

# Description of raw materials for manufacturing candles and grave candles and their influence on the environment

Joanna GUZIAŁOWSKA-TIC – Department of Environmental Engineering, Opole University of Technology in Opole, Poland

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## Introduction

The first candles probably appeared in the ancient civilisations-3000 BC. At that time animal fat was used as a raw material for manufacturing candles. In Poland, tallow candles with a wick made of a leaf were mentioned for the first time in the 16<sup>th</sup> century. In the 19<sup>th</sup> century, spermaceti wax obtained from liquid within the head of a sperm whale started to be used. In the middle of the 19<sup>th</sup> century, the first stearin candles were obtained from fatty acids separated from animal fat, and paraffin candles derived from processing crude oil also appeared.

The mass production of stearin candles began in 1831. The first braided wicks appeared in 1825, and mordanted wicks have been commonly used since 1834. In 1854, a mixture of paraffin (made from petroleum) and stearin was used for manufacturing candles. The production of candles with synthetic wax began in the second half of the 20<sup>th</sup> century, and from the 1990s, candles and grave candles have been produced from soy wax and palm wax, obtained by hydrogenating adequate vegetable oils [1].

Oils and fats are an important element of food and feed products. They are also used as a raw material in the chemical industry. Products are typically classified as oils and fats on the basis of their state at ambient temperature. Mixtures of liquid triglycerides, usually of plant origin, are classified into the oil category; whereas solid triglycerides regardless of their origin belong to fats. A common chemical feature of both oils and fats is their susceptibility to hydrolytic degradation to glycerol and fatty acids [2]. Moreover, they are characterised by the following features: hydrophobic nature, greasiness to the touch, lubricity, possible combustion without mineral residues (ash, dust, etc.).

Some types of oils and fats are used as the raw material in the industry, and with carbohydrates and lipids, they are an important group of so called renewable raw materials. Regarding an ecological evaluation of safety, renewable raw materials are usually predominant over their petrochemical equivalents [3].

Glycerol and fatty acids are decomposition products of fats and oils (Fig. 1). Triglycerides are decomposed in the presence of water and acid or alkaline catalysts [4].

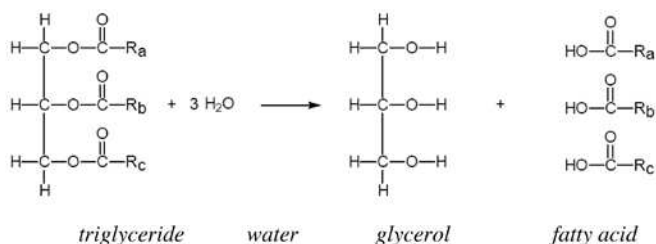


Fig. 1. Decomposition products of triglycerides [2]

Although many fatty acids present in natural oils and fats have been discovered, only few of them are commercially significant. They are, among other things, myristic acid, lauric acid, palmitic acid, stearic acid, oleic acid, linoleic acid and linolenic acid (Tab. 1).

In practice, fats and oils are usually a mixture of triglycerides in various proportions. In some cases, one of triglycerides is dominant; however, the source where natural oil or fat would contain only one glyceride has not been found so far.

Table 1

The chemical formula of the major fatty acids

Acid	Empirical formula	Structural formula
Lauric acid	C <sub>12</sub> H <sub>24</sub> O <sub>2</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> COOH
Myristic acid	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>12</sub> COOH
Palmitic acid	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOH
Stearic acid	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> COOH
Oleic acid	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> (CH) <sub>2</sub> COOH
Linoleic acid	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>12</sub> (CH) <sub>4</sub> COOH
Linolenic acid	C <sub>18</sub> H <sub>30</sub> O <sub>2</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> (CH) <sub>6</sub> COOH

## Raw materials for manufacturing candles and grave candles

The process of manufacturing candles and grave candles is rather simple; but it is very important which raw materials are used. High quality granules and properly selected wicks can greatly contribute to the success of a product sale.

