ISSN NO. 2320-5407

*Journal homepage: http://www.journalijar.com*

*INTERNATIONAL JOURNAL OF ADVANCED RESEARCH*

**RESEARCH ARTICLE**

**Production application of paraffin waxes refining process in Iraq and used as phase change materials**

**Hussein J. Akeiber[1], Mazlan A. Wahid[1], Taha Mahdi[2,*], Naser N. Jassim[3], Mohammed M. Obeid[4]**

**1.** Department of mechanical engineering, Universiti Teknologi Malaysia, skudai 81310, Johor, Malaysia.
**2.** Studies Planning & Flow up Directorate, Ministry of Oil, Baghdad, Iraq.
**3.** Midland Refineries Company, Ministry of Oil, Daura, Baghdad, Iraq.
**4.** Materials Engineering, University of Babylon, Babylon- Iraq.

***Manuscript Info***

***Manuscript History:***

Received: 15 November 2015
Final Accepted: 22 December 2015
Published Online: January 2016

***Key words:***
Applications,
Phase change materials
De-waxing process

* Corresponding Author

**Taha Mahdi**

***Abstract***

There are large numbers of Phase Change Materials (PCMs) that melt and solidify at a wide range of temperatures, making them attractive in a number of applications. This paper summarizes the investigation of the available thermal energy storage systems incorporating PCMs for use paraffin wax. We also present a production of paraffin waxes base on petroleum refining process through Iraq given increasing economy globalization and stricter environmental regulations. Different subsequent refining techniques including solvent de-waxing have been used to produce paraffin wax base oil from residue crude oil waste by-product. The solvent de-waxing technique was performed using two different solvent mixtures of methyl ethyl ketone and toluene.



## Introduction:-

Petroleum products are among the most significant material flows in the economy by magnitude and by environmental impact (Adriaanse et al., 1997). Iraq's petroleum refining industry produces a wide variety of petroleum products and uses many types of processing equipment, such as catalytic cracking, hydrocracking, hydrotreating, and coking units to upgrade heavier feedstocks to more valuable lighter fractions. However, the end product from the vacuum distillation was satisfactory. Paraffin wax oil is one of the most important materials that have been used in many different ways since the early days of humankind.

Paraffin waxes are petroleum products, consisting mostly of straight-chain hydrocarbons, thus the melting point and the latent heat of paraffin waxes increase with the number of carbon atoms. Paraffin waxes have been found to exhibit many desirable characteristics for use in thermal energy storage, for example, their reasonably high volumetric storage density (around 200 kJ/kg or 150 MJ/m3) and their availability in a large temperature range. Their need for sub-cooling is negligible since they are self-nucleating, they are chemically inert and stable, give raise to no phase segregation, and they are commercially available at reasonable cost. Due to their promising properties, Paraffin waxes have received increasing attention in recent years as phase change materials (PCMs) (Pal et al., 1999). It compared to ice storage, these PCMs are used in a passive manner such as the stabilization of room temperature by means of the thermal inertia of phase change.

The PCMs, usually meaning solid-liquid phase change materials (because the latent heat change for a solid-to-solid transition is usually considerably less than that for a solid-to-liquid transition), have received considerable attention in recent years due to their high heat storage capacity (Salyer et al., 1987). Various forms of PCMs have been utilized as thermal storage media for cooling and heating applications (Marinković et al., 1998; Bo et al., 1999). They have shown a promising ability to reduce the size of a storage system compared with water storage that uses sensible heat to store energy. The candidates for PCM are generally divided in two groups: organic and inorganic compounds. Inorganic compounds include salt hydrates, salts, metals and alloys. Organic compounds are categorized into paraffins and non-paraffins (Farid et al., 2004; Hasnain, 1998).

The purpose of this project is to review the basic aspects dealing with heavy crude oil and residua processing for production of useful Paraffin waxes which can be used as the base PCM storage in a passive method.

## Types of Waxes:-

The word "wax" usually refers to a variety of organic substances that are solid at ambient temperature but become free-flowing liquids at slightly higher temperatures. The chemical composition of waxes is complex, but normal alkanes are always present in high proportion and molecular weight profiles tend to be wide. Paraffin and Microcrystalline waxes are types of waxes which they derived from petroleum. They are easy to recover and offer a wide range of physical properties that can often be tailored by refining processes.

Iraqi products offer different types of petroleum waxes are given in Table 1 (Ministry of oil, 2013). Paraffin was which are distinguished by large well-formed crystals; micro-crystalline, which are higher melting waxes with small irregular crystals; and "intermediate" wax, in which the boiling range is cut where the transition in crystal size and structure occur. It was observed that the addition of oil leads to reduction of milting point. Petroleum wax production characterizes wax by degree of refinement; fully refined paraffin has oil content generally less than 0.5%, and fully-refined micro-crystalline less than 3%. The melting temperature can be changed by adjusting the concentrations of oil as illustrated in Table 1. Also the paraffin wax changes from white to black as the fraction of oil content increases as shown in Figure 1.

