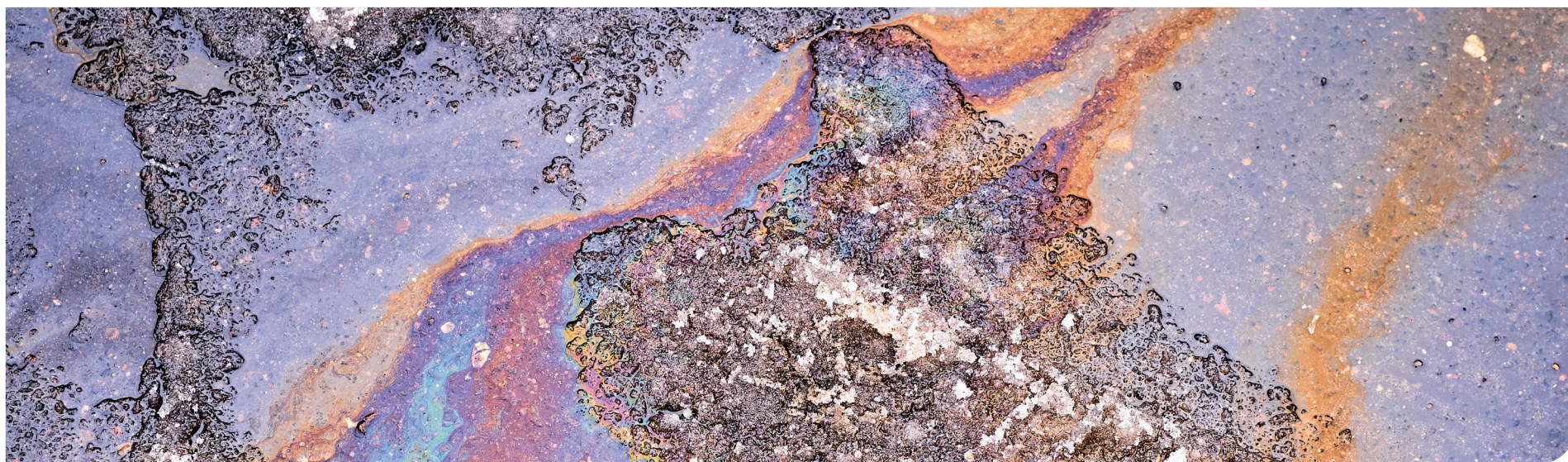


REVOLUTIONIZING CLOUD AND POUR POINT MEASUREMENTS



Introduction

The cloud point and pour point of fuels correspond to the lowest temperature at which lubricating greases and other petroleum products can be utilized. Testing methods for these indicators involve a small sample of grease being cooled and periodically examined within an apparatus, with the reported results being the highest temperature at which haziness is observed (cloud point) and the lowest temperature at which movement of the oil is observed (pour point)[1]. These two parameters go hand in hand when assessing the behavior of these fuels for use in low temperature conditions. Cloud point haziness indicates the initial separation of waxes which solidify on cold surfaces and decrease fluidity of the fuel, until the pour point is reached where filters and injectors become clogged and consequently decrease engine performance[2]. With the significance of these two parameters, it is essential that these points are predetermined for lubricating oils before being supplied on the market so that necessary changes to formulations can be made[3]. Here, we will explore the ASTM testing methods for both cloud and pour point determinations through the advanced techniques of cloud point extraction and nanocomposite pour point depressants, respectively, as well as their roles in furthering green technology.

ASTM D5771 (Cloud Point)

ASTM D5771 assesses the cloud point of transparent petroleum and diesel fuels in layers of 40 mm thick samples through the use of an automatic optical apparatus. This test method covers temperatures ranging from -60 to 49°C with the cloud point being declared at the lowest temperature where liquid petroleum and diesel fuels first form wax crystals, additionally offering a reference point for the lowest temperature at which a tested fuel could be used. The procedure calls for first heating up a sample to at least 14°C above its expected cloud point temperature with a hot water bath to a limit of 69°C. After heating, the sample is filtered through dry, lint-free filter paper until the liquid appears transparent. Next, the sample is deposited into a marked, cylindrical glass test jar placed in a test cell of the apparatus, and a cork disk is positioned below the jacket of the test cell with a cork ring around the jar 25 ± 3.0 mm from its base. The jar chamber is then connected to a cooling circulating bath with a controlling device in between to monitor the jacket temperature such that the bath is always at least 10°C below the jacket temperature as shown in Figure 1.

Once the apparatus begins the test, it will regulate the jacket temperature such that it will move onto the next jacket temperature level within 90 seconds and alarm the experimenter of a cloud point detection to 0.1°C accuracy.