Figure 2 illustrates various types of raw materials for manufacturing candles and grave candles, their origin and properties. Figure 3 shows a percentage share of individual raw materials for manufacturing candles and lights.

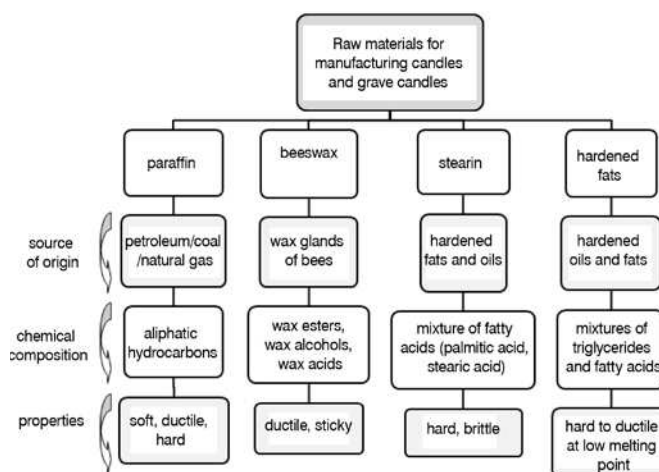


Fig. 2. Raw materials for manufacturing candles and grave candles [7]

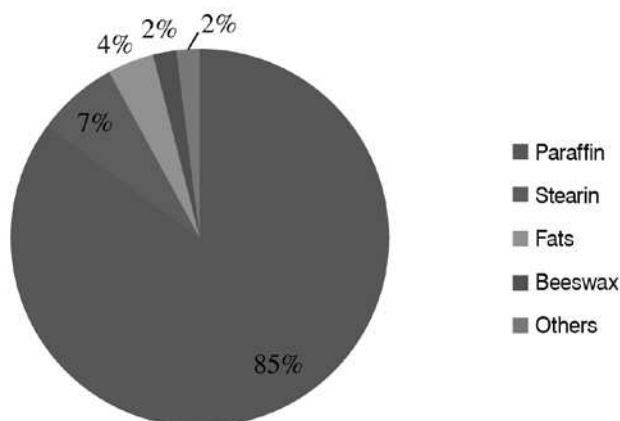


Fig. 3. Percentage share of raw materials for manufacturing candles [7]

Paraffin is a relatively cheap and ordinary raw material, but candle manufacturers are getting interested in using more available, renewable resources [5]. As petroleum belongs to non-renewable energy sources, a drop in its production is inevitable [6]. Cheap and alternative raw materials are thus being searched for manufacturing candles and inserts for grave candles. In recent years, an interest in using modified vegetable oils as a material for manufacturing such products has been observed. The performed tests included, among other things, partially hydrogenated soybean oil and hydrogenated cottonseed oil with added hydrogenated palm oil. There were also attempts to improve functional properties of hydrogenated palm oils by their modification (epoxidation and esterefication).

### Combustion process

The combustion process of candles and grave candles, even if occurs in accordance with laws of physic, brings many problems regarding chemical aspects. During combustion of exposed surfaces (wicks) in the presence of air and under standard pressure, gaseous products and particulate matter are released to the surrounding environment. The thermal balance of such process is unfavourable which results from incomplete combustion of organic matter. The complete combustion process requires a satisfactory dispersion of fuel and a quick mixing with air. Soot can be released if there is lack of air [8].

The combustion process depends on many parameters: a type of combusted fuel; the amount of supplied air; a volume of released combustion gases.

Such factors determine, whether the whole quantity of flammable substance present in fuel, will be transformed into the end products of combustion, that is, carbon monooxide (IV), steam or other (desirable or undesirable) chemical compounds. Combustion of solid fuel differs from gas or liquid combustion. This process consists of the following stages: melting of paraffin; transforming a liquid into a volatile phase; forming ash from the wick (its inorganic components), which is emitted to the surrounding environment; releasing soot from unburned parts of paraffin fuel.

