

## Food & Beverage Analysis

### Solvent recovery from edible oil: How to be more efficient with flash point testing

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Cooking food in our kitchen, frying and deep frying, or making salads is part of our daily life. A world without edible oils is unimaginable. Also, for a lot of industrial food manufacturing – think of products such as margarines or baked and cooked goods – edible oils are a key component. Have you ever thought about the amount of edible oil you consume? In numbers, global edible vegetable oil production in 2024 was estimated at 224.2 million tons. Palm oil was number one, with 80 million tons, followed by soybean oil with 65.5 million tons, rapeseed oil with 34.2 million tons, and sunflower seed oil with 20.6 million tons [1]. And the market is growing! Looking at the numbers, it is clear that oil extraction from vegetables and seeds has to be highly efficient. It has to be fast, and of course the oil yield from the raw material must be maximised. Initially, during edible oil production, mechanical pressing was used to extract the oil from the seeds. Nowadays, following mechanical pressing, oil extraction by solvent is performed, to increase the oil yield – from roughly 60% to 70%, to even 95%, depending on the oil pressing method used. However, solvent extraction necessitates recovery of the solvent and subsequent checks for solvent traces within the edible oil. Flash point limit testing allows quick checks on the solvent concentration within an intermediate product to make sure that the recovery process is working according to specifications and that those intermediate products can be handled with the necessary precaution. Flash point limit testing makes the edible oil extraction process more efficient while improving the product quality.

#### Edible oil extraction by solvent

How does edible oil extraction by solvents work? In short: Soy beans, as an example of an oil source, are cleaned, cracked, cooked, and dried. Subsequently, the flaked soy beans are washed with hexane which dissolves the oil from the seed flakes [2]. There are different types of solvent extraction plants and procedures, but in general the solvent used is commonly hexane. It is used because of its solubilising nature, low boiling point, low costs, good miscibility with oil, and relatively easy recovery and reuse. However, studies are investigating the exchange of hexane for less harmful solvents [3].

Solvent extraction by hexane increases the oil yield significantly compared to mechanical pressing only, and therefore it is the most common method for producing edible oils in large quantities. The drawback with solvent oil extraction is the fact that hexane has to be removed from the edible oil once the oil extraction process is finished. Hexane is highly toxic and should not be considered as part of our diet. Thus, there is a limit for hexane that is tolerated in edible oil. For example, according to European Directive EC 2009/32, a maximum of 1 mg of hexane is allowed in 1 kg of edible oils [4]. After the oil extraction process, the hexane is removed from the edible oil via rising film evaporators and final vacuum distillation [5]. In fact, the solvent recovery process involves several steps: recovering more and more hexane via different extraction methods [6].

#### Measuring the residue hexane in edible oil

To prove that the amount of hexane does not exceed amounts specified in food regulations, the hexane content in edible oils has to be measured. Typically, the final concentration of hexane in edible oils is determined by gas chromatography, which enables precise measurement of small hexane traces in edible oil [7] [8].

However, as mentioned, the hexane recovery process includes several steps. Between them, the hexane content within the edible oil diminishes continuously. To monitor if the recovery processes are working according to specifications it makes sense to measure the hexane content in between the recovery steps. Measuring the hexane content of an intermediate product can also be necessary due to safety reasons or internal requirements if it will be transported to another production site. Here, the drawback of gas chromatography is that it has to be conducted by well-trained lab staff and often is only available within limited working hours. Thus, gas chromatography is expensive and not always available in a plant operating 24/7.