Figure 2 correlates the sample temperature to the expected jacket temperature in a table and shows a graph of a steady rate of depression in the jacket temperature (represented as a staircase configuration) alongside a curved, gradual descent in the sample temperature. To understand the inner workings of this test method, note that the testing jar contains a light emitting and receptive device, a mirror, and a temperature probe (Figure 3). As the temperature dwindles, the collected light reflectance off the mirror will decline due to the obstructive formation of wax crystals at the bottom of the test jar just above the mirror. In short, the reflective optical system serves to reveal the presence of wax crystals through sensing the disturbance of light reflectance and recording the initial temperature at which such phenomenon occurs[2].

ASTM 5950-14 (Pour Point)

ASTM 5950-14 evaluates the pour point of petroleum fuels through cooling the sample from a range of -66°C to 51°C and administering a tilt test with an automatic optical apparatus. The pour point ascertains the lowest temperature at which movement of a fuel sample is detected before the increase in viscosity or shaping of wax crystals hinders its motion (the no-flow point). Similar to the

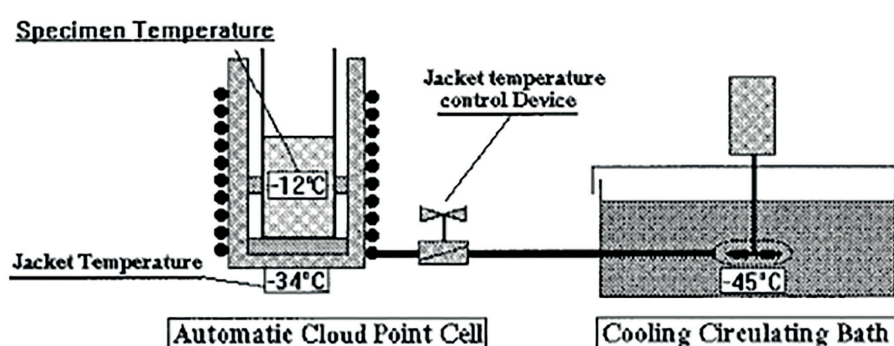


Figure 1. Cloud Point Test Setup[2]

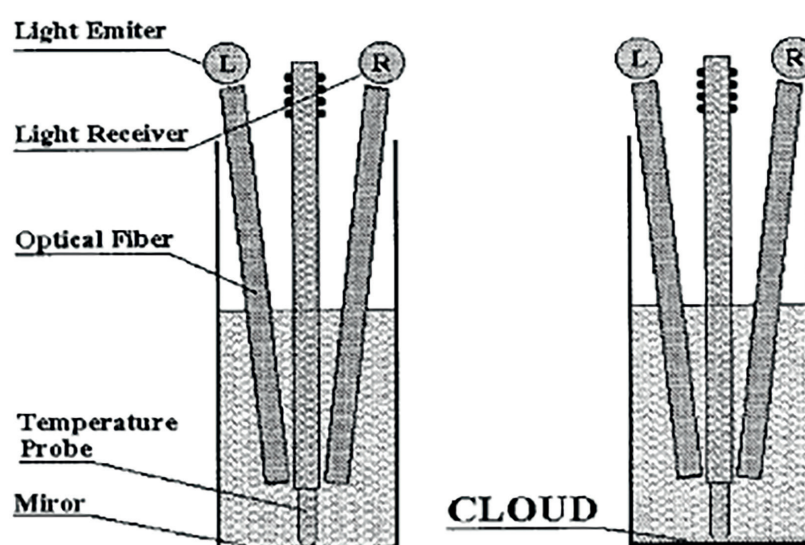


Figure 2. Cloud Point Sample Temperature and Jacket Temperature Correspondence[2]

Specimen Temperature, °C	Jacket Temperature, °C
ST > +10	0 ± 0.5
+10 ≥ ST > -7	-17.2 ± 0.5
-7 ≥ ST > -24	-34.2 ± 0.5
-24 ≥ ST > -41	-51.2 ± 0.5
-41 ≥ ST > -58	-68.2 ± 0.5
-58 ≥ ST > -75	-85.2 ± 0.5

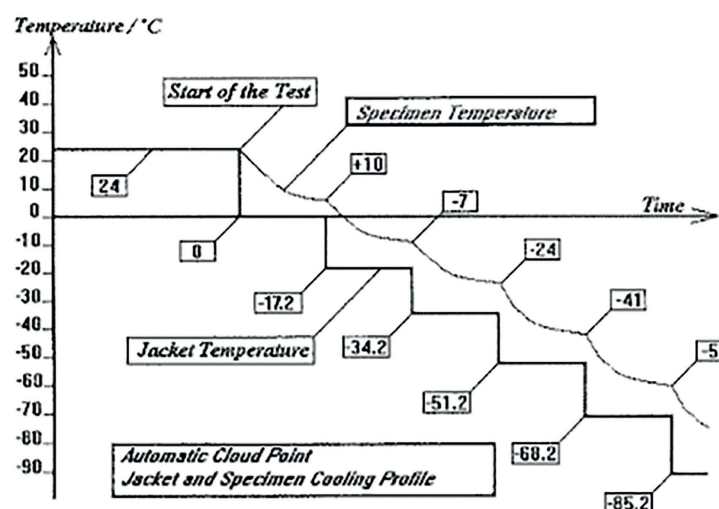


Figure 3. Inside of Testing Jar[2]