A mechanism of chain cleavage within a candle flame.

Cleavage of a paraffin chain takes place using the same mechanism as the pyrolysis of petroleum naphtha. This mechanism can be described with the use of an example of naphthas cracking – one of the most widespread industrial processes for producing ethylene. The process starts at a temperature between 800°C and 900°C with the cleavage of a single C-C-bond resulting in the formation of two alkyl groups. Each of these groups then eliminates an ethylene molecule and forms a new radical with at least two carbon atoms, which can again remove an ethylene molecule. Thus the main process is depolymerisation of paraffin wax molecules. By thermal dehydrogenation of ethylene, acetylene is formed, which decomposes into carbon and oxygen.

Alkyl groups can also react in other ways, e.g. by eliminating hydrogen atom (Fig. 4). In this case, depolymerisation and dehydrogenation are classified as endothermic processes. Nevertheless, the temperature within the candle flame increases from 800°C in zone 1, through 1000°C, up to 1300°C in zone 3. The reason is the combustion of hydrogen. From each  $C_2H_4$  molecule, two molecules of hydrogen are formed which in turn split into four hydrogen atoms by thermal dissociation. Combustion of hydrogen results in such a heating of zones 2 and 3 that the carbon particles reach incandescence.

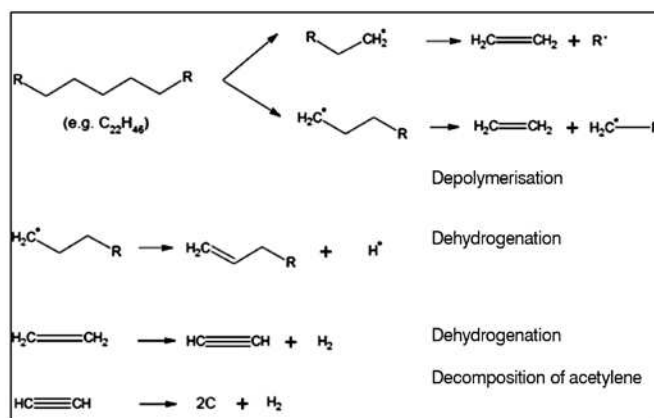
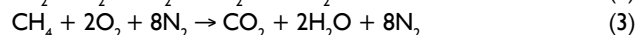
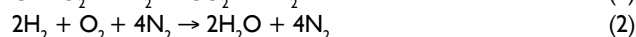


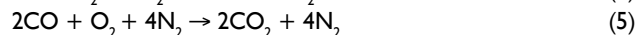
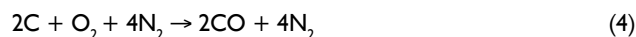
Fig. 4. Mechanism of chain cleavage within the flame [7]

During combustion of candles and grave candles, organic matter flowing towards the wick is not subjected to complete degradation due to interference in the diffusion of atmospheric oxygen to its surface. Paraffin contains many carbon atoms which require a suitable amount of oxygen for its complete combustion, and this condition is not met for candles. Combustion is thus accompanied by emission of unburned soot molecules – smoke.

Reactions occurring during the complete combustion are shown with the use of an example of methane:



If there is an insufficient amount of air, carbon monooxide is formed in the first phase, which in a subsequent course of the process can be transformed into carbon dioxide.



These equations are typical for changes in the composition of reactive substances assuming that the whole amount of carbon is transformed into carbon dioxide, and the whole amount of hydrogen is transformed into water [8].

The supply of oxygen to the outer zone of the flame is different compared to deeper layers, and particularly to the wick surface. Other factors which can affect the process of complete combustion of paraffin may result from the fact that at high temperatures, combustion reactions do not come to an end because of dissociation of formed carbon dioxide molecules and steam. Factors related to the combustion rate and resulting from the non-steady course of reactions in the area where combustion occurs may be regarded as another reason for the presence of such unburned parts as soot, aldehydes, and alcohols in combustion gases. This can be caused by an insufficient amount of air during combustion, its improper distribution, not thorough mixing of gases and too early cooling of gases in the surrounding environment.