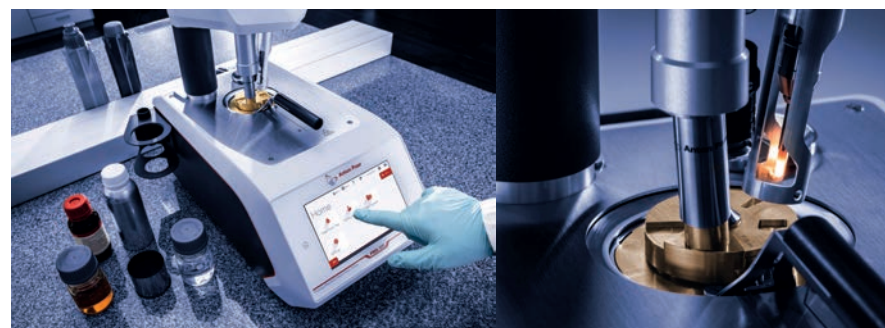
Luckily, there is an alternative. A fast check of the hexane content can be conducted by flash point limit testing. Hexane content in edible oils, down to several hundred ppm, can be determined by flash point limit testing according to ISO 15267: 'Animal and vegetable fats and oils – Flash point limit test using Pensky-Martens closed-cup flash tester' [9]. Moreover, flash point limit testing can be conducted with only little training, by almost everybody involved in the production process. It does not require any pre-treatment of the sample and is always readily performable. It is a time-efficient and cost-saving way to test hexane limits during the edible oil production of intermediate products.

Another benefit of having equipment that measures according to ISO 15267 is that you can also measure the flash point of the finished product according to ISO 2719 or ASTM D93 for transportation and storage classification.

#### Flash point limit testing according to ISO 15267

Flash point testing in general is a very straightforward testing method. For flash point testing you need to have: the sample within a sample cup, a heater, a temperature measuring device, sometimes a stirrer, and an ignition source. The procedure usually involves heating the sample and the application of the ignition source at a defined temperature to the gas phase above the sample. The lowest temperature at which the application of the ignition source leads to an ignition of the gas phase above the sample, without subsequent combustion, is called the flash point. If a subsequent combustion for at least five seconds is observed, the temperature is called fire point. Such fire points can only be measured with an open cup flash point tester without any lid on the sample cup. There are plenty of different flash point testing methods such as closed or open cup methods and equilibrium temperature or temperature ramp methods. It is important to know that different methods will lead to different results as the flash point is not a physical property of the sample but strongly depends on the measurement setup.

A typical setup of a Pensky-Martens flash point tester used for measurements according to ISO 15267 is shown in *Figure 1*.



*Figure 1: Pensky-Martens flash point tester PMA 500 with test cup and the application of the ignition source.*

How is flash point limit testing according to ISO 15267 conducted? First of all, a Pensky-Martens flash point tester is needed. It is recommended to use an automatic flash point tester with automated heating, ignition testing, temperature measurement, barometric pressure correction, flash point detection, and sophisticated data handling. It is also strongly recommended to use an instrument with pre-defined testing standards. Manual instruments are sensitive to human error and again require well-trained operators. Secondly, 70 mL of the sample to be tested is required. With this, the measurement is ready to go. The sample is filled into the sample cup, the filled test cup is placed onto the heater of the flash point tester and the sample is heated at a rate of 5°C per min to 6°C per min. At a defined temperature, for hexane testing often 121°C, the ignition source is applied to the test cup.

How do we know the temperature at which an edible oil with a defined amount of hexane flashes? The same hexane concentration in edible oils of different sources can lead to different flash points. Therefore, it's necessary to determine the temperature at



which a certain hexane concentration leads to a flash within the edible oil of choice by preliminary tests. However, it is not required to find the exact flash point. For example, to ensure that the hexane concentration is below or equal to 800 ppm, an oil sample with 800 ppm hexane is prepared and measured according to ISO 15267, e.g. at 121°C. If no flash occurs, the testing temperature of 121°C refers to a hexane concentration of 800 ppm or below. If the sample flashes, the testing temperature has to be set to a lower value.

#### Test results for soy bean oil (flash point found)

EFLP	700 ppm	800 ppm	900 ppm	1,000 ppm
121 °C	no	no	no	yes
150 °C	no	yes	yes	-

#### Test results for rapeseed oil (flash point found)

EFLP	700 ppm	800 ppm
121 °C	no	yes
150 °C	yes	-

Figure 2: Results of ISO 15267 measurements of hexane in soy bean oil and rapeseed oil.

