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Sea Transportation of Some Agriculture Products Liable to Self-heating

M. Popek
Gdynia Maritime University, Gdynia, Poland

ABSTRACT: Propensity of cargoes to self-heating is determined by many factors which can be divided into two main types - properties of the cargo and environment/storage conditions.
Some agricultural products are susceptible to self-heating which can cause many serious problems during handling, storage and sea transportation of such commodities.
Palm kernel shells (PKS) have been shipped in bulk since 2007 but they are not a currently listed cargo in the IMSBC. PKS are a natural by-product of palm oil processing and differ materially from the palm kernel expellers currently regulated by the IMSBC Code. However, their specific characteristics and negative external influences may cause them to behave like a substance from Class 4.2 (Substances liable to spontaneous combustion) or MHB cargo.
Due to the importance of spontaneous combustion, particularly with respect to the storage and sea transportation of PKS, an investigation has been conducted.

1 INTRODUCTION

1.1 *Hazard in transport of agriculture products*

The marine transport industry tonnage accounts for 90% of world trade. Whether it involves the delivery of raw product to a manufacturer, or final goods, marine transport is a critical part of the supply chain [Kelman 2008].

The agriculture sector has been growing rapidly over the years. Agriculture products shipments are to a large extent determined by weather conditions in producing and exporting countries. However, other factors are increasingly influencing the volume and structure of these cargoes. They include: the shift in demand and usage for industrial purposes, environmental and energy policies that promote the use of alternative energy source such as biofuels and evaluation in consumption and demand patterns.

Apart from grains, oilseeds, and pulses, and besides timber and paper products and refrigerated products, there remains a whole range of agricultural products which together comprise large and valuable sectors of seaborne trade. Most agriculture products are transported with minimal loss of quality. However, a part of raw vegetable and grain products that are transported in bulk, when subjected to high humidity levels and mild heat tend to self-heat, which contributes to a reduction of their quality. Cargoes with a high tendency to self-heating are listed as Class 4.2 Substance Liable to Spontaneous Combustion.

Self-heating is a catalytic process that occurs when the heat generated by the oxidation of cargo and other mechanisms is not effectively dissipated to the surrounding environment, causing local temperature to rise. The increase in temperature occurs in two phases. Phase one is a biological heating, which normally occurs up to 55°C and exceptionally up to 75°C. Biological heating is caused by activity of plant cells, bacteria and insects. Phase two is a chemical heating caused by exothermic chemical reaction between goods and oxygen up at least 150°C [Ramirez et al. 2010]. If the heat is removed or absorbed by the surrounding environment, then only low temperature oxidation may occur.

Self-heating of agriculture cargoes depends on numerous controllable and uncontrollable factors such as: chemical composition, porosity, exposed surface area.

The original condition of these products is the most important factor affecting its transport. The product moisture content and temperature influence and even direct events that occur during storage and transportation may lead to self-heating.

Also, handling conditions such as changes in moisture content of surrounding environment, large variation in the temperature and movement of air through the cargo may contribute to self-heating of the cargo.

Moisture within the product reaches an equilibrium with the air within and between the product particles and produces a relative humidity level that may be suitable for the growth of deteriorative organisms.

Biological organisms that cause transported products to deteriorate require different levels of relative humidity for normal development.

Both relative humidity and moisture content depend on temperature. The excess moisture in the product coupled with elevated temperature promotes microbial activity that exudes heat and moisture.

In some cases, self-heating may not only lead to a decomposition of the material, with a release of flammable gases, but also major fires and risk of explosion. This phenomenon is known as spontaneous combustion or self –ignition [Sturaro et al. 2003]. Situations involving fire are very serious and may cause major losses of products and human injury.

In order to secure storage and transport, the self-heating and self-ignition in different types of coal wood products and biomass have been studied [Jones 2001, Krause &Schmidt 2001]. However, there is still a lack of research that would characterize the risk of self-heating of agriculture products. Therefore, not enough data regarding the properties of the goods stored and transported by sea.

The increased sea transportation of agriculture raw materials for the biofuels industries and the distribution of alternative energy products present new challenges for the maritime industry.

Some agriculture goods are more susceptible to self-heating than others, and this can lead to severe problems during storage, handling and transportation of such commodities.

The mechanism behind the reaction which leads to self-heating is not completely understood but is probably connected to the biomass extractives.

1.2 *Seed cakes*

Seedcake is the residue remaining after removal of oil from any oil-bearing seeds, grains, cereals and other cereals products. It is a by-product and principally used as an animal feed and fertilizer.