Additionally, at the temperature of the burning wick, often saturated with various types of compounds and strengthened by metal ribbons or wires, chemical reactions can occur. They are often catalysed with these metals, resulting in the formation of harmful volatile substances (aldehydes, ketones, peroxides and polycyclic aromatic hydrocarbons).

It has been confirmed that burned candle products release significant amounts of soot having particles of  $0.06 \mu\text{m}$ , which are easily inhaled by human respiratory system. The sorption of various chemical compounds can be observed on these types of aerosols [8].

Derudi et al. [9] described the emission of pollutants from burning pure paraffin candles and candles with aroma additives (cedar wood, oriental spices, aloe and rhubarb). Figure 5 illustrates the emission of polycyclic aromatic hydrocarbons (PAHs) from burning pure and scented candles.

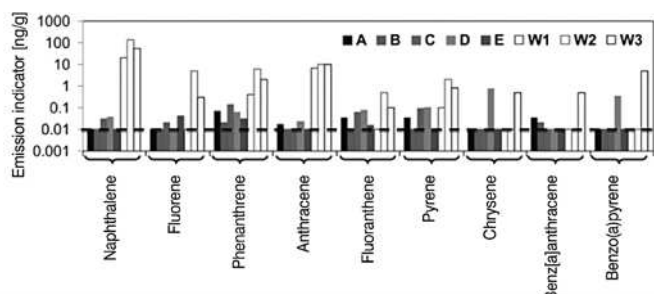


Fig. 5. PAHs emission factors for the tested scented candles (A-E) and pure paraffin candles (W1-W3) [8]

The diagram (Fig.5.) shows various types of scented candles marked with letters A÷E, and pure paraffin candles marked with letters W1 – W3. Limit values are marked with a dashed line. The limit values were exceeded by pure paraffin candles. Scented candles also exceeded the limit values, but at a lower level compared to pure paraffin candles.

Rezaei K. et al. [10] presented burning characteristics of three types of candles: made of paraffin wax, soy wax and beeswax and described changes in the size of a pool of melted wax (melt pool) depending on the used raw material (Fig. 6). Soy candles produced larger melt pools compared to paraffin wax candles (Figs. 6A, 6B). Melt pools of beeswax were the smallest ones (Fig. 6C). The size of these melt pools depended on a few parameters. As it was illustrated in thermographs prepared using DSC (differential scanning calorimetry) technique, melting and freezing curves had a significant impact on the size of melt pools (Figs. 6D÷6F). It was observed that soy wax began to melt at a lower temperature than paraffin wax and beeswax. Therefore, the largest melt pool was observed for candles made of soy wax.

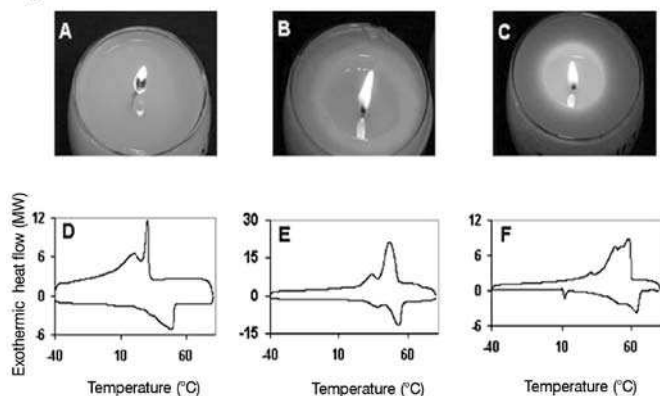


Fig. 6. Typical differences in liquid wax pool size and flame size among the Three types of candles: (A) soy-wax; (B) paraffin; (C) beeswax; (D), (E) and (F) are the DSC thermograms of these waxes, respectively [10]

Another parameter influencing the size of a melt pool, was the diameter of a wick. Paraffin candles and soy candles with thicker wicks formed larger melt pools and their burning was more intensive.

