Application of High-Resolution NMR and GC–MS to Study Hydrocarbon Oils Derived from Noncatalytic Thermal Transformation of e-Waste Plastics

Uttam Kumar, Vaibhav Gaikwad, Mohammad Mayyas, Martin Bucknall, and Veena Sahajwalla

Centre for Sustainable Materials Research and Technology (SMaRT@UNSW), School of Materials Science and Engineering, UNSW Sydney, Sydney, New South Wales 2052, Australia
Mark Wainwright Analytical Centre, UNSW Australia, Sydney, New South Wales 2052, Australia

ABSTRACT: The increases in the volumes of electronic waste have become an aggravating environmental, economic, and social health issue in recent times. This study investigates the conversion of e-waste plastics into hydrocarbon oils via noncatalytic thermal transformation followed by an in-depth characterization of these oils using diverse analytical techniques such as gas chromatography–mass spectrometry (GC–MS), Fourier transform infrared (FTIR) spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy. In particular, NMR spectroscopy is a key analytical tool utilized in this study to gain a comprehensive insight into the chemical nature of the resultant oils along with a semiquantitative investigation of the changes in their composition over a temperature range of 800–1200 °C. The one-dimensional (1D) $^1$H and two-dimensional (2D) heteronuclear single-quantum correlation spectra were acquired for the oils, wherein the 2D NMR spectrum provided improved resolution of peaks to address the overlaps encountered in the 1D spectrum. The experimental results obtained from GC–MS, FTIR spectroscopy, and NMR spectroscopy were found to align well with each other. The oils produced in this study have a high calorific value of 38.27 MJ/kg and thus may find use in several applications. A detailed mechanism for the thermal degradation of styrene acrylonitrile plastics and the formation of major products is elucidated in this study.

1. INTRODUCTION

E-Waste has been growing at a dramatic rate in the last two decades and has been regarded as an exacerbating environmental and economic problem around the world for a long time. Globally, generation of e-waste is forecasted to reach a volume of around 50 million metric tons in 2018, which is roughly 1.5 times as high as the volume of the e-waste generated in 2010. In 2014, Australia alone produced around 468 000 metric tons of e-waste. In another study, in the same year, the amount of e-waste disposed of in Australia has been reported to be ~25 kg per person. All the electronic devices and equipment have a finite useful lifetime after which they are considered as e-waste. E-Waste is mainly constituted of end-of-life electronics such as computers, TVs, printers, mobile phones, washing machines, air conditioners, and refrigerators. The life span of such devices has been shortened drastically in the recent past because of the frequent advent of newer, faster, and smarter devices facilitated by rapid advancements in the technology. E-Waste is a very complex type of waste and contains a large variety of precious metals, toxic metals, and other useful materials. If not recycled properly, these toxic components from the e-waste can severely degrade the environment and may exert biological effects on both plants and animals because of the leaching of these toxic elements into the soil, crops, groundwater, and rivers. Conversely, the recycling of e-waste by adopting proper techniques can provide a range of economic and environmental benefits. Various valuable materials can be extracted from the e-waste through recycling, which can be used in the manufacturing of new products, effectively reducing the consumption of finite primary resources. Majority of the research on e-waste recycling has been focused on the extraction of highly valuable elements such as precious metals for economic benefits. Plastics being less valuable have generally been dumped into landfills or incinerators, after initial dismantling, which are not environment-friendly options because of the toxic emissions and loss of valuable resources.

Typically, plastics take up a large proportion of e-waste, and their content in different types of e-wastes has been reported to be in the range of 10–30%. In the case of printers, plastics account for almost a quarter of the total weight of the printers. The major different types of plastics found in e-waste are acrylonitrile butadiene styrene (ABS), styrene acrylonitrile (SAN), polystyrene (PS), polypropylene, polycarbonate blends, low-density polyethylene, and polyurethane foam. Various attempts have been made by researchers to utilize these e-waste plastics in different applications. Onwudili and Williams used supercritical water to degrade two of the most
commonly used e-waste plastics, brominated ABS and brominated high impact polystyrene (Br-HIPS), into oils, solid residue, and gases. Incineration has also been employed as a way to generate energy from the e-waste plastics; however, it can be potentially very harmful to the environment because of the toxic emissions. These plastics have also been utilized as the filling materials alongside quartz sand and gravel to obtain a polymer concrete. The study found that the mechanical properties of the concrete were not negatively affected for a composition of plastics of up to 5%. Acomb et al. used the e-waste plastics (ABS and HIPS) to produce hydrogen gas via gasification using a two-stage reaction system.

