



Achievements in Co-pyrolysis of Oil Sludge with Additives: A Pathway to Enhanced Waste Processing Efficiency

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Abstract

Oil sludge, a by-product of the petroleum industry, presents serious environmental and health risks due to its content of benzene cycloalkanes, polycyclic aromatic hydrocarbons, and other toxic compounds. At the same time, its high crude oil content offers potential for recycling. Thus, selecting an effective treatment method is crucial. Among available options, pyrolysis is notable for its favorable product distribution and low pollutant emissions. This review highlights recent progress in the co-pyrolysis of oil sludge with a diverse range of materials, including biomass, tires, plastics, ash, activated carbon, and steel slag. It explores how additives influence product yield and quality, with particular focus on synergistic interactions. Additionally, the article assesses the impact of additives on adsorption properties of activated carbon, catalytic activity, activation energy, carbon conversion, and heavy metal immobilisation in solid residues.

Keywords: Oil sludge; Co-pyrolysis; Additives, Biomass; Product yield.

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1. Introduction

Oil sludge is a product of petroleum activities and is classified as semi-solid complex waste in the form of water-oil emulsions with solid particulates inter dispersed.^[1,2] The substance is generated during different processes like oilfield development, crude oil refining, transportation, and storage. Annually, the global production of oil sludge has surpassed 60 million tons, and the accumulated volume has surpassed 1 billion tons.^[3–7] OS contains 30–85% water, 5–46% solids, and high hydrocarbon contents with 30–80% oil content.^[8,9] OS also has valuable hydrocarbon fractions such as saturated hydrocarbons, aromatic hydrocarbons, asphaltenes, and resins which make it a potential candidate for fuel and chemical recovery.^[10]

OS is therefore a very promising petroleum resource with

a lot of interest in its safe disposal. Yet, oil spills have high levels of hazardous and carcinogenic compounds, some of which are heavy metals,^[11,12] along with other organic pollutants characterized by high biological toxicity. TPHs, heavy metals, and radioactive pollutants are the principal causes of the hazards,^[13,14] whereas TPHs are the main cause of flammability of oil spills.^[15]

As a result, OS is one of the major pollutants in the oil and petrochemical industries.^[16,17] The TPHs in oil sludge exhibit strong soil adsorption capabilities, and gases released by microbial activity are extremely harmful to the environment and human health.^[18,19] Improper disposal of OS poses significant threats to humans, plants, and aquatic organisms. Therefore, OS represents a persistent environmental risk and is classified as hazardous waste in many countries.^[20,21]

At the same time, the high oil content and calorific value of OS highlight its immense energy potential.^[22,23] Given the global energy demands and environmental protection imperatives, the ultimate goal of OS treatment is to immobilize hazardous elements in the residue while maximizing crude oil recovery.^[17,23]

Consequently, research into the reduction and safe treatment of OS has been a critical issue in the oil industry.^[24] Developing technologies that simultaneously enable resource recovery and harm reduction is vital for addressing OS disposal challenges.^[25]

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Various treatment and disposal methods of oil sludge have been reviewed thoroughly in a number of review articles.^[25–34] Nowadays, OS treatment processes can be categorized into physical separation, chemical separation, and thermal conversion processes.^[35–37]

In addition to international reviews, several Kazakhstani research groups have contributed to this topic by investigating the pyrolysis and co-pyrolysis of local petroleum waste and biomass, including oil shale and oil sludge. For instance, Yermagambet *et. al*^[38–43] have explored thermal decomposition processes of hydrocarbon-rich wastes and the synthesis of adsorbents and semi-coke from Kazakhstani feedstocks.

Physical separation techniques include mechanical separation, ultrasonic treatment, microwave assisted processing and freeze-thaw treatment. Chemical separation mainly includes solvent extraction and surfactant-assisted methods. However, these techniques have significant limitations, such as limited potential for OS utilisation, generation of significant amounts of liquid waste, etc.^[44,45]

On the other hand, thermal conversion methods, particularly pyrolysis, have proven to be more effective in reducing the bulk of organic solid waste and fostering resource recovery.^[46,47] Pyrolysis has the advantage of converting aromatic compounds into gas products, hence facilitating the production of high-grade fuel for usable purposes.

Pyrolysis is a process of thermal decomposition conducted at intermediate temperatures (500–800 °C) under anoxic conditions, producing liquid oil, synthesis gas, and solid residues (char).^[48] Due to the high organic content of organic waste materials (OS), pyrolysis allows them to be converted into valuable products like premium fuels,^[49] fractions susceptible to enzymatic digestion,^[50] aromatic distillates, and char. Pyrolysis products can undergo further processing and application in different industries.

For example, pyrolysis gas can be utilized as a fuel to generate heat and electricity or as synthesis gas (CO, H₂).^[40] Moreover, char carbon has various applications in the manufacture of activated carbons, battery anodes, and catalysts.^[51–55] Further, the byproduct from organic material pyrolysis can also find application as an adsorbent precursor, semi-coke, catalysts, and soil remediation agents.^[39,56–59]

Pyrolysis's flexibility and efficiency render it an attractive strategy for tackling OS disposal issues while concurrently enhancing resource recovery and environmental sustainability.