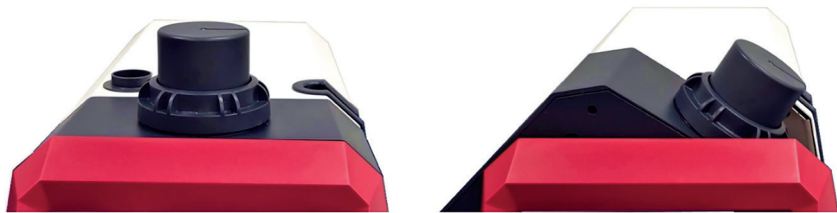
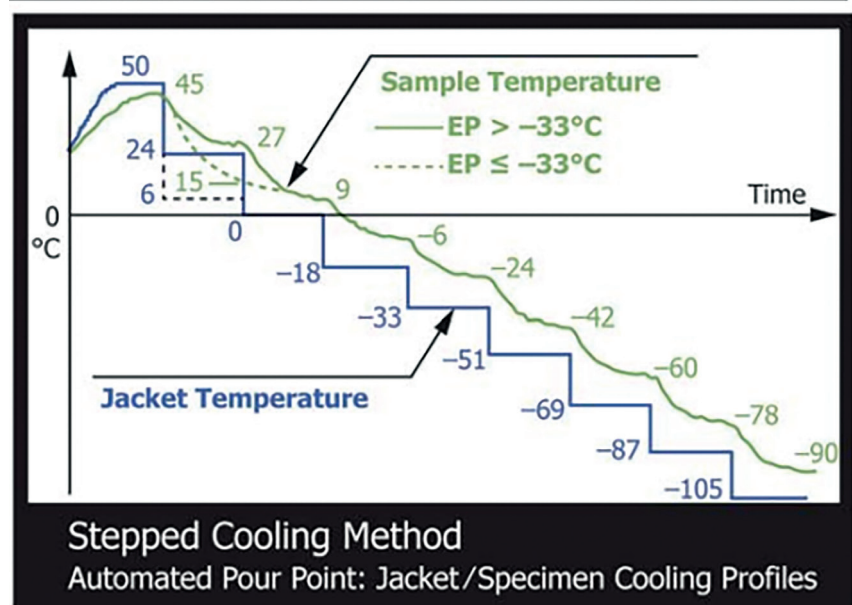


Figure 4. Side by Side Comparison of K77000 Tilt Method

Specimen Temperature, °C	Jacket Temperature, °C
+27 >= ST > +9	0 ± 0.5
+9 >= ST > -6	-18 ± 0.5
-6 >= ST > -24	-33 ± 0.5
-24 >= ST > -42	-51 ± 0.5
-42 >= ST > -60	-69 ± 0.5
-60 >= ST > -78	-87 ± 0.5



Stepped Cooling Method
Automated Pour Point: Jacket/Specimen Cooling Profiles

Figure 5. Pour Point Sample Temperature to Jacket Temperature Correspondence[4]

cloud point determination procedure, fuel samples should be preheated to a liquid phase no more than 70°C before settling it into a test jar. Pour point testing utilizes the same experimental setup as that of the cloud point with the inclusion of the same automatic optical apparatus, jacket, cork disk, cork ring, jacket temperature controlling device, and cooling circulating bath. The automatic optical apparatus allows the pour point to be measured in intervals of 1°C or 3°C depending on the user's preference.

Once the test commences, the apparatus will automatically alter the jacket temperature in accordance with the measured sample temperature at intervals summarized in Figure 5[4], recording a consistent, stepwise decrease in jacket temperature (at intervals of 1°C or 3°C) alongside a trickling decline in sample temperature similar to that of the cloud point test. Meanwhile, the apparatus will also automatically conduct its tilting test at 9°C above the expected pour point as displayed in Figure 6. The sample will start off at a vertical position before tilted horizontally to inspect any fluid flow. If the no-flow point has been reached, the sample will undergo no movement at its horizontal position for at least five seconds, implying that the pour point was the temperature preceding that of the no-flow point[5].