A styrene-based polymer accounts for a significant part (∼55%) of the e-waste plastics and needs a special attention to deal with them. Although there has been considerable work done on converting plastics to hydrocarbon oils, there is still an existing knowledge gap with regard to converting complex e-waste plastics to high calorific value oils and more so on understanding the chemical nature of the oils. In the present study, we intend to contribute in bridging this gap. We have performed noncatalytic thermal transformation of SAN plastics, obtained from the end-of-life printers, to produce hydrocarbon oils between 800 and 1200 °C and an in-depth study of the chemical composition of the oils through 1H and two-dimensional (2D) heteronuclear single-quantum correlation (HSQC) nuclear magnetic resonance (NMR) spectroscopy, gas chromatography–mass spectrometry (GC–MS), and Fourier transform infrared (FTIR) spectroscopy.

2. RESULTS AND DISCUSSION

2.1. X-ray Fluorescence Analyses. According to X-ray fluorescence (XRF) analysis, the SAN plastics had an ash content of 2.56% at 815 °C. The composition of different elements in the ash (reported in the form of oxides) is shown in Table 1. The XRF data reveal that the major elements present in the ash are Si, Mg, Al, and Fe. The XRF data were also used to calculate the alkali index (AI) of the ash obtained from the SAN plastics. AI is a very important parameter in the gasification studies of carbonaceous materials and is defined as (eq 1) the sum of the fractions of the basic oxides (CaO, MgO, K₂O, Na₂O, and Fe₂O₃) in the ash to the mass fraction of the acidic and amphoteric compounds (Al₂O₃ and SiO₂) multiplied by the ash content of the material. This index is used to describe the overall influence of catalytically active species in the ash. The AI for the ash produced from the SAN plastics was calculated to be 1.45. This value can be used to compare the gasification of SAN with other carbonaceous materials. A higher AI means a higher gasification reactivity for the carbonaceous material. In a study conducted by Porada et al., the AI value for the bituminous Janina coal was found to be 2.53.

\[
AI = \frac{\text{CaO} + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O} + \text{Fe}_2\text{O}_3}{\text{SiO}_2 + \text{Al}_2\text{O}_3} \times \text{ash content (\%)}
\] (1)

Next, transformation experiments were performed under isothermal conditions at 800, 1000, and 1200 °C to observe the changes in the composition of these oils produced at different temperatures. The main products of the thermal transformation of SAN plastics were oils, gases, and solid residue. The oils generated in the process were trapped using dichloromethane (DCM) as the solvent.

The color of the solvent turned to reddish black after the emissions from the thermal transformation interacted and dissolved in it. The impinger assembly containing the solvent with the trapped oils was disconnected from the furnace outlet after 5 min as the gas emissions had stopped indicating that the SAN sample had completely degraded. After the removal of the particulate solid matter from the trapped oils using a centrifuge, the oils exhibited different colors as shown in Figure 1. The oils obtained at 800 °C had a brownish color, and the oils obtained at 1000 and 1200 °C showed dark black colors (in DCM solvent). Similar colors have been widely reported in various studies involving the conversion of plastics to hydrocarbon oils. The composition and the chemical nature of the oils produced were evaluated using analytical tools such as GC–MS, attenuated total reflectance (ATR)–FTIR, and NMR spectroscopy.