An analysis of conducted studies highlights the potential of pyrolysis for OS treatment, demonstrating its ability to:

Efficiently recover oil while suppressing pollutant emissions, aligning with OS management objectives;^[60]

Completely remove total petroleum hydrocarbons from OS and recover valuable resources that can be utilized either independently or in combination with other technologies;^[15]

Break down oil into high-value liquid and gaseous fuels in an oxygen-free environment, with minimal formation of NO_x or SO_x emissions, while most heavy metals are

immobilized in the solid residue.^[29]

Pyrolysis is regarded as a relatively environmentally friendly method due to the minimal formation of pollutants such as dioxins and particulates.^[60] Current studies indicate that compared to other treatment methods, pyrolysis offers higher energy utilization efficiency and simpler operational processes when treating OS.^[61] Pyrolysis not only reduces the volume of OS but also enables energy recovery, alleviating the pressure caused by the depletion of petrochemical energy resources.^[62–64]

Despite these advantages, pyrolysis is associated with several drawbacks like high energy input, high ash yield, and low value addition of products due to the origin and nature of OS.^[65] Moreover, three main issues are related to the quality of pyrolysis products: pyrolytic oil quality, oil in solid residue, and migration of toxic elements and heavy metals.^[13]

Corrosive materials (such as asphaltenes, sulfur compounds, and carboxylic acids) and heavy fractions of oil are two major issues related to oil quality.^[66] Heterocyclic and oxygenated compounds in pyrolytic oil are undesirable since they are of low heating value, heat unstable, and corrosive.^[67] Further, secondary processing on these constituents lowers the pyrolytic oil yield and increases its aromaticity.^[68]

The results of the literature review showed that the number of publications on oil sludge pyrolysis has increased significantly over the past few years. At the same time, most review articles in this field are devoted to various methods of oil sludge processing and disposal aimed at reduction, recycling and harmlessness. The main purpose of these studies is to discuss the development of these processing methods, summarise and compare their advantages, limitations, disadvantages and mechanisms of action of the processes under study, the future direction of development of these methods, as well as the characteristics of oil sludge and valuable oil sludge processing products. Moreover, in recent years, some researchers have taken a keen interest in the co-processing of oil sludge with various additives in the context of improving resource efficiency and environmental safety in waste processing. However, there is currently insufficient research in this area, which is mainly limited to analysing the yield and/or quality of products.

Some existing review articles tend to focus on narrow areas, in particular, involving only biomass,^[69] subcritical and supercritical water.^[70] In this regard, this review article takes a comprehensive approach: it covers a wide range of different types of additives and considers their impact not only on the yield and quality of liquid and gaseous products, but also on the kinetics of the process, the catalytic effect of additives, the characteristics of solid pyrolysis residue, the degree of immobilisation of heavy metals, etc. In addition, special emphasis is placed on a comparative analysis of the yield of pyrolysis products depending on the type of additives. Attention is also paid to the synergistic effect of the interaction between oil sludge and additives. Thus, this review

systematises and compares diverse data, identifying universal patterns and dependencies, which makes it a valuable basis for further research and the development of effective technological solutions in the field of joint pyrolysis of oil sludge with additives.

This review paper deals with recent progress in co-pyrolysis of oil sludge with various feedstocks like biomass, tyres, plastics, ash, steel slag, etc. It examines the influence of various additives in detail with a particular emphasis on synergistic interactions between OS and additives. Additionally, the article also takes into account the effect of additives on other parameters, such as adsorption properties of resultant activated carbon products, overall catalytic activity in the co-pyrolysis reaction, activation energy, OS carbon conversion, heavy metal immobilization in solid residues, and others.

2. Materials and methods

In the present study, data collection methods were applied in accordance with the PRISMA 2020 (Preferred Reporting Items for Systematic Reviews and Meta-Analyses) guidelines, which ensure objectivity and completeness of the research process. This methodology comprises several stages (such as literature search, selection, data extraction and analysis, among others), of which the following were employed:

1. Information sources. To ensure scientific rigour and comprehensive coverage of the literature on the co-pyrolysis of oil sludge with additives, a systematic search was conducted in major international bibliographic databases, including *Web of Science* and *Scopus*. Additionally, *ScienceDirect*, *SpringerLink*, and *Google Scholar* were consulted (the latter used selectively for grey literature analysis). The literature search was conducted between April and May 2025.

2. Search strategy. To identify relevant journal articles within the above databases, the following search terms and phrases were employed: “petroleum sludge”, “oil sludge”, “pyrolysis of oil sludge”, and “co-pyrolysis of oil sludge with additives”.