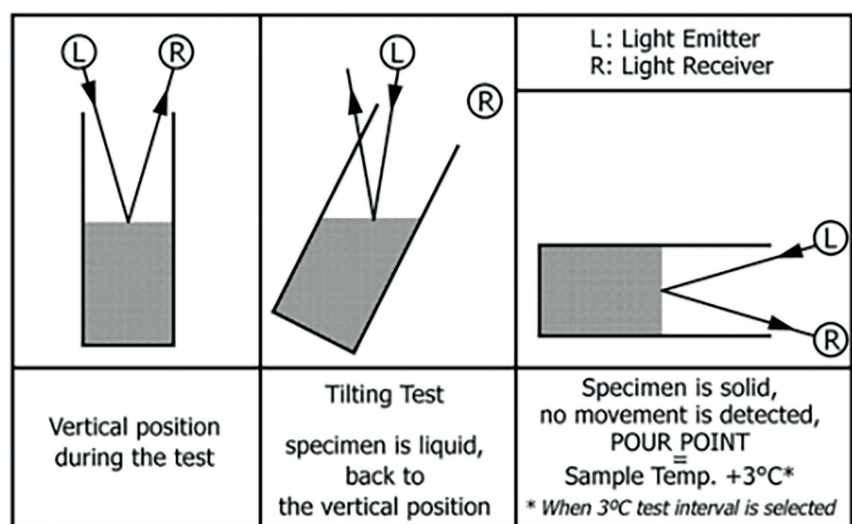


Figure 6. Tilt Test Method[4]

Automatic Cloud and Pour Point Analyzer K77000, K77001

Koehler Instrument Company's Automatic Cloud and Pour Point Analyzer (Figure 7) conforms to both ASTM D5771 and ASTM D5950 test procedures while having excellent correlations to ASTM D97, D2500, D5853, D6074, D6158; ISO 3015, 3016; IP 15, 219; DIN 51597; FTM 791-201; NF T 60-105; JIS K2269. Depending on which model, the product includes either a wireless cloud or pour point head for sample insertion and a wireless head holder at the side to act as a resting stop for the head during the loading of samples, consolidating the purpose of cloud and pour point determination through the use of optical detection and tilt method, respectively, in one product. The instrument encompasses a temperature range from -105°C to 50°C within 0.1°C accuracy

and a tilt test at every 1°C to 3°C interval, as outlined in ASTM D5950. Moreover, this instrument incorporates an internal cooling system and a 10.4-inch color touchscreen displaying electronics and jacket calibration settings as well as a sample and bath temperature vs. time graph.



Figure 7. Automatic Cloud and Pour Point Analyzer K77000, K77001

Cloud and Pour Point Breakthroughs

To tackle the problem of wax crystallization in fuels affecting their flowability, pour point depressants (PPDs) are added into crude oils to permit flowability through resisting the gelification of crude oil. Conventional PPDs fall under two categories, nonpolar and polar PPDs. Nonpolar PPDs, like alkyl chains, modify the crystallization patterns of wax crystals to avert deposition through nucleation and co-crystallization. On the other hand, polar PPDs, like esters and vinyl acetates, disrupts and quenches wax crystal growth. Nonetheless, new research within the last few years introduced nanocomposite pour point depressants (NPPDs), PPDs laced with nanoparticles. Although little is understood about the interaction between NPPDs and waxy oils, studies have confirmed that NPPDs are capable of weakening gel structures essential for wax crystallization, reducing oil viscosity, and diffusing wax particles, demonstrating improved flowability and wax crystallization prevention compared to traditional PPDs[5][6].

In recent years, the use of cloud point has also evolved beyond its simple definition and into a biocompound extraction method known as cloud point extraction. In 2019, the Journal of Food Science and Technology published by the Association of Food Scientists and Technologists of India recognized cloud point extraction as a new, green, inexpensive technique to swiftly extract organic and inorganic compounds from solutions using surfactants, compounds that mitigate surface tension and assist in the entrapment of other compounds. When a non-ionic surfactant is added to an aqueous organic solution and heated at cloud point temperature, the surfactant forms micelles or congregations of molecules that envelope biocompounds within it as portrayed in Figure 8.

These micelles result in the separation of two phases: surfactant-rich and surfactant-lean. Furthermore, factors that affect this mechanism include concentration, temperature, pH, extraction time, pressure, bonding strength, etc. The food industry, in particular, is looking into the use of this revolutionary technology to extract biocompounds with antioxidant, antimicrobial, and anti-allergic characteristics that better preserves their essence compared to traditional enzyme assisted, ultrasound assisted, microwave assisted, liquid-liquid, and solid-liquid extractions. In doing so, food waste could be processed to reuse and purify these compounds and food continents could be easily extracted for future research analyses[7].

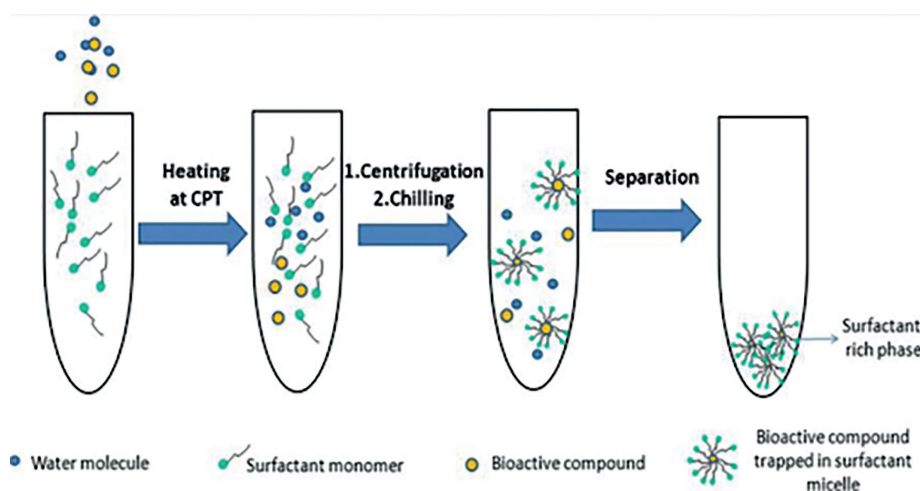


Figure 8. Cloud Point Extraction Process[7]