2.2. GC–MS Analyses. The GC–MS chromatograms of the resultant oils are as represented in Figure 2. The peaks in the spectra correspond to various aromatic hydrocarbons. Although more than 20 different aromatic compounds were detected in the first 40 min of the GC–MS spectra acquisition, we will be discussing only the compounds that had an area % of more than 0.18. The area % of the peak for a compound was correlated with the percentage of that compound in the oil. The major aromatic hydrocarbons detected in these spectra were found to be toluene, ethylbenzene, styrene, α-methylstyrene, phenol, 1-propynylbenzene, naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, biphenyl, acenaphthylene, fluorene, and anthracene. The data obtained from the chromatograms were used to calculate the percentage of these
Three compounds were the major components in the mixture of gases such as CH$_4$, H$_2$, CO, and CO$_2$. When the expected degradation products included various hydrocarbons, SAN Plastics and Major Products Formation.

3. The toluene and ethylbenzene content (%) in the oils from the data in Table 2.

The content of other aromatic hydrocarbons can also be observed increased with the increase in temperature. This trend and the (%) of naphthalene, biphenyl, and anthracene in the oils temperature of thermal transformation. However, the content decreased quite dramatically with the increase in the temperature of thermal transformation. However, the content (%) of naphthalene, biphenyl, and anthracene in the oils increased with the increase in temperature. This trend and the content of other aromatic hydrocarbons can also be observed from the data in Table 2.

2.3. Mechanism of the Thermal Degradation of the SAN Plastics and Major Products Formation. SAN is a styrene-based copolymer, and its degradation is likely to be similar to the PS degradation. When SAN plastics undergo a heat treatment at the temperatures employed in this study, the expected degradation products included various hydrocarbons, oligomers, different-sized carbon chains and chains, and a mixture of gases such as CH$_4$, H$_2$, CO, and CO$_2$. When the thermal energy is greater than the energy barrier of a reaction and the bond energy of a bond, the bond will break, resulting in chain scission. Depending on the temperature, the bonds can dissociate in different ways to form different products. Generally, single bonds are the easiest to break as compared to double bonds, triple bonds, and aromatic rings. Figures 4 and 5 demonstrate the possible schemes for the decomposition of SAN into various aromatic hydrocarbons such as toluene (C$_7$H$_8$), styrene (C$_8$H$_8$), and naphthalene (C$_{10}$H$_8$). These three compounds were the major components in the hydrocarbon oil mixture as demonstrated by the GC–MS data. Naphthalene is the simplest polycyclic aromatic hydrocarbon (PAH) and has the highest concentration among the PAHs generated in the present study. There were various other PAHs such as anthracene, fluorene, and so forth that were generated in smaller quantities.

Hydrocarbons such as acetylene (C$_2$H$_2$) are also expected and reported to be some of the degradation products of SAN plastics and play an important role toward the formation of PAHs through a hydrogen abstraction acetylene addition (HACA) mechanism. The HACA mechanism leads to the formation of additional aromatic rings via ring closures and has been widely reported in the literature. The mechanism in Figure 4 accounts for the formation of styrene and naphthalene. A noncatalyzed thermal degradation generally takes places via a free-radical mechanism. At first, the C–C bond scission in the SAN polymer chain leads to the formation of two chains with a free radical at one end. Further to that, a β scission takes place to form a styrene molecule and another free-radical chain. Styrene was one of the major degradation products and worked as a precursor toward the formation of PAHs. Consequently, there is a high probability of the conversion of styrene into phenylacetylene by hydrogen elimination. This step is likely to be followed by the addition of an acetylene molecule to phenylacetylene, which ultimately yields naphthalene. Similarly, Figure 5 represents the scheme for the generation of toluene. The generation of toluene from the styrene-based polymer has been reported in the literature. The scheme displayed here involves hydrogenation, β chain scission, and molecular rearrangement reactions. The mechanisms shown in this study are some of the probable mechanisms for the thermal degradation of SAN copolymers; however, as the thermal degradation results from a number of competing decomposition reactions, it is difficult to predict the real mechanism underlying the degradation.