Cereals and cereal products defined as seedcake are those derived from several products such as: coconut, maize, sunflower seed, copra, corn gluten, linseed palm kernel and soya bean.

Seedcake is transported as dry bulk cargo, in the form of pulp, meal, cake, pellets and expellers. There are four types of seedcakes listed in IMSBC Code defined by the oil, moisture content and the method of production. Three of them are classified as hazardous materials class 4.2 and represents cargoes liable to spontaneous combustion.

Seed cake is regarded as hazardous good and liable to self-heating due to high presence of moisture, residual oil. Although the process is slow, it can cause the temperature of the cargo to rise to the point at which it may spontaneously ignite. Furthermore, high moisture content of seedcake promotes microbiological activity, which may be responsible for the initial rise in temperature up to about 70°C. It may accelerate oxidation of the residual oil, which can cause the temperature to rise to the value at which the seedcake will spontaneously ignite.

Oxidation of the oil in seedcake causes a subsequent reduction of the concentration of oxygen in the air inside the cargo space. Additionally, carbon dioxide and carbon monoxide may be produced.

Palm Kernel Shells (PKS) have been shipped in bulk since 2007, but they are not a currently listed cargo in the IMSBC. PKS are a natural by-product of palm oil processing and differ material from the Palm Kernel Expellers currently regulated by the IMSBC Code. However, their specific characteristics and negative external influences may cause them to behave like a substance from Class 4.2 (Substances liable to spontaneous combustion) or MHB cargo.

The purpose of the research was to examine factors, which contribute to the self-heating of Palm Kernel Shells.

2 PALM KERNEL SHELLS

2.1 *Characteristics of Palm Kernel Shells*

There are two kinds of oil in palm nut: one is palm oil, which remains in outer core of the nut and the other is palm kernel oil which is extracted from the inner core, known as palm kernel. Palm Kernel Shells (PKS) are the hard endocarps, which cover palm kernel [Olanipekun et al. 2006].

The palm oil industry produces wastes after oil extraction process. The type of waste produced from oil palm industry includes: empty fruit bunches, fiber, shell, wet shell, palm kernel fronds and trunks. They consist mainly of hemicellulose, cellulose and lignin, with some biopolymer extractives being minor components [Ninduangdee et al. 2015].

PKS as a cargo are the shell fraction left after the nut has been removed after crushing in the Palm Oil mill. This cargo should not be confused with PK Expellers, which can contain more residual oil and therefore regulated in IMSBC Code as Seed Cake.

Kernel shells are fibrous material and can be easily handled in bulk. The average oil content is below 1%, but individual cargoes may vary.

Moisture content in PKS is low compared to other biomass residues with different sources and is between 11% and 13%. Due to the fact that the exporting countries are located in the tropical zone, the cargo can take up a large quantities of moisture content after heavy precipitation.

The studies have shown that PKS is characterized by that the relative high absorbency of water, as the material is an organic aggregate and contains many pores. The 24 –h water absorption varies in the range 21%-25% with varying PKS sizes. [Alengaram et al. 2010].

Specific gravity of PKS depends on the origin but has never crossed the value 2,0 and the range of it is around 1,17-1,60 [Mannan & Ganapathy 2002].

PKS has wide range of particles from 3 to 14 mm. The shape of the material depends on the extraction method and breaking of the nut. The thickness of PKS varies between 0,15 and 8 mm. Bulk densities are affected by the size of PKS and vary in the range of 500-600 kg/m^3 and 600-740 kg/m^3 for loose and compacted material respectively [Alengaram et al. 2010].

Furthermore, PKS contain residues of Palm Oil, which accounts for its slightly higher heating value than average lignocellulosic biomass.

2.2 *Major application of PKS*

In view of increasing population, the energy consumption derived from fossil fuel resources increases too. Nowadays one of the serious problems related to the environment is the increasing pollution, caused by the use of fossil fuels (Olivier et al. 2012). Global warming has emerged as a major problem due to increasing rate of greenhouse gases emissions generated from fossil fuel combustion [Hosseini et al 2013].

Furthermore, facing the challenge of depletion of fossil fuels reserves, there are a lot initiatives to promote the development and dissemination of renewable energy [Dhillon & von Wuehlisch 2013].

In order to promote greater energy efficiency, renewable energy should be part of the climate change solution as long as the renewable energy is developed in a sustainable way.

Use of biomass fuels in stationary combustion chambers is recognized as an environmental friendly production of energy [Lasek et. al 2017].

This has led to significant number of different source of biomass to be applied as an energy resource.