CPE of Olive Oil Wastewater to Salad Dressing

Mediterranean countries are responsible for more than 98% of the world's olive oil production through a two-phase and three-phase centrifuge systems, creating 0.2-0.3 and 0.3-1.2 cubic tons of olive oil wastewater (OMW) every four-month season. Nonetheless, OMW contains various phenol compounds, such as tyrosol and hydroxytyrosol, that offer several health benefits by the European Food Safety Authority. In 2022, Karadag, Ayse, et al from the Department of Food Engineering and TUBITAK Marmara Research Center of Istanbul, Turkey experimented the use of cloud point extraction (CPE) to recover the phenol compounds from OMW, a simpler, energy-efficient, eco-friendly method compared to membrane filtration, liquid-liquid extraction, liquid-solid extraction, and supercritical-CO₂ extraction that utilize flammable, toxic solvents at higher costs. In this case, lecithin, a fatty substance readily found in soybeans, sunflower, egg, and rice, acts as the extraction solvent due to its role as an amphiphilic surfactant that can solubilize OMW phenols.

Furthermore, the effects and optimization of the extraction temperature, pH, NaCl concentration, lecithin concentration, and equilibrium time on phenol recovery were explored. OMW was first mixed with lecithin to form a homogenous solution before the addition of NaCl (0% to 20% weight/volume) and adjustments to pH values (2.5 to 7.5). The solution was then held in a controlled water bath (50°C to 90°C) for a determined time period (20 min to 90 min) before phase separation occurred for 30 minutes at 4°C. Lastly, the aqueous phase was separated from the lecithin phase, and the total phenolic content (TPC) in the lecithin phase was recorded via

Parameters	Unit	Contents
Total phenolic content (TPC)	mg Tyrosol/L	7545.25 ± 766.89
	mg Hydroxytyrosol/L	5220.22 ± 390.68
	mg GAE/L	4830.50 ± 414.18
Antioxidant capacities		
ABTS	mg TE/L	6892.05 ± 222.64
FRAP	mg Fe ²⁺ E/L	5010.54 ± 216.90
DPPH	mg TE/L	4315.06 ± 237.73
Phenolic compounds		
Hydroxytyrosol	mg/L	592.91 ± 8.39
Tyrosol		167.34 ± 2.23
3-hydroxybenzoic acid		26.70 ± 4.46
Catechin		14.96 ± 0.57
Vanillic acid		4.93 ± 0.24
Rutin		1.09 ± 0.08
4-hydroxybenzoic acid		0.99 ± 0.06

Figure 9. OMW Components From HPLC[8]

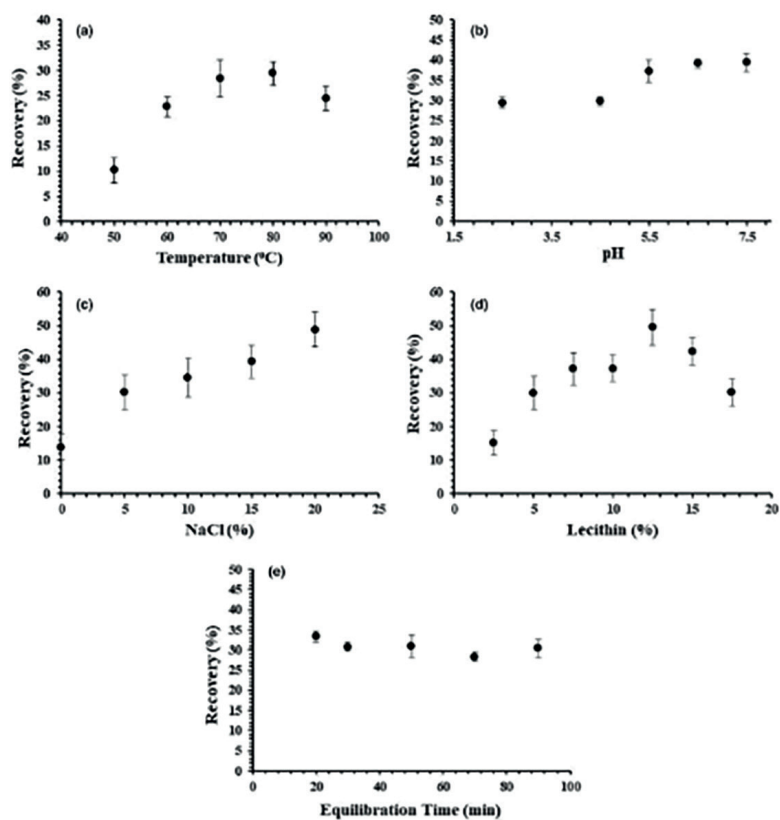


Figure 10. Phenol Recovery vs. a) Extraction temperature b) pH c) NaCl % d) Lecithin % e) Equilibration time[8]