3. Eligibility criteria. Priority was given to peer-reviewed journal articles published in English between 2010 and 2025 that reflect current scientific approaches and trends, thereby covering recent advancements in co-pyrolysis and the treatment of oil-containing wastes. Key earlier studies in English—particularly those from the 1990s and 2000s—that provided theoretical and methodological foundations for modern pyrolysis approaches were also included. Unpublished manuscripts, conference abstracts, and irrelevant sources were excluded.

4. Selection process. The selection process involved several stages: removal of duplicate records; initial screening based on article titles, indicative keywords, abstracts, and stated research objectives to eliminate non-relevant sources; and a full-text review to further exclude unsuitable articles.

5. Data collection process. For the statistical analysis of

the retrieved data, Microsoft Excel templates and the software *VOSviewer 1.6.20* were employed.

6. Data items. From the selected sources, the following data were extracted: type of additive; experimental conditions (temperature, reactor type, nature and concentration of additive in the mixture, etc.); yield, characteristics and quality of co-pyrolysis products; presence of catalytic and synergistic effects; as well as additional factors such as char adsorption properties, activation energy, carbon conversion from oil sludge, and heavy metal immobilisation in solid residue.

To broaden the scope of the literature review, the snowballing method was additionally employed. This involved tracing references from a key publication (backward snowballing) and identifying newer studies that cited the selected article (forward snowballing) in order to reveal both foundational and the most recent relevant research, including those with novel experimental data or methodological approaches reflecting current trends in the field.

Furthermore, the following methods of data analysis were utilised:

- Quantitative methods:
 - *Meta-analysis* – a generalised statistical evaluation of effects or phenomena (in this case, assessing the impact of additives on the co-pyrolysis process);
 - *Parameter-based analysis (tabular/graphical)* comparison of numerical data (e.g. comparison of product yields depending on additive types);
 - *Bibliometric analysis* – quantitative analysis of scientific publications.
- Qualitative methods:
 - *SWOT analysis* – overall assessment of the object under study (e.g. interpretation of additive properties in terms of their advantages and limitations);
 - *Risk of Bias assessment* – critical appraisal of data, used here to identify reliable sources and ensure correct data interpretation.

The retrieved literature was categorised as follows: review articles; articles highlighting the advantages of co-pyrolysis of oil sludge with additives; articles identifying effective additives for co-pyrolysis; and articles focused specifically on the co-pyrolysis process itself. The latter were further divided into two subcategories (Level 1): (1) studies on the influence of additives on yield, distribution, and quality of products; and (2) studies on the impact of additives on other factors. These two Level 1 subcategories were further divided into Level 2 subcategories according to additive types. A complete classification system, including all categories and subcategories, is presented in [Table 1](#). Classification of Scientific Articles from Bibliographic Databases.

Additionally, the second Level 1 subcategory (influence on other factors) was further subdivided into Level 3 subcategories, based on the specific factors affected by the additives.

Each identified publication was initially assigned to one of these categories based on analysis of the article title,

Table 1: Classification of Scientific Articles from Bibliographic Databases.

Main Category	Subcategory 1 – Additive Influence Area	Subcategory 2– Additive Types	Subcategory 3– Affected Parameters
Literature review	–	–	–
Key benefits of co-pyrolysis	–	–	–
Effective additives for co-pyrolysis	–	–	–
Co-pyrolysis of oil sludge with additives	Effect on product yield, distribution, and quality	Microalgae residue, sawdust, wood waste, rice husk, rice straw, walnut shell, apricot shell, fly ash, oil sludge ash, activated carbon, waste tires, steel slag, red mud, hemicellulose, cellulose, lignin, polyethylene waste	–
Co-pyrolysis of oil sludge with additives	Effect on other process factors	Walnut shell, coconut shell, wheat straw, peanut straw, corn stalks, wood residues, poplar sawdust, waste tires, inert solids (e.g., silica, clay minerals)	Adsorption capacity of activated carbons, catalytic activity, activation energy, iron recovery efficiency, OS carbon conversion, heavy metal immobilization, oil sludge viscosity

indicative keywords, abstract, and research objectives. Where this information was insufficient (particularly for Level 2 and 3 classifications), the full text of the article was reviewed. A similar procedure was applied to classify publications into subcategories at Levels 1 to 3.

3. Key advantages of co-pyrolysis of oil sludge with additives

To solve the above-mentioned main problems, co-pyrolysis with other additives is widely used, with both organic and inorganic waste from industrial production and agriculture often serving as additives. An effective method for improving the oil sludge pyrolysis process is the addition of catalysts to the co-pyrolysis with other substances.^[71–73] Co-pyrolysis is considered to be a simple and effective way of improving the quality and yield of pyrolysis products.^[74] The introduction of an appropriate additive, which can act as a catalyst in the process of pyrolysis, allows the time of the pyrolysis reaction to be shortened, pyrolysis temperature lowered, oil and gas yield increased, and the quality of pyrolysis products improved.^[45,57,75]