It is important to understand that the test can be adapted to your needs. The amount of hexane in edible oil which will pass the ignition test is determined by the testing temperature. With a higher testing temperature, lower amounts of hexane will lead to a flash. To be clear, ISO 15267 is not a method to determine the flash point but to find a maximum hexane concentration in the tested oil. It only conducts an ignition test once the test temperature is reached. The flash point of a hexane-containing oil sample cannot be determined by a standard Pensky-Martens flash point method, such as ASTM D93. Ramp methods involve multiple ignition tests and with every ignition test, volatiles can leave the sample cup, which would artificially increase the flash point temperature. This bias is observed if the volatile amount within a mixture is very low.

Equilibrium flash point test methods such as ISO 1516, ASTM D3934, or ISO 3679 could be used to find the exact flash point, however this would involve several measurements and would not deliver important information when looking at the hexane concentration in vegetable edible oil.

In this article, measurements with a dilution series of hexane in rapeseed and soy bean oil are reported and the results of the measurements are shown in Figure 2. For rapeseed oil with 800 ppm hexane, a flash was found at 121°C, while 700 ppm hexane did not lead to a flash at 121°C, but did at 150°C. With soy bean oil, at a testing temperature of 121°C, a flash was only found for a hexane concentration of 1,000 ppm. 800 ppm of hexane in soy bean oil led to a flash at a testing temperature of 150°C. For flash point limit testing and flash point testing we used an Anton Paar Pensky-Martens flash point tester PMA 500 with a standard brass cup and cover. Pre-defined methods according to ISO 15267 and ASTM D93 were used. The set testing temperatures were 121°C and 150°C.

The flash point of neat rapeseed oil was found to be 272°C while for neat soybean oil it was 248°C. Hexane has a flash point of -20°C. The exact flash point values of the neat product were measured for edible oils with a Pensky-Martens flash point tester PMA 500 according to ASTM D93-A. The flash point of hexane was measured by an Abel flash point tester ABA 500 according to ISO 13736.

Of course, there are limits to the ISO 15267 method. The typical hexane concentration at which flash point limit tests are conducted is 800 ppm hexane in edible oil. The final check of the edible oil with a hexane content below 1 ppm must be performed via gas chromatography as this is below the detection limit of flash point limit testing. Nevertheless, flash point limit testing according to ISO 15267 can be a perfect tool to quickly check if the hexane recovery process is working according to given parameters.

## References

1. "https://www.ofimagazine.com/news/global-vegetable-oil-production-continues-to-grow," [Online].
2. "https://www.andersonintl.com/understanding-hexane-extraction-of-vegetable-oils/," [Online].
3. C. Cravotto, A.-S. Fabiano-Tixier, O. Claux, M. Abert-Vian, S. Tabasso, G. Cravotto and F. Chemat, Towards Substitution of Hexane as Extraction Solvent of Food Products and Ingredients with No Regrets, Foods, 2022.
4. "https://eur-lex.europa.eu/eli/dir/2009/32/oj/eng," [Online].
5. A. G. Serrato, Extraction of oil from soybeans, JAOCS, 1981.
6. "https://www.spectecindia.com/blog/what-is-solvent-extraction-plant/," [Online].
7. M. Yousefi and H. Hosseini, Evaluation of Hexane Content in Edible Vegetable Oils Consumed in Iran, JECT, 2017.
8. A. H. Samsuri, M. Y. Ang and S. Y. Ng, Optimization of Residual Hexane in Edible Oils Analysis Using Static Headspace Gas Chromatography, Int. J. Anal. Chem., 2021.
9. Animal and vegetable fats and oils - Flashpoint limit test using Pensky-Martens closed-cup flash tester, Standardization, ISO - International Organization for Standardization, 1998.