high-performance liquid chromatography (HPLC). Other tests, such as ferric reducing antioxidant powder (FRAP), ABTS assays, and DPPH assays were also performed to assess the antioxidant capacity of the OMW. To measure the effects of the extraction temperature, pH, NaCl concentration, lecithin concentration, and equilibrium time on phenol recovery, a series of single-factor experiments, processes in which a single independent variable was altered while the rest were controlled, were conducted with each experiment repeated four times. Figure 8 summarizes the data collected from all the individual tests and experiments mentioned above with hydroxytyrosol as the dominant phenol compound responsible for the high antioxidant capacity in OMW.

Figure 10 graphically exhibits the contribution each independent variable had on the percent recovery of phenol compounds. The bell curve in Figure 10a illustrates that increase in extraction temperature from 50°C to 80°C caused an initial increase of 10.21% to 29.45% phenol recovery with a drop to 24.49% when the temperature exceeded 80°C, explained by the deterioration of phenol compounds at high heat and broken hydrogen bonds between the surfactant (lecithin) and water molecules that decreased the solubility of phenols in lecithin micelles. Figure 10b displays a direct, positive correlation between the increase in pH value from 2.5 to 7.5 and phenol recovery with the highest recovery occurring at 5.5 pH, a condition optimal for the phenols to engage in deprotonation stages and greater hydrogen bonding activity with water. Figure 10c indicates an increase in phenol recovery from 13.93% to 48.92% as the concentration of NaCl increased from 0% to 20% since NaCl eases the separation of phases through lowering the cloud point temperature of the surfactant and solubility in aqueous phase while increasing the aqueous phase's density. Figure 10d shows another bell curve between phenol recovery and lecithin concentration with the highest recovery rate of 49.47% at 12.5% lecithin concentration, justified by decrease in mass transfer rate between phases with higher solution viscosity. Finally, Figure 10e found no correlation between the equilibration time in bath water from 20 to 90 minutes due to the rapid entrapment of phenol compounds by the lecithin surfactant during the initial homogenizing phase.

When calculating the optimal condition for phenol recovery, it was found that a 65°C extraction temperature, 4.5 pH, 10% NaCl concentration, and 15% lecithin concentration would offer the highest phenol recovery value of 41.87%. Later, the enriched lecithin procured by the optimized

CPE process of OMW was used for salad dressing, laced with xanthan gum, deionized water, sugar, salt, sunflower oil, and lecithin. Both a control salad dressing sample and the enriched lecithin salad dressing sample were tested for its oxidative stability at 70, 80, 90, and 100°C using an OXITEST device to obtain their induction period (IP) or the time needed from the start of a reaction to when a substance reaches a crystallization stage. Oxidative stability is proportional to a higher induction period and can be determined by kinetic factors: the change in enthalpy (ΔH^{**}), the change in entropy (ΔS^{**}) and change in Gibbs free energy (ΔG^{**}). Figure 11 organizes the respective ΔH^{**} , ΔS^{**} , and ΔG^{**} and for the control lecithin and enriched lecithin at various temperatures. Although the positive ΔH^{**} seen in both samples only reveals the endothermic nature of the reaction, the salad dressing of the enriched lecithin had a noticeable greater negative ΔS^{**} , a higher ΔG^{**} , and longer IP values than that of the control salad dressing, implying an overall slower oxidation rate and a higher oxidative stability in the salad dressing prepared with enriched lecithin.

Sample	Temperature (°C)	IP (h)	E_a (kJ/Mol)	ΔH^{**} (kJ/Mol)	ΔS^{**} (J/Mol/K)	ΔG^{**} (kJ/Mol)
Control	70	16.35 ^{5B}	38.77 ± 0.09 ^B	83.057 ± 0.65 ^A	-27.71 ± 0.91 ^A	93.39
	80	7.44 ^{5B}				93.11
	90	4.15 ^{5B}				92.84
	100	1.33 ^{5B}				92.56
Enriched lecithin	70	27.82 ^{5A}	40.88 ± 0.23 ^A	73.259 ± 0.52 ^B	-59.89 ± 0.78 ^B	95.59
	80	11.53 ^{5A}				94.99
	90	6.89 ^{5A}				94.40
	100	3.03 ^{5A}				93.80

Figure 11. Oxidative Stability Component Values[8]

This research success not only uses the CPE method to withdraw phenol compounds in OMW that would otherwise be considered food waste, but it also further recycles the enriched lecithin carrying those phenol compounds to produce a more stable salad dressing. In the end, messages promoting resourcefulness and future application of the CPE method to other food products are well conveyed[8].