Here, in recent years, scholars have conducted studies on improving the pyrolysis process and the distribution of pyrolysis products, studying the synergistic effect of oil sludge with various additives.^[76,77] Considering environmental protection and economy, the choice of inexpensive and non-toxic catalysts and various additives is crucial for improving the efficiency of OS pyrolysis. For example, the high oxygen

content in pyrolytic oil derived from biomass makes bio-oil a low-quality byproduct, limiting its commercial application. However, biomass is a hydrogen donor and a supplier of alkaline metals, and thus can be effectively used in co-pyrolysis with OS to improve the quality of pyrolytic oil.^[78]

- Analysis of the conducted studies has shown that when additives are introduced into oil sludge pyrolysis, there is:
 - An increase in the yield of pyrolysis products;
 - Improvement in the quality of pyrolytic oil (e.g., reduction in the yield of heavy hydrocarbons and an increase in the yield of light hydrocarbons, improvement in the calorific value of pyrolysis products, reduction in the distribution of sulfur and nitrogen in the oil phase, etc.);^[79]
 - Control over the formation and emission of pollutants, especially gaseous products such as ammonia and hydrogen sulfide.^[79]

For example, it is reported that in the pyrolysis process, the breakdown of aromatic compounds is enhanced in the presence of solids such as chemical halite,^[80] metal oxides,^[81,82] and zeolites.^[81,83,84] This allows for the processing of OS with the production of a large amount of valuable fuel. There have been few scientific studies on co-pyrolysis of oil sludge and additives, much less comparison of the effect of various additives on OS pyrolysis.

4. Effective additives for co-pyrolysis with oil sludge

Due to its broad range of sources and high productivity, biomass is an ideal raw material as an alternative to fossil

fuels.^[79,85] Biomass has a low cracking temperature.^[17] However, bio-oil still lacks production specifications because the H/C ratio is too low and the O/C ratio is too high for bio-oil generated solely from biomass.^[17,86] Acidity, low calorific value, high oxygen content (up to 35–60%), and high viscosity are ubiquitous characteristics of bio-oil.^[79,87–89] Low thermal stability and strong corrosive activity restrict biofuel utilization in practical applications in industrial production and daily life.^[17,90] Pyrolytic oil (oil sludge) has high hydrogen and high calorific value in comparison to biomass.^[17] Biomass and oil sludge are also different in chemical and physical properties such as ash content, volatile matter, and oxygen content, which can produce synergistic interaction in co-pyrolysis.^[91] Co-pyrolysis of biomass and petroleum wastes (waste plastics, waste tires, and oil sludge) is a simple, effective, and economic method for improving the yield and quality of petroleum products.^[92] Hydrocarbons from the pyrolysis of oil sludge can react with oxygen-containing compounds generated from the degradation of biomass. Therefore, co-pyrolysis of oil sludge and biomass is an effective method for reducing the oxygen content in the petroleum products. Additionally, minerals present in oil sludge can act as catalytic agents in co-pyrolysis, inhibiting coke formation and facilitating the cracking of heavy gaseous species.^[92] This can enable the co-pyrolysis of biomass and oil sludge.^[78] Availability of high volatile matter content in biomass can ensure a higher petroleum product yield and process efficiency in biomass and oil sludge co-pyrolysis.^[92] The most important aspect of oil sludge and biomass co-pyrolysis is catalysis and enhancement of oil sludge pyrolysis, improvement of the extraction rate of oil and gas, and improvement of oil and gas quality. One should keep in mind that biomass, with a relatively higher H/C ratio, can provide a significant number of free radicals (*i.e.*, -H and -OH) for suppressing secondary reactions and promoting the pyrolysis of char, thereby increasing the oil yield.^[93] Thus, co-pyrolysis of oil sludge and biomass has an extremely high potential in OS processing in an efficient manner and energy production.

The most commonly used biomass wastes for co-pyrolysis with oil sludge are walnut shells, sawdust, apricot pits, and rice husks.^[91,94–96] Utilization of such biomass waste, such as sawdust, along with pyrolysis of oil sludge increases the quality of the produced gaseous products.^[6] Sawdust may be mixed with oil sludge to reduce viscosity by breaking intermolecular forces.^[97] Sawdust also has a high volatile matter content and low ash content, which can improve the pyrolysis characteristics of oil sludge when mixed.^[15,98,99]

Alkali metals in rice husks have been beneficial for catalyzing oil sludge, resulting in higher-calorific gas, *i.e.*, H₂, CO, C₁–C₂ hydrocarbons, and improved oil quality,^[95] while hydroxyl radicals from rice husks lowered the cracking temperature of oil sludge, whereas hydrogen radicals from oil sludge increased the cracking degree of rice husks during co-pyrolysis.^[15,18]

In addition to biomass, rich fuel and industrial wastes, such

as coal, polyethylene, and tire waste, are also common feedstocks for co-pyrolysis with oil sludge.^[23,100,101] It has been reported that rubber, tires, and plastic have the potential to be used in a joint thermal reaction to improve the quality of pyrolysis products.^[102–105]

Studies^[75,106,107] have observed the catalytic effect of oil sludge ash, the addition of which in the pyrolysis of oil sludge not only increases the yield of petroleum products but also improves the quality of the oil, particularly by reducing carbon residues (or asphaltene) in the petroleum products.