The most intensive burning was observed for paraffin candles, and the least intensive one for beeswax candles (Fig. 7A). Also the highest burning rate was observed for paraffin candles which were continuously increasing over time (Fig. 7B). The burning rate of the soy candle was dropping for the first 60 minutes, and then a slow increase in this parameter was observed. The drop was connected with a smaller production of soot. For the beeswax candle, the burning rate remained at the same level.

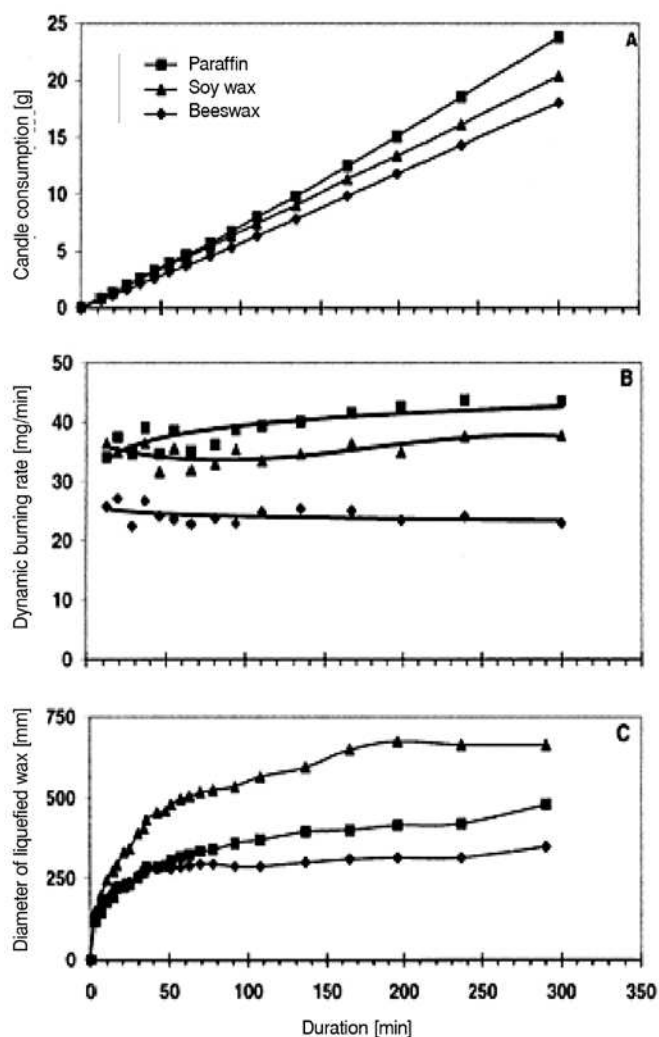


Fig. 7. (A) Characteristics for the consumption of paraffin, soy wax and beeswax in candles over time; (B) Dynamic burning rate of paraffin, soy wax, and beeswax; (C) Changes in the size of melt pools in three different types of candles [10]

The size of a melt pool around the flame was changing during five hours, whereas the most dynamic change was observed during the first 40 minutes (Fig. 7C). The largest melt pool was noted for the soy candle. However, the paraffin and beeswax candles had a very similar size of the melt pools for the first 50 minutes. Just later, a diameter of the melt pool started to increase for the paraffin candle, whereas the one of beeswax candle remained constant.

## Conclusions

This paper describes the raw materials for manufacturing candles and grave candles as well as their influence on the environment. On the basis of the data presented in this paper, it can be found that the selection of a raw material has a significant impact on the emission of pollutants and the combustion nature during candle burning.

As prices of petroleum naphtha are increasing, and consequently the prices of paraffin are also higher, the candle industry is trying to modify formulae of their products in order to influence prices of the end products. Therefore, we can observe synthetic and plant waxes, which are added to candles in larger amounts, more often.