**Table 1. Iraqi products of petroleum waxes**

| | **Hard paraffin wax** | **Soft paraffin wax** | **Microcrystalline wax** |
|---|---|---|---|
| Oil content wt% | 3 | > 4 | < 2 |
| Milting point $^{o}$C | 60 - 65 | 50 – 55 | 70 - 75 |
| Penetration @ 25 $^{o}$C | 20 | 34 | 18 |
| Color (ASTM-1500) | 3.0 | 2 | 4 |

Figure 1. Optical image of the color of the paraffin wax

## Characterization of Paraffin Wax:-

Paraffin waxes are saturated hydrocarbon mixtures that usually consist of a mixture of different alkanes. They are characterized by straight or branched carbon chains with generic formula $C_nH_{2n+2}$, the crystallization of the ($CH_3$) - chain release a large amount of latent heat. Both the melting point and latent heat of fusion increase with chain length, thus it has melting temperatures ranging from 23 to 67 °C (Akgün et al., 2007; Krupa et al., 2000; Hato and Luyt, 2007). They are white, semi-transparent, tasteless and odor less solids with common properties such as smooth texture, water repellency, low toxicity, safe, reliable, predictable and non-corrosive. They are combustible and have good dielectric properties. They are soluble in benzene, ligroin, warm alcohol, chloroform and carbon disulfide, but insoluble in water and acids. They have commercially available, ecologically harmless, readily available and inexpensive (Akgün et al., 2007, Krupa et al., 2007, Sari, 2004). Their specific heat capacity is about 2.1 kJ/(kg* K), and their enthalpy lies between 180 and 230 kJ/kg, quite high for organic materials. The combination of these two value results in an excellent energy storage density (, Krupa et al., 2007). They have chemical stability, show little volume changes on melting and have low vapor pressure in the melt form. Moreover, they have low thermal conductivity (Sari, 2004, Xiao et al., 2002) and large volume change during a phase transition (Elgafy and Lafdi, 2005). Because of these desirable characteristics of paraffin waxes, it is used as PCMs in latent heat storage systems (Xiao et al., 2002; Xing et al., 2006). The application of phase change materials has found importance in various systems from energy storage to thermal protection (Krupa et al., 2007).

## Application of Paraffin Wax in Iraq:-

Waxes have been used in many different ways since the early days of humankind. The most important application of waxes is for candles. Although no longer used for primary illumination, candles are currently the fastest growing segment of the wax market. The different types of waxes process have been established as the leading technology for the production of high-purity paraffin waxes. Thus there are many other applications for high-purity waxes: Waxes are widely used in cosmetic products such as lipstick, mascara, moisturizing creams, and sun blocker. They are used for the paper coating, glass cleaning preparations, hot-melt carpet backing, biodegradable mulch, lubricants, and stoppers for acid bottles, as well as electrical insulation (Krupa et al., 2000, Hato and Luyt, 2007). Fully refined wax is non-toxic and many products are approved for direct use in food and personal care formulations. Wax is used to cover certain types of cheese that would dehydrate if not properly protected. It is sprayed on citrus and other types of fruit to protect the fruit from oxidation and enhance its appearance. Waxes are present in most hot-melt adhesive formulations, where they control the viscosity of the adhesive and contribute to open time, flexibility, and elongation. Wax is a vital component in rubber tire formulations. It is added for protection against atmospheric ozone that "dries" unprotected rubber, leading to cracking that compromises the strength of the tire. Nowadays, paraffin waxes in particular are of recent research interest due to their promising properties as phase change materials.

## De-Waxing Process:-

Waxes are part of the residues of the crude oil atmospheric distillation unit because of their higher boiling ranges. In processing the residues to lubricating oils, waxes are obtained in all fractions of the vacuum distillation unit. Waxes must be removed from the lubricating oil, due to they cause a high pour point of the oil because of their poor solubility. If the oil temperature is below the pour point, solid waxes will begin to precipitate. Depending on the source of the crude oil, the content of solid waxes can vary between 3% and 15%. The flow characteristics of the oil will be adversely affected and oil filters will be blocked. Slack waxes are produced through the de-waxing of lubricating oil distillates as illustrated in Figure 2. During the de-waxing, the paraffin waxes are separated from the lubricating oil by solvent extraction processes. The paraffin enriched by-products of these processes are a mixture of oil and wax, the so-called slack waxes.