Another feedstock for effective pyrolysis with oil sludge is fly ash, a byproduct of industry formed during the combustion of solid fuels.^[108] Fly ash has also been reported as a suitable additive in the majority of the hydrocracking, hydrocarbon oxidation, pyrolysis of solid plastic, and solventless organic synthesis.^[109] Fly ash is complicated in nature with sufficient quantity of metals available in the form of aluminum, iron, calcium, chromium, copper, zinc, nickel, and lead. It contains alkali and alkaline earth metals (Mg, Ca, K, and Na), which directly affect the product distribution of the pyrolysis products. It may promote polymer structure degradation and result in enhanced yields of low-molecular-weight products.^[110]

Co-pyrolysis of hydrocarbon feeds enables hydrogen to be transferred from the feed to gaseous and liquid products, concentrating the carbon in the solid residue.^[111] Co-pyrolysis of oil sludge with other additives can possibly be a functional material because it possesses an appropriate amount of functional groups such as C–O and C=O, and possesses a very good porous structure.^[112–115]

Iron-rich wastes are generally generated in water treatment plants, steel-making, and water treatment.^[116,117] They contain various iron-bearing compounds,^[118,119] including iron oxyhydroxides, hematite, magnetite, and even have the ability to catalytically adsorb and/or decompose organic compounds directly.^[120] Particularly in catalytic decomposition, surface iron participates in redox reactions and shows the Fe²⁺/Fe³⁺ cycling behavior to activate the catalyst,^[121,122] which catalyzes the decomposition of organic matter. As the redox reaction of iron-containing compounds also occurs at high temperatures, iron-rich residues are promising to be used in co-pyrolysis of oil sludges, although there are limited reports on this type of co-pyrolysis. One more iron-containing substance is steel slag—a type of solid waste with a high decomposition temperature of around 800–1600°C, which is inevitably produced in the steel industry.^[123,124] Steel slag contains high amounts of metals such as Fe, Ca, Al, and Mg,^[125] which can be utilized as catalysts.

5. Co-pyrolysis of oil sludge with additives

5.1 The effect of additives on the yield of products during co-pyrolysis of oil sludge

The co-pyrolysis of oil sludge with microalgae residue (MR) was conducted using TGA and a custom-designed tube furnace reactor system.^[126] When MR was added (up to 30%),

the yields of pyrolysis oil and gas increased (~5%), while the char content decreased (~10%).

Experiments on the co-pyrolysis of OS and sawdust (SD) and their mixtures were carried out using a TG-MS analyzer and a fixed bed reactor at temperatures up to 900°C.^[91] Low temperature (below 700°C) favored the generation of gas, mainly CO and CO₂. SD additives from 20 to 80 wt% assisted in enhancing oil yield by 8.65 wt% (from 20.65% to 29.33%) and syngas yield by 8.08 wt% (from 31.48% to 39.56%), and reduced solid residue yield by 16.76 wt% (from 47.87% to 31.11%). The highest syngas yield was 39.59 wt% with 60 wt% SD, and the H₂+CO composition was as high as 61.34 vol%. Oil production was also improved when sawdust was used in the OS pyrolysis process in a rotary kiln reactor equipped with fins under,^[15] where oil and gas yields were 14.5% (from 22.4% to 36.9%) and 11.2% (from 11.9% to 23.1%), respectively, as sawdust composition ranged from 20 to 80 wt%. Sawdust also enhanced the yield of oil products in co-pyrolysis with OS in a fixed-bed reactor, where, with sawdust content between 25% and 75%, oil yield was enhanced by 8.7% (from 40.2% to 49.2%), and gas yield decreased by 9.7%.^[91] A similar study on the use of wood waste in co-pyrolysis with OS was carried out in a fixed bed reactor.^[11] However, compared to the previously described studies, adding wood waste to OS (10% and 20% by mass) did not increase, but rather decreased the total petroleum hydrocarbon extraction, which the authors attributed to the role of alkaline and alkaline earth metals in the wood waste. The results indicated that the co-pyrolysis of OS with 20% wood waste at 400°C was the most effective for OS processing, with satisfactory oil extraction and an acceptable risk index of 54.1.