In the nearest 15 years, the global demand on wax will be increasing at a rate of 1% per year according to prognoses of Kline&Company experts. They also warn that at the same time deliveries of this raw material will be diminishing at a rate of 1.5% per year. The paraffin industry is thus looking for alternative solutions for supporting candles manufacture not only at the current level, but also at an increasing level [11].

"The green sector" is one of the most developing sectors in the USA and Europe; and its average annual growth amounts to ca. 20%. Consumers demand that also such products as candles should be ecological and free of any pollutants; that traditional wax is replaced by palm oil-based products which are the renewable sources of raw materials [11].

### Literature

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Joanna GUZIAŁOWSKA-TIC – Ph.D. (Eng.), graduated from the Faculty of Mechanical Engineering, Department of Environmental Engineering at Opole University in Technology in 2004. She completed her doctorate studies at the Faculty of Mechanical Engineering at Opole University of Technology in 2008. He is currently employed in the Department of Environmental Engineering, in the Waste Management and Chemical Technology Teaching. Research interests: catalysts for environmental protection, management of chemicals, environmental protection. She is the author and co-author of 9 chapters in monographs, 18 articles published in scientific and technical journals, 3 patents and over 30 papers and posters presented at national and international conferences.

e-mail: j.guzialowska@po.opole.pl.

## Wyróżnienia AGRO ARCA

W dniach 30.08–01.09.2013 r. Instytut Nafty i Gazu uczestniczył w międzynarodowej wystawie wynalazków: 6<sup>th</sup> International Fair On Innovation, Eco Ideas, Products and Technologies in Agriculture and Food Industry, AGRO ARCA, Biograd na Moru, Chorwacja.

Najwyższą nagrodę Wystawy, tzw. Wielką ARCĘ, otrzymał wynalazek pt. Uniwersalny pakiet dodatków do bioestrów (zgłoszenie patentowe nr. P.39283., twórcy: Winicjusz Stanik, Ireneusz Bedyk, Zofia Łukasik, Katarzyna Sikora, Rafał Konieczny, Maria Łenyk, Grażyna Żak), a wyróżnienia otrzymały wynalazki: Biodegradowalny smar plastyczny (twórca: Anna Zajezierska, nr patentu: P.400119), Biodegradowalny smar dla trakcji szynowej (twórcy: Franciszek Steinmec, Anna Zajezierska, nr patentu: P.371309), Biopaliwo do silników z zapłonem samoczynnym (twórcy: Zofia Łukasik, Iwona Skręt, Winicjusz Stanik, Leszek Ziemiański, Marta Baranik, Anna Duda, Jan Lubowicz, nr patentu: P.353663), Olej napędowy zawierający biokomponenty (twórcy: Winicjusz Stanik, Zofia Łukasik, Leszek Ziemiański, Iwona Skręt, Marta Baranik, Anna Duda, Jan Lubowicz, nr patentu: P.353662), Paliwo stałe zawierające komponenty biogenne uszlachetnione wielofunkcyjnym pakietem dodatków (twórcy: Leszek Ziemiański, Anna Duda, Grażyna Żak, Winicjusz Stanik, Iwona Skręt, Michał Wojtasik, Jan Lubowicz, Wojciech Mazela, Michał Pajda, Celina Bujas, nr patentu: P.398944), Sposób otrzymywania biokomponentu oleju napędowego oraz paliwo do silników wysokoprężnych zawierające ten biokomponent (twórca: Łukasz Jęczmionek, nr patentu: P.396590), Wielofunkcyjny pakiet dodatków do paliw stałych zawierających komponenty biogenne (twórcy: Leszek Ziemiański, Anna Duda, Grażyna Żak, Winicjusz Stanik, Iwona Skręt, Michał Wojtasik, Wojciech Mazela, Elżbieta Szałkowska, Wojciech Krasodmski, nr patentu: P.398377). (kk)

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