2.4. FTIR Analyses. FTIR spectroscopy is a very important characterization technique used to identify various functional groups present in a sample. The ATR–FTIR spectra obtained for the oils generated from SAN plastics at 800, 1000, and 1200 °C and for DCM are shown in Figure 6. The spectra at all the three temperatures have similar peaks because of the presence of essentially the same functional groups in the oils. The strong peaks in the range of 680–760 cm$^{-1}$ for DCM are due to the C–Cl stretch. The absence of this band in the spectra for oils indicates that all the DCM had evaporated by heating the oils to 45 °C before the ATR–FTIR spectra were acquired for these samples. The peaks observed in the spectra for oils at ~3050 cm$^{-1}$ can be attributed to alkene stretching. The band in the region 3250–3420 cm$^{-1}$ is present only in the 800 °C sample and accounts for the −OH stretch in alcohols and phenols. The peak at 1222 cm$^{-1}$ implies the presence of C–C stretching vibrations, which may have originated from the C=C bond in 1-propynylbenzene. The wide overtone bands between 1760 and 1990 cm$^{-1}$ indicate the substituted benzene rings. These bands are more pronounced for the 1200 °C sample. The sharp peak at 1593 cm$^{-1}$ is attributed to the benzene ring stretching in aromatic compounds. Additionally, the band at 1511 cm$^{-1}$, for the 800 °C sample, also indicates the benzene ring stretching in aromatic compounds. The bands in the range 1400–1480 cm$^{-1}$ represent the CH$_2$ scissor vibrations and CH$_3$ antisymmetric deformation in aliphatic compounds. According to GC–MS analysis, many aromatic compounds showed the presence of these groups attached with the polycyclic carbon rings.
The bands in the range of 1015−1220 cm\(^{-1}\) may be arising because of the C−O stretch in the C−OH bond present in phenol. These bands are more pronounced at a lower temperature, and the same can be observed through the GC−MS data, which show that the phenol content decreased with the increase in thermal transformation temperatures. The peak in the region 950−1000 cm\(^{-1}\) is coming from \(\equiv\text{CH}\) out-of-plane vibrations from the \(\equiv\text{CH}−\equiv\text{CH}_2\) group present in vinyl compounds such as styrene and \(\alpha\)-methylstyrene. The sharp bands between 690 and 770 cm\(^{-1}\) imply the presence of CH out-of-plane deformation in monosubstituted benzenes. The sharp peak at 690 cm\(^{-1}\) can be assigned to OH out-of-plane deformation in phenols. The results from GC−MS and ATR−FTIR analyses are matching and thus corroborate each other.

### Table 2. Composition of the Oils Resulting from the Thermal Transformation Process at 800, 1000, and 1200 °C

| Name          | Molecular Weight | Structure | Area % (800°C) | Area % (1000°C) | Area % (1200°C) |
|---------------|------------------|-----------|----------------|-----------------|-----------------|
| Toluene       | 92.1             | ![Structure](image) | 35.74          | 30.17           | 20.01           |
| Ethylbenzene  | 106.2            | ![Structure](image) | 5.69           | 2.10            | 1.79            |
| Styrene       | 104.1            | ![Structure](image) | 38.33          | 31.15           | 36.01           |
| \(\alpha\)-Methylstyrene | 118.2 | ![Structure](image) | 2.15           | 1.33            | 1.35            |
| Phenol        | 94.1             | ![Structure](image) | 1.88           | 0.84            | 0.20            |
| 1-Propynylbenzene | 116.2 | ![Structure](image) | 0.53           | 1.42            | 1.97            |
| Naphthalene   | 128.2            | ![Structure](image) | 1.87           | 7.56            | 10.78           |
| 2-Methylnaphthalene | 142.2 | ![Structure](image) | 0.56           | 0.40            | 0.20            |
| Methylnaphthalene | 142.2 | ![Structure](image) | 0.23           | 0.34            | 0.18            |
| Biphenyl      | 154.2            | ![Structure](image) | 0.61           | 2.96            | 3.02            |
|acenaphthylene | 152.2            | ![Structure](image) | 0.20           | 0.84            | 1.25            |
| Fluorene      | 166.2            | ![Structure](image) | 0.33           | 1.17            | 1.02            |
| Anthracene    | 178.2            | ![Structure](image) | 1.18           | 4.55            | 5.64            |