Low-temperature co-pyrolysis of OS with various agricultural biomasses (rice husk, sawdust, walnut shell, and apricot shell) was conducted in a horizontal quartz reactor (placed in an electric furnace) at 723 K for 3 hours.^[96] The recovery efficiency was in the direction of going up with biomass content 0-0.2 wt%, but down with increases in biomass addition above 0.2 wt% to 1.0 wt%. For example, in co-pyrolysis with rice husk, the recovery efficiency went up from 53% to 60% with the addition of small quantities of rice husk (≤ 0.2 wt%). The presence of sawdust and rice husk during co-pyrolysis with oil sludge resulted in higher oil recovery than when walnut shell and apricot shell were used, which have a higher lignin content than cellulose. Rice husk (RH) was also used in co-pyrolysis with OS (in a fixed-bed reactor) at various weight ratios (OS/RH = 2/1, 1/1, 1/2) at 600°C to study the interaction effects on the products and to improve the quality of pyrolysis oil.^[95] The results showed that with a rise in the proportion of rice husk in the mixture, the oil yield went down (from 59.8% to 49.0%), while the residue yield went up (from 18.9% to 27.7%). The gas yield increased due to the promotion of secondary reactions of volatile matter (from biomass ash) and water-gas shift reactions, resulting in the enhancement of H₂, CO, CO₂, and C₁-C₂ fractions in the

gas. An increase in pyrolysis product yields was also observed in the co-pyrolysis of rice straw with oil sludge (at 250°C) using torrefaction, where the oil and gas yields increased by 3.22% and 5.4%, respectively, compared to pyrolysis of rice straw alone.^[78]

The effect of adding fly ash on the thermal behavior, distribution, and properties of OS pyrolysis products was studied using a fixed-bed reactor and TG at 600°C to achieve higher oil yield.^[14] The addition of fly ash (up to 50 wt%) increased the oil and gas yields by 13.85% and 2.24%, respectively. The maximum oil and gas yields were 30.43% and 11.56% (wt%), respectively, when the fly ash content was 50 wt% (Fig. 1).

A similar oil yield using oil sludge ash was obtained in a study,^[127] which proposed a sustainable method for fuel production from oil sludges, such as oil field sludge (OFS) and oil tank sludge (OTS), through a pyrolysis-reforming process. The highest oil yield of 35.5% was achieved in the co-pyrolysis of OTS with OFS ash, which may be attributed to the presence of iron and sulfur elements in the OFS ash. Compared to OFS, oil extraction from OTS was more substantial.

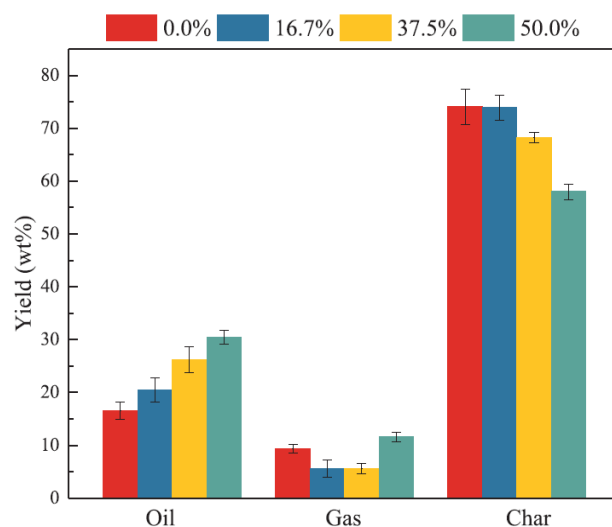


Fig. 1: The product distribution from oily sludge pyrolysis with different rate of fly ash additive. Values are given as averages with standard deviations ($n = 3$, shown as error bar). Reproduced from.^[12] Fig. 3.

Oil sludge ash was also used in the pyrolysis of OS with steam injection under inert conditions at 450°C in a reactor with a stirrer.^[128] It was found that injecting steam from 0 to 0.8 mL/min led to an increase in oil yield (from 12.45% to 18.33%), and the addition of OS ash (up to an OS/ash ratio of 1/1.5) increased the oil yield to 17.82%. However, when the ash ratio was increased to 1/2, the oil yield slightly decreased. The yields of gas and coke generally decreased with increasing steam flow. The yield of organic gas (C_xH_y) decreased as the steam flow rate increased (from 63.59% to 44.86%) and as the

amount of OS ash increased (from 63.59% to 48.06%). The coke yield decreased in the ranges of 5.82–1.72% and 5.82–1.3% with increasing steam flow and OS ash amount, respectively.

The addition of granular activated carbon (GAC) also promoted higher oil product yields during the microwave pyrolysis of OS. When the GAC was raised to 10%, the oil yield increased from 56.3% to 77.5% (with approximately 70.0% diesel and gasoline fractions), the residue yield decreased from 32.3% to 8.3%, and the gas yield rose gradually from 11.4% to 14.2%.^[129]

When the GAC was further raised (from 10% to 15%), however, the oil yield decreased by 8.9% (from 77.5% to 68.6%). The authors explained this result by the fact that a larger amount of GAC could lead to excessive coking due to the very high heating rate. The leaching of heavy metals, such as Cr, As, and Pb, was suppressed in the solid residue after pyrolysis.