The two countries: Indonesia and Malaysia produce 85% of world's oil palm total production. Indonesia is the world's largest producers of palm oil and the industry has been the economy's most valuable agricultural export sector for the past decade [World Growth, 2011].

PKS is one of the products of waste during palm oil production. The huge quantities of waste generated from oil palm industry resulted in investigation the possibility of converting that waste into biofuel. PKS have a high dry matter content, therefore are generally considered as a good fuel for the boilers because of low ash amounts and minimum emission in combustion process.

The estimation of biomass-based renewable energy potential generated from solid waste od palm oil (PKS) are approximately 54.8 GJ/year which could replace the use of fossil fuels [Prastowo 2012].

Currently compacted briquettes obtained from palm kernel shells are formed. Because of the uniform shape and size this product, it can be more easily transported and used as a fuel.

In the opinion of scientist hydrogen may be considered as the most important bio-fuel that is expected to be a major source of energy and play significant role in the economic development [He et al. 2009, Pinto et al. 2009].

One of the serious problems, related to the environment, is the increasing amount of plastic waste. Currently the possibility of hydrogen production by blending Palm Kernel Shells with the polyethylene waste is studied. The production of hydrogen-rich gas from mixed feedstock may mitigate the carbon emissions to the environment, preventing further global warning and reducing the dependence on fossil fuel. [Moghadam et al.2013].

The investigation indicates that palm kernel shells would make good alternative pore agents in insulating refractory bricks. Very low water absorption rate and hardness have the potentialities of producing controlled size and independent pores [Ekong 2013].

The high demand for concrete in construction using normal weight aggregates, such as gravel and granite, has reduced natural stone deposits and caused damage to the environment [Alengaram et al. 2013]. During the past years researches has been focused on investigation on the use of palm kernel shells as lightweight aggregates, to replace conventional normal weight aggregates in structural elements and road construction [Mannan et.al 2006]. It served the purpose of both the structural stability and economic viability.

Palm Kernel Shells are currently the most common biomass energy good transported by sea. PKS are generally shipped in bulk vessels.

Recent incidents during sea transportation of PKS in last years have demonstrated that this cargo emits very high level of methane, when is subjected to the fermentation process and oxidation. This situation occurs, when the moisture content exceeds 11%. The experience in shipment of these goods indicates that the cargoes are subjected to oxidation leading to depletion of oxygen and increase of carbon monoxide and carbon dioxide.

Due to the importance of self-heating, particularly with respect to the storage and sea transportation of the PKS, an investigation has been conducted. The IMO standard has been used in this investigation.

3 EXPERIMENTAL

3.1 *Materials and methods*

For the research, Palm Kernel Shells coming from Indonesia were used.

It is important to characterize the risk of self-heating and self -ignition of these cargoes before loading them on ship. Dry and oily (contaminated with oils) samples of PKS were used in studies. The possibility of self-heating of Palm Kernel Shells was estimated by using *The Test Method for self-heating substances* of the Model Regulations [UN 2009]. The test procedure outlined adequately assesses the relative hazard of goods liable to spontaneous combustion so that an appropriate classification for transport can be made. The ability of a substance to undergo oxidative self-heating is determined by exposure of it to air at temperature of 140^{o}C in 25 mm wire mesh cube.

The sample of PKS in its commercial form was filled to the brim of the sample container and the container tapped several times. The container was housed in the cover and hung at the center of the oven. The oven temperature was raised to 140^{o}C and kept for several hours. The temperature of the sample and of the oven was recorded continuously. Positive results are obtained if spontaneous ignition occurs or if the temperature of the sample exceeds the oven temperature by 60^{o}C.

3.2 *Results and discussion*

The result of investigation on the ability of self-heating are presented on figures 1 –3.

Dry sample of PKS (sample A) , wet (10 % of moisture content – sample B), wet (15 % of moisture content – sample C) and oily contaminated (oils content:10% – sample D; 15% sample – E) samples of PKS were used in studies.

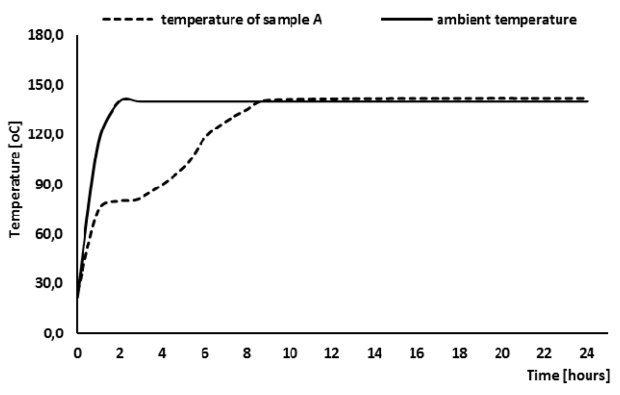

Figure 1. Self-heating curve of tested sample A at a constant temperature 140^{o}C.