NPPs from Waste Plastic

According to research done by Kamal, Rasha S., et al. from the Egyptian Petroleum Research Institute and University for Modern Sciences and Arts, polyethylene (PE), labeled as the most healthy-to-use plastic used for plastic bags and packaging, was part of the 236 million tons of total plastic in global circulation in 2023. At the time, petrochemicals from fossil fuels were turned into plastic and took part in 4% of petroleum production annually, causing long-lasting environmental harm with its non-biodegradable nature. Hence, Kamal, Rasha S., et al. experimented with including magnetic nanoparticles (MNPs) and PE from waste plastic to heavy and light crude oils to assess the additive's crystallization impedance power and the revamped oil's effectiveness as pour point depressants. In the study, two sets of samples were prepared such that the first set consisted of 10 samples with liquified PE, crude oil, and no MNPs while the second set consisted of 30 samples with liquified PE, crude oil, and MNPs. Samples of various concentration ratios of liquified PE and MNPs were created with Liquified PE set at concentrations of 0.25, 0.5, 1, and 2% and MNPs at concentrations of 0.5, 1, and 2%.

Among the numerous testings done on these samples, two of great importance were photomicrographic analysis to inspect wax crystallization progress and pour point determination to evaluate the samples' effectiveness as pour point depressants. Figure 12a and 13a are photomicrographic analysis photos of a sizable, dark spot representing wax crystals that were ubiquitous in light and heavy crude oil samples, respectively, at 0.25% PE without the addition of nanoparticles. Meanwhile, Figure 12b and 13b captures the appearance of miniscule wax crystals in light and heavy crude oil samples, respectively, at 0.25% PE and 2% MNPs, proving the effectiveness of MNPs in being a wax crystal inhibitor through changing the crystals' growth structure.

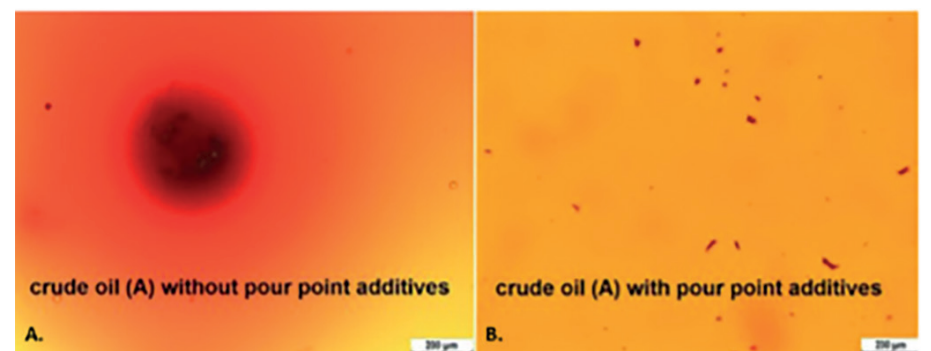


Figure 12. Light Crude Oil Photomicrographs[9]

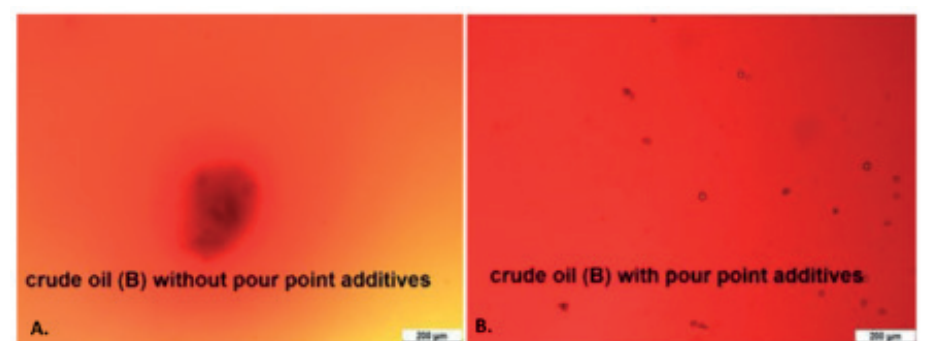


Figure 13. Heavy Crude Oil Photomicrographs[9]

Figures 14 and 15 graphically represent the pour points of light and heavy crude oil, respectively, with added relative PE and MNPs concentrations. In both cases, it is observed that the crude oils serve as optimal PPDs with 0.25 to 0.5% PE and 1 to 2% MNPs as seen by the minimum pour point value of -36°C. The increase in PE concentration unfavorably raised the pour point temperature, but the increase in MNPs aided in depressing the pour point temperature regardless of PE levels when viewing the trend of the colored bars in each set.