The results of co-pyrolysis of side wall waste tires (SWWT) and offshore oil sludge (OOS) showed that the 75SWWT/25OOS ratio was optimal due to the stimulating surface properties of char and lower oxygen and nitrogen content in the pyrolysis oil.^[130] The highest oil yield of 64.9 wt% was observed at 500°C with a 100% OOS ratio (SWWT/OOS = 0/100), while with a 100% SWWT ratio (SWWT/OOS = 100/0), the oil content decreased to 56.8 wt%, due to the higher carbon content, which forms more volatile

compounds during decomposition (Fig. 2). Therefore, SWWT is not as productive for oil recovery as OOS; however, when using 100% SWWT, the highest char yield of 33.4 wt% was obtained, due to the higher soot (carbon black) content in SWWT.

The study on the influence of steel slag (SS) on the pyrolysis of OS using a continuous pyrolysis-magnetic separation process revealed that the addition of SS up to 15 wt% at 550°C increased the tar yield from 10.63% to 14.03% (Fig. 3,b).^[72] However, when the temperature was raised to 650°C, the tar yield slightly decreased to 9.79% (Fig. 3,a), which was attributed to the intensification of secondary thermal cracking of the volatile compounds at higher temperatures.^[131] The maximum gas yield was 25.79% when the steel slag content reached 20%.

Compared to the previously described study,^[72] the addition of steel slag (SS) led to a decrease in oil yield in another study.^[131] In the research on the effects of steel slag (SS) and red mud (RM) on the OS co-pyrolysis, it was found that SS and RM addition (30 wt%) reduced the yield of oil from 95.98 wt% to 89.22 wt% and 84.59 wt%, respectively, while the yield of gas was enhanced from 3.60 wt% to 18.28 wt% and 19.55 wt%, respectively.^[131] The addition of RM enabled oil extraction at lower temperatures (400–500°C) and resulted in greater gas yield at higher temperatures (600°C). Thus, the studies described above showed different results due to the varying properties of the additives and the technological

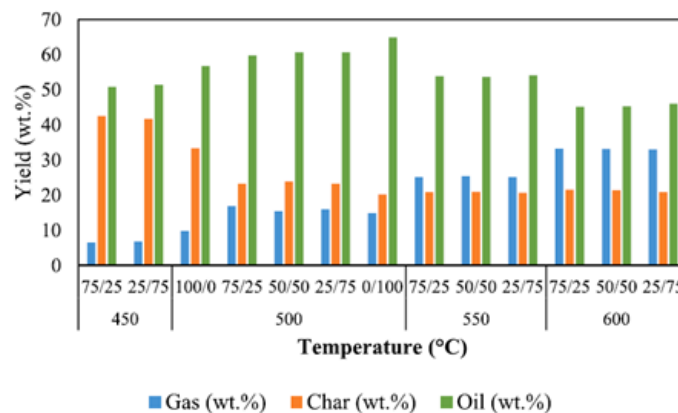


Fig. 2: Product distribution from co-pyrolysis of SWWT and OOS. Reproduced from.^[116] Fig. 5.

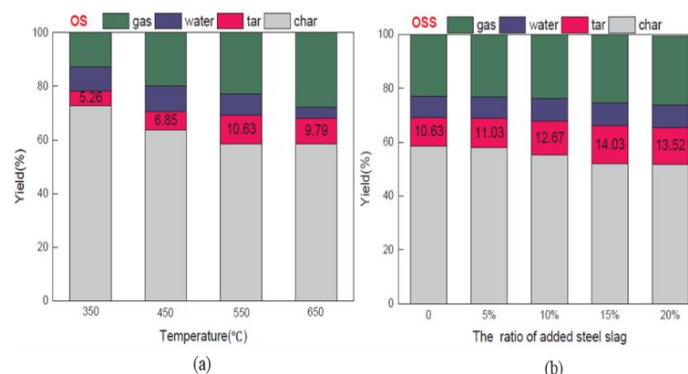


Fig. 3: The pyrolysis products yield and non-condensable gas of OS and OSS in the CPM. Reproduced from.^[57] Fig. 4.

conditions of the co-pyrolysis with OS. In this context, Table 2 provides a brief overview of some studies on the impact of additives and operational parameters on the product yields of co-pyrolysis with OS. As seen, in works^[126] and^[15] the addition of sawdust leads to a significant increase in both oil and gas yields under different co-pyrolysis conditions. This could be due to one operational parameter compensating for another. For example, the lower temperature (500°C) in study^[15] is offset by the rotary kiln reactor compared to the higher temperature (900°C) and fixed-bed reactor in study^[126] and vice versa. This is further confirmed by the fact that in study^[126] on the co-pyrolysis of OS and sawdust at the lower temperature (500°C) and in a fixed-bed reactor, a relatively modest increase in oil yield and even a decrease in gas yield were observed. Another additive that resulted in a relatively high oil yield (Significant increase in oil yield from 56.3% to 77.5% when added from 0 to 10%) was activated carbon.^[129] Other additives showed either insignificant increases or reductions in oil yield.