**Figure 4.** Mechanism of SAN degradation into styrene and naphthalene.

**Figure 5.** Mechanism of thermal degradation of SAN into toluene.

### 2.5. NMR Analyses

NMR spectroscopy is a powerful tool for determining the chemical nature of hydrocarbon oils, including functional groups and molecular bonding. As is evident from the GC−MS results, the hydrocarbon oils are...
mixture of several compounds, which makes the unequivocal
identification of compounds in NMR very challenging. However, using a highly sensitive 2D NMR technique, that
is, HSQC spectroscopy, it is possible to overcome some of the
challenges and to characterize the oils in further detail. The
HSQC spectra essentially depicts the correlation (direct
bonding) between the \( ^1H \) and \( ^{13}C \) NMR spectra, which
enables us to understand the interaction between carbon and
hydrogen within the hydrocarbon oils. In the present spectra, it
is also possible to distinguish the CH\(_2\) groups from the CH and
CH\(_3\) groups, wherein the CH\(_2\) groups are marked in red color
compared to the blue color for the CH and CH\(_3\) groups.
Although the aliphatic and aromatic content of the oils was
found to vary with temperature, it was observed that
qualitatively the spectra did not change much, and thus, the
HSQC NMR spectra for oils produced at 800 °C were utilized
as a representative spectrum for the present analyses. Figure 7
shows the HSQC spectra for the oil produced at 800 °C. The
results of the semiquantitative analyses performed on the \( ^1H \)
spectra of oils produced at 800, 1000, and 1200 °C are
presented after the HSQC NMR analyses. The \( ^1H \) NMR
spectra for the oils are depicted in Figure 8. The sharp peaks at
a chemical shift of 7.26 ppm in the \( ^1H \) spectra and at a
chemical shift of 77.2 ppm in the \( ^{13}C \) spectra (as shown in
HSQC) represent deuterochloroform (CDCl\(_3\)), which has
been used as a solvent for NMR analyses.

The HSQC NMR spectra depict four major regions of
correlation between \( ^1H \) and \( ^{13}C \), which will be labeled as A, B,
C, and D for the present analyses. Region A (0.84–3.01 \( ^1H \)
and 11–44 ppm in \( ^{13}C \)) comprises signals mainly from the
CH\(_3\) groups and some from the CH\(_2\) groups. The correlation
region between 0.89 and 1.83 in \( ^1H \) and 14.1–31.5 ppm in \( ^{13}C \)
may be attributed to CH\(_3\) and CH\(_2\) groups from the short- and
long-chain aliphatic compounds, respectively. For example, the
CH\(_3\) correlation at \( \sim 29 \) ppm in \( ^{13}C \) and 1.34 ppm in \( ^1H \) can be
due to the presence of compounds such as methyl hexane.
Furthermore, the correlation region at \( \sim 21 \) ppm in \( ^{13}C \) and
\( \sim 2.4 \) ppm in \( ^1H \) can be attributed to the CH\(_3\) groups attached
to the aromatic rings and may represent compounds such as
toluene. Region B (3.37–4.43 in \( ^1H \) and 34.5–42.1 ppm in
\( ^{13}C \)) comprises predominantly CH\(_2\) groups, more
specifically CH\(_2\) groups in the vicinity of aromatic/phenyl
rings. It is possible that the CH\(_2\) groups from compounds such as
fluorene and diphenylmethane exhibit their signature in this
region. Region C (5.06–5.95 in \( ^1H \) and 110–116 ppm in
\( ^{13}C \)) can be said to be characteristic of the \( =CH_2\) groups from
compounds such as styrene or methyl styrene. Region D (6.4–
9.5 in \( ^1H \) and 109–151 ppm in \( ^{13}C \)) largely comprises peaks
from the aromatic CH groups. Several compounds such as
toluene, styrene, methyl styrene, naphthalene, and fluorene
exhibit the peaks from the aromatic CH groups in this region,
and hence, there is a considerable overlap of peaks.

