increases to form the required blend the naphthalene rings break and on one ring of naphthalene the kerosene group is attached as a side group and thus it contains less aromatics and more olefins [6, 12, 15, 17].

It was concluded that the blend of kerosene with 17.5 wt.% of naphthalene was showing properties near to those of turpentine and could be used as an

alternative for it. The study also included flash point, boiling point, fluorescent indicating, density and pH tests of kerosene and our blends.

CONCLUSION

In this research, blends of naphthalene and kerosene were made to achieve the properties of turpentine used in the paint industry for reducing the viscosity of paint for better coating and fabrication. The results showed that on increasing the amount of naphthalene the flash point of the blend is decreasing. It was observed that at 17.5 wt. % the flash point of the blend was exact 43 °C, the same as turpentine. The boiling point temperature of the 17.5 wt. % blend was 180 °C and that of turpentine was 184 °C. The fluorescent indicator test revealed the quantity of olefins, aromatics and saturates present in the blends, turpentine and kerosene. The results showed that turpentine had 2 % of aromatics 74% of olefins and 26 % of saturated hydrocarbons. Blend of 17.5 wt. % had 20.93 % of aromatics, 63.95% of olefins and 15.11% of saturates. The density of turpentine was 0.767 g/ml and that of the sample with 17.5 wt. % was 0.751 g/ml, just close to the required. The pH of turpentine was 7.66 and that of the 17.5wt.% blend was 7.16. The future recommendation for this study is to perform a liquid FTIR study to get a know-how of the mechanism going inside it. Few additives could also enhance its properties.

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