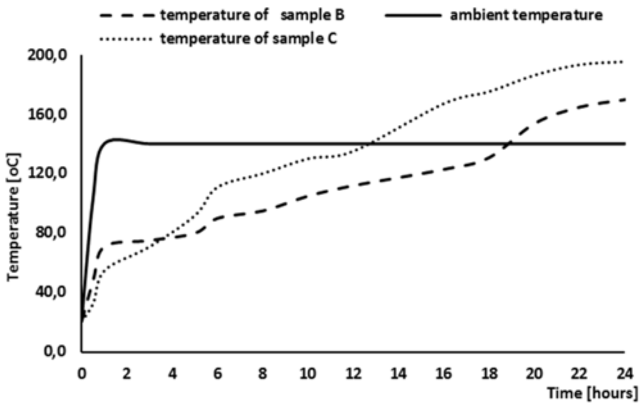

Figure 2. Self-heating curves of tested samples B and C at a constant temperature 140^{o}C.

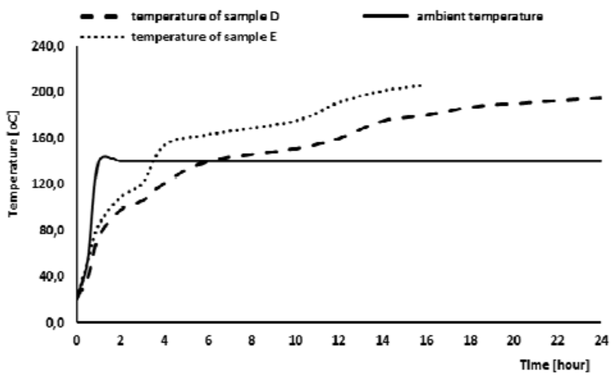

Figure 3. Self-heating curves of tested samples D and E at a constant temperature 140^{o}C.

The primary component of tested material is cellulose that is a kind of a polymer mainly composed of C, H, and O. Despite such chemical composition, the result indicates that the dry PKS are not self-heating materials. After the test period, there was no visible change in the sample.

Based on the criteria defined in *The Test Method for self-heating substances, PKS* is not a self-heating substance (in the conditions of the experiment, the sample temperature has not increased to 200^{o}C). Self – heating of biomass can occur either by chemical oxidation reaction or microbiological decay.

Self-heating processes of PKS which were recorded during sea transportation were probably caused by microbiological processes.

According to the test, wetted PKS cannot be classified as a substance capable of self-ignition. The experimental data may suggest that moisture enhances oxidation of materials by oxygen.

15% moisture content caused that the temperature of PKS approached the limit values of 200^{o}C. The conditions of shipping: large mass of the load and the long transportation time can cause self-heating of moist cargo.

Nevertheless, for PKS the content of fatty acid is predominant from the point of view of safe storage and transportation. Once contaminated with dry oils, its thermal stability was decreased with larger heat generation which could result in spontaneous combustion.

The results of experiments confirmed that the level of propensity PKS to self-heating strongly depends on the degree of purity of tested materials. The high content of oil as a contaminant (10 %) accelerates exothermic reaction which may cause self-heating of material. When oil content in PKS was approximately 15%, the temperature grew rapidly and has initiated the self-heating process.

4 CONCLUSION

The maritime transport continues to evolve, new products and new methods introduce new and less well understood hazards. It is recognized that risks associated with this growth in the transport of these raw materials depend on two major parameters: temperature and their moisture sensitivity.

Self-heating of biomass is a serious problem and has been a cause of several incidents.

Oil palm biomass such as Palm Kernel Shell can be used to produce steam for processing activities and for generating electricity. It is important to characterize the risk of self-heating and self-ignition of these cargoes before loading them on ship.

The results of investigation provide information important for preventing the self-heating in the PKS. The data presented in the paper could be useful in estimation of the thermal stability during storage and transportation of these cargoes. It should be recommended to avoid storage and sea transportation of large volumes of PKS if its tendency for self – heating is unknown.

The IMSB Code need continual upgrading because crews and shipping agency need more information on the behavior of the new products and their carriage in new ways.

Factors, such as cargo volume, the level of compaction of the transported cargo and external heat source should be taken into account when determining the risk of self-heating.

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