For semiquantitative analyses, each \( ^1H \) spectrum was
integrated between identical chemical shifts, that is, 0–9.08
ppm, and the total integral was calibrated as 100. The aromatic
content was then determined by integrating the area between
the 6.59 and 9.08 ppm chemical shift. The aromatic content of
the oils produced at 800, 1000, and 1200 °C was calculated to
be 80.5, 94.1, and 88.74%, respectively. It thus indicates that
the aromatic content in the oils increased with an increase in
temperature from 800 to 1000 °C; however, a further increase
in the temperature to 1200 °C resulted in a drop in the
aromatic content. This drop may be attributed to the
decomposition of aromatic compounds to smaller and low-
molecular-weight compounds at such high temperatures, an
observation which has been noted in some of our previous

Figure 6. ATR–FTIR spectra of DCM and the oils produced during the thermal transformation of SAN plastics at 800, 1000, and 1200 °C.

Figure 7. HSQC spectrum of the hydrocarbon oil produced at 800 °C.

Figure 8. \( ^1H \) NMR spectra of oils produced from the noncatalytic single-step transformation of SAN plastics at 800, 1000, and 1200 °C.
research as well. Overall, it can be said that the results from GC–MS and NMR spectroscopies align very well and reinforce each other.

Furthermore, despite being a noncatalytic process, the presence of methoxy groups was not detected in the oils, which is highly advantageous as it might lessen the need for intensive downstream upgrading processes.

2.6. Gross Calorific Value. According to the findings of $^1$H NMR spectroscopy, the oils produced at 1000 °C had the highest aromatic content among the three oil samples. The aromatic content started to decrease because of the thermal transformation performed at temperatures higher than 1000 °C. The experimental calorific value for the oil sample derived from the SAN plastics at a thermal transformation temperature of 1000 °C was found to be 38.27 MJ/kg, which can be considered high from the energy utilization point of view. Although this oil has a significantly higher aromatic content, its calorific value is very close to the commercial fuel-grade criteria for gasoline (43.4−46.5 MJ/kg), kerosene (43.0−46.2 MJ/kg), and diesel (42.8−45.8 MJ/kg). The heating values obtained by Ahmad et al. for the aliphatic chain hydrocarbon-based plastics HDPE and PP were 30.6 and 35.5 MJ/kg, respectively. Szabo et al. reported the calorific value of 34.4 MJ/kg for the oils produced by the thermal decomposition of the polymethylmethacrylate−ABS waste. In another study, the gross calorific value for the bio-oil produced from rice straw was found to be 13.41 MJ/kg. Some of these gross calorific values are significantly lower as compared to the values obtained in the present study and thus indicate that SAN plastics may serve as a potential feedstock material for fuel generation.

3. CONCLUSIONS

NMR [one-dimensional (1D) and 2D] and GC–MS techniques were utilized to gain a comprehensive understanding of the chemical nature of hydrocarbon oils produced by the noncatalytic thermal transformation of SAN plastics from end-of-life printers between 800 and 1200 °C. Toluene and styrene were the two most dominant compounds present in the oils. The toluene and ethylbenzene content (%) in the oils decreased with the increase in the temperature of thermal transformation; however, the content of naphthalene, biphenyl, and anthracene increased with the increase in temperature. NMR and GC–MS analyses complement each other, thus reinforcing the validity of the results presented in this study. FTIR analyses of the oils too concurred these results. The XRF data were used to estimate the AI, which is a very important parameter in the gasification studies of carbonaceous materials. The AI of SAN plastics was calculated to be 1.45. Additionally, the gross calorific value for the oil sample obtained at a thermal transformation temperature of 1000 °C was found to be 38.27 MJ/kg. The results obtained in the present study suggest that the waste SAN plastics can potentially be used as a feedstock for producing hydrocarbon oils, which could be blended with commercial grade fuels after suitable upgrading. This will contribute to address the problems associated with the safe disposal of these end-of-life plastics and provide alternative avenues for their diversion from landfill.

4. MATERIALS AND METHODOLOGY

The plastics retrieved from the end-of-life printers were supplied by an electronic waste management company named TES ANZ. The plastics were first sorted out based on the color and physical appearance. Following that, an FTIR spectrum was acquired for these plastics and has been reported in our earlier published work. SAN was found to be the dominant plastic in the mixture and was selected to be used in this study. The as-received SAN plastics were pulverized using CryoMill (Retsch Mixer Mill). The ash composition of SAN plastics was investigated with the help of XRF spectroscopy and is shown in Table 1. The XRF data were used to calculate the AI of the SAN plastics. For this study, all percentages are presented as weight %, unless specified otherwise.