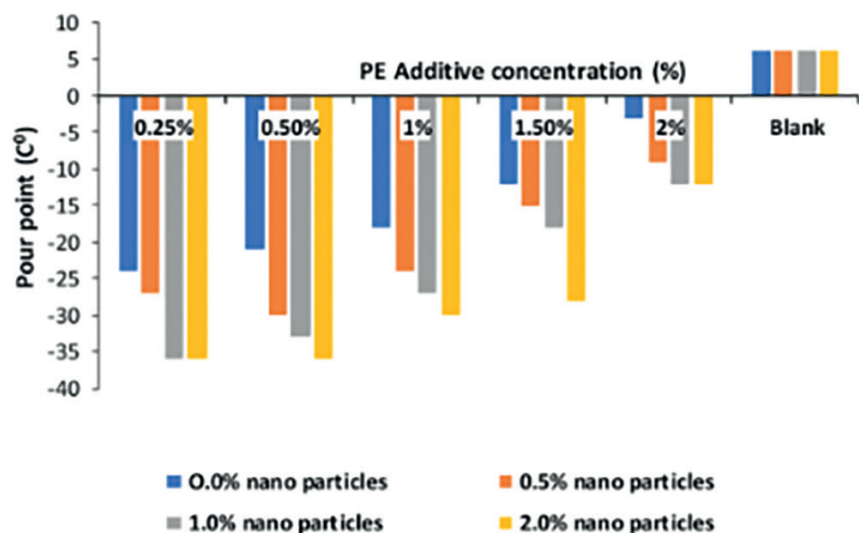


Figure 14. Light Crude Oil Pour Points[9]

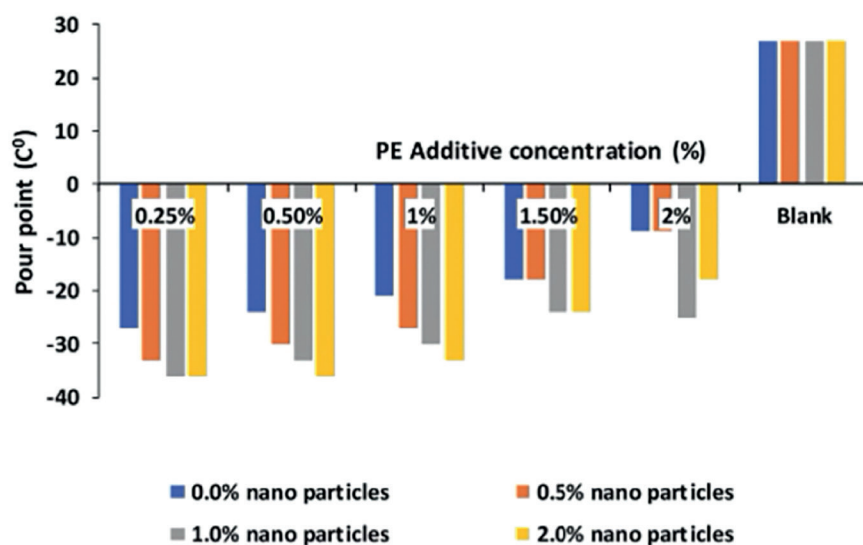


Figure 15. Heavy Crude Oil Pour Points[9]

The empirical data gathered from photomicrographic analysis and pour point determination are evidence of a viable approach to the enhancement of PPDs with the addition of MNPs and PE. Not only does this research expand the limited realm of NPPDs, but it also challenges the thought of tackling plastic waste, one of the world's leading environmental concerns, simultaneously[9].

Conclusion

Although cloud and pour point are merely terms to describe the lowest temperature at which wax crystals form and impede flowability, researchers worldwide are constantly working towards searching for more applications or ameliorating current designs related to these two parameters. With the successes of applying cloud point extraction of phenols to olive oil wastewater and further making a salad dressing of high oxidative stability or including polyethylene and magnetic nanoparticles in crude oil to prove the wax crystal inhibition abilities of nanocomposite pour point depressants, there is the hidden message of two-fold recycling by incorporating current waste materials into research explorations and reusing those products as raw materials at the next step. Impressive performance in solving problems presented by the petroleum industry is apparent, but hopefully entwining green technology with it and applying their collaboration on an industrial scale will be the next challenge that revolutionizes modern science.

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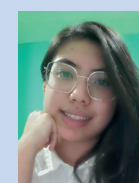
ASTM Eagle Award recipient, Dr. Shah recently coedited the bestseller, "Fuels and Lubricants Handbook," details of which are available at "ASTM's Long-Awaited Fuels and Lubricants Handbook 2nd Edition Now Available" (<https://bit.ly/3u2e6GY>). He earned his doctorate in Chemical Engineering from Pennsylvania State University and is a Fellow of The Chartered Management Institute, London. Dr. Shah is also a Chartered Scientist with the Science

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More information on Raj can be found at <https://bit.ly/3QvfaLX>.

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