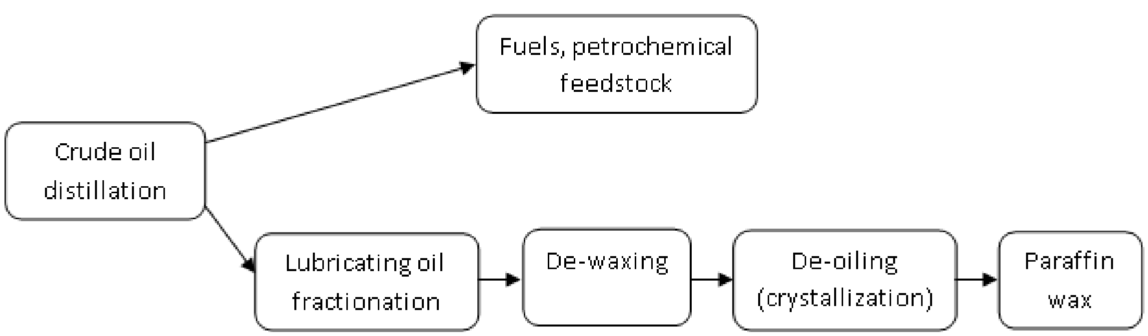


Figure 2. typical refining scheme for paraffinic wax production

The characteristics of ideal de-waxing solvent include the following: low solvent power of wax, high solvent power for oil, low freeze point, low viscosity, less in cost, non-toxic and have chemical and thermal stabilities (Wauquier, 2000). The waxy raffinate from the solvent-extraction process is a physical process which is usually mixed with two solvents are used: toluene, which dissolves the oil and maintains fluidity at low temperatures, and methyl ethyl ketone (MEK), which dissolves little wax at low temperatures and acts as a wax precipitating agent.

A simplified flowsheet of MEK de-waxing process is shown in Figure 3. It consists of the three basic sequential processing steps: i) crystallization (dilution and chilling of the feedstock), b) filtration (separation of wax and de-waxed oil filtrate) and c) solvent recovery (separation of solvent from wax and oil). The feedstock is mixed with two to four volumes of solvent by a double dilution controlled shock chilling procedure are used. About 60 % of the chilling is obtained by heat exchange between the feedstock and solvent with cold filter from filtration being used as the chilling medium in the double-pipe exchangers. The remainder of the refrigeration required for chilling is obtained by indirect heat exchanger with a refrigerate in the double pipe chillers. The slurry leaving the chillers at a temperature of 5 to 20 $^{o}$F below the desired pour point is filtered using rotary vacuum filters and the wax cake is washed with a spray of cold solvent before being discharged by a gas blow back. The solvent is recovered from the resultant de-waxed oil filtrate and wax cake by flash vaporization and recycled in the process.

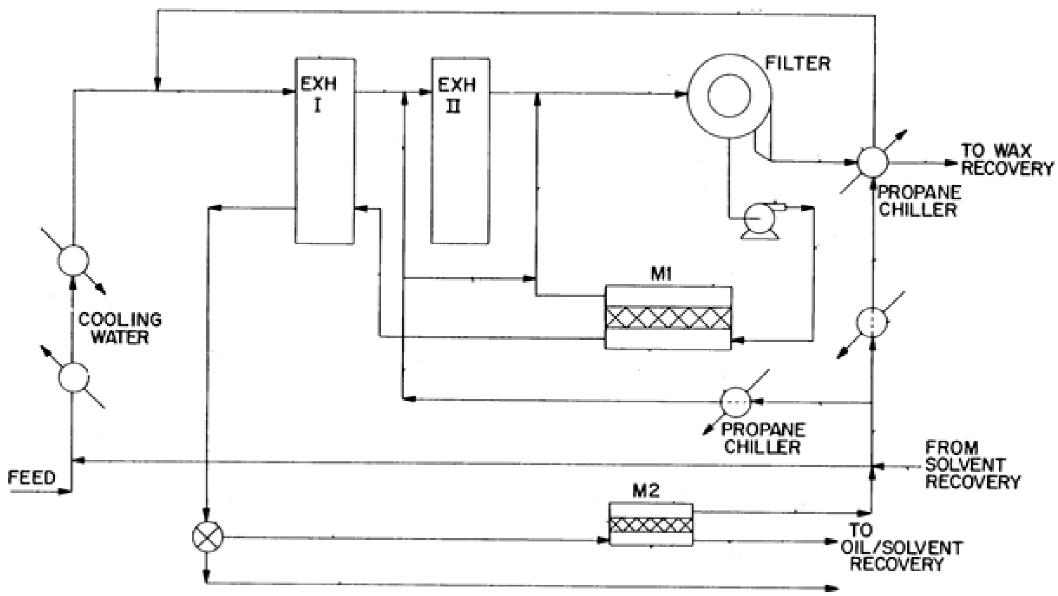


Figure 3. A simplified flowsheet of de-waxing process.

## Result and Discussion:-

Fierce competition due to the globalization of the world economy, the fast depletion of domestic crude oil, and increasingly stricter environmental regulations are providing challenges to the sustainable development of petroleum refining business. This review paper is focused on the production of paraffin waxes in Iraq with different applications. The processing of Iraqi oil refineries by de-waxing process has produced a significant yield of a high quality wax material. This product is very beneficial for the humans as well as for thermal energy storage technology with phase change materials (PCMs). The application of PCMs is one of prospective techniques of storing thermal energy. It is used for cool storage has obtained considerable attention, since they can be designed to melt and freeze at a selected temperature and have shown a promising ability to reduce the size of storage systems compared with a sensible heat storage system because they use the latent heat of the storage medium for thermal energy storage.

## Acknowledgment:-

The authors are grateful to Universiti Teknologi Malaysia, Skudai. Authors are also thankful to the Studies Planning & Flow up Directorate, Ministry of Oil, Republic of Iraq.

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