The thermal transformation experiments were performed at isothermal conditions at the temperatures 800, 1000, and 1200 °C. Argon gas was used at a flow rate of 1 L/min to create and maintain an inert atmosphere inside the horizontal tubular furnace, which was used to conduct these thermal transformation experiments. The schematic and the setup of the furnace are described in detail in our earlier publication. An alumina crucible with 2 g of SAN plastic sample was inserted in the preheated furnace. The emissions generated, during the transformation of these plastics in the furnace, were transferred to an impinger, which was linked to the gas outlet of the furnace. The impinger was filled with 15 mL of DCM, which was used as an organic solvent to trap the hydrocarbons generated during the thermal transformation of SAN plastics. The impinger was disconnected from the gas outlet of the furnace after an interval of 5 min as the plastics in the furnace had completely decomposed and gas emission had stopped. The solvent and hydrocarbon mixtures thus obtained from the impinger were transferred to 15 mL conical centrifuge tubes. An HERMLE Z206A centrifuge (Hermle Labortechnik GmbH) was employed to centrifuge these oil-bearing solvents to remove the suspended particulate matter, for 30 min.

At all the temperatures used in the present study, the yield of solid carbonaceous residue was found to be similar, at ∼5%. This solid residue was used in metallurgical and energy storage applications in our earlier published works. After suitable additional treatments, it can be used in a variety of other value-added applications such as high-performance carbon anode in alkali-ion batteries, carbon capture and storage, and gas separation.

The solvents obtained after the removal of the particulates were analyzed by GC–MS. A Thermo FOCUS DSQ II GC–MS (Thermo Fisher Scientific Inc.) instrument equipped with a split/splitless heated GC inlet and a TriPlus autosampler was employed to perform the GC–MS analysis. The system was operated in the electron impact mode for all the analyses and was used to identify the unknown components trapped in the DCM solvent. A Thermo Electron TR-50MS 60 m column with an inner diameter of 0.25 mm and a film thickness of 0.25 μm was installed in the split inlet of the GC with an SGE Split Focus liner. High-purity helium was used as the carrier gas at a constant flow rate of 1.5 mL/min. The GC inlet was maintained at a temperature of 305 °C and the ion source of the MS at 200 °C. Heptane was used as a syringe wash in the autosampler. The centrifuged samples were diluted 10 times, and 1 μL of the diluted sample was injected into the preheated GC inlet at a split ratio of 50:1. The initial temperature of the oven was held at 45 °C for 30 s before it was increased to 310
°C, at a rate of 5 °C/min, where it was held for an additional 12 min. Additionally, the temperature of the GC transfer line was maintained at 315 °C throughout the run. The m/z values between 45 and 550 were scanned by a mass spectrometer at a rate of 3.5 scans/s. To protect the filament, the mass spectrometer was switched off during the first 6.5 min of the run. The components present in the solvent were identified by comparing their mass spectra with the ones stored in the Wiley 9/NIST 2011 Mass Spectral Library.

Prior to FTIR and NMR spectroscopies, the DCM solvent (boiling point, 40 °C) from the oil samples was evaporated by heating the mixtures up to 45 °C. A Fourier transform infrared spectrometer (PerkinElmer Spotlight 400 FTIR) fitted with an ATR accessory was used for this analysis. The spectra were recorded in the wavenumber range of 4000–650 cm⁻¹ and were studied to identify the various characteristic functional groups present in the oils.

NMR spectroscopy was performed to determine the chemical nature of hydrocarbon oils. The oil samples obtained after DCM evaporation were dissolved in deuteriochloroform (CDCl₃, 99.8%), which contained silver foil as a stabilizer. 1D and 2D HSQC NMR spectra were acquired on a Bruker Avance III Cryo NMR spectrometer operating at 600 MHz at a rate of 3.5 scans/s. To protect the Bruker TopSpin 3.5 software was used for the processing of the NMR spectra.

Lastly, the oil samples were analyzed for the gross calorific values (MJ/kg) using the Parr 6400 calorimeter by the ASTM D240 test method.

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