5.2 The influence of additives on the distribution and quality of co-pyrolysis products.

The addition of microalgae residue (MR) in the co-pyrolysis with OS^[132] led to an increase in the oil-to-gas ratio, which the authors attributed to MR's ability to suppress the secondary

cracking of heavy hydrocarbons, preventing the decomposition of oil products into gas-phase products. As the MR proportion increased, the content of CO and CO₂ increased, while the content of H₂ and C_xH_y decreased. With increasing MR content in the composition of C_xH_y, the proportion of C₄₊ hydrocarbons decreased, while the levels of C₂ and C₃ hydrocarbons increased, especially C₂H₂. With the addition of MR (from 5 to 30 wt%), the proportion of light oil increased (from 38% to 45%), while the proportion of heavy oil decreased (from 62% to 55%). Thus, the addition of MR improved the quality of the pyrolysis oil.

The addition of rice husk also had a positive effect on the quality of the final oil in OS co-pyrolysis, as it increased the content of saturates (15-55%) and aromatic hydrocarbons (55-86%), while the content of resins (25-31%) and asphaltenes (11-68%) reduced (Fig. 4). Gas chromatography/mass spectrometry analysis revealed that co-pyrolysis not only increased the concentration of chain hydrocarbons but also significantly reduced the content of oxygenated compounds by 46-93%. The observed synergistic effect was explained by the catalytic action of the ash and alkaline metals (from the rice husk), which promoted secondary reactions of liquid products. Additionally, although the release of H₂S was inhibited, the distribution of sulfur between the oil and gas phases improved due to the synergistic effect.

Table 2: A Brief Overview of Studies on the Effect of Additives and Operating Parameters on the Product Yields of Co-pyrolysis with Oil Sludge.

No.	Additive Type	Quantity/ratio	Type of reactor	Temperature(°C) and time of pyrolysis	Heating rate (°C/min)	Change in the yield of co-pyrolysis products, wt% (↑ increase, ↓ decrease)			Ref.
						Oil	Char	Gas	
1	Sawdust	0-20wt%	Fixed bed reactor	900(n.r.)	n.r.	9.80(10.85-	15.63(63.50-	5.83(25.65-	[126]
		20-40 wt%				20.65)	47.87)	1.48)	
		40-60 wt%				2.31(20.65-	6.04(47.87-	3.73(31.48-	
		60-80 wt%				22.96)	41.83)	35.21)	
		80-100 wt%				0.16(22.96-	4.54(41.83-	4.38(35.21-	
		23.12)	37.29)	39.59)					
		6.21(23.12-	6.18(37.29-	0.03(39.59-					
		29.33)	31.11)	39.56)					
		2.61(29.33-	4.57(31.11-	1.96(39.56-					
		31.94)	26.54)	41.52)					
2	Sawdust	0-20 wt%	Rotary kiln reactor (with fins inside)	500(n.r.)	10	6.5(15.9-	11.8(77.5-	5.3**(6.6-	[15]
		20-40 wt%				22.4*)	65.7*)	11.9)	
		40-60 wt%				7.0(22.4*-	16.8(65.7*-	9.8**(11.9-	
		60-80 wt%				29.4*)	48.9*)	21.7)	
		80-100 wt%				5.9(29.4*-	1.7(48.9*-	4.2**(21.7-	
		35.3*)	47.2*)	17.5)					
		1.6(35.3*-	7.2(47.2*-	5.6**(17.5-					
		36.9*)	40.0*)	23.1)					
		8.2(36.9*-	8.5(40.0*-	0.3**(23.1-					
		45.1)	31.5)	23.4)					

No.	Additive Type	Quantity/ratio	Type of reactor	Temperature(°C) and time of pyrolysis	Heating rate (°C/min)	Change in the yield of co-pyrolysis products, wt%			Ref.
						Oil (↑ increase, ↓ decrease)	Char	Gas	
3	Sawdust	0-25 wt%	Fixed bed reactor	500(n.r.)	20	4.0(36.2-40.2)	1.1(13.7-14.8)	5.1(50.1-45.0)	[91]
		25-40 wt%				0.6(40.2-40.8)	0.4(14.8-15.2)	1.0(45.0-44.0)	
		40-50 wt%				5.6(40.8-46.4)	0.9(15.2-16.1)	6.5(44.0-37.5)	
		50-60 wt%				1.8(46.4-48.2)	0.4(16.1-15.7)	1.2(37.5-36.3)	
		60-75 wt%				0.7(48.2-48.9)	0.1(15.7-15.8)	1.0(36.3-35.3)	
		75-100 wt%				0.3(48.9-49.2)	0.4(15.8-16.2)	0.7(35.3-34.6)	
4	Microalgae residue	0-5wt%	Fixed bed reactor	600 (30 min)	20	1.60(19.29-20.89)	3.37(54.43-51.06)	1.77(26.28-28.05)	[132]
		5-15wt%				1.41(20.89-22.30)	2.12(51.06-48.94)	0.70(28.05-28.75)	
		15-30wt%				1.95(22.30-24.25)	4.97(48.94-43.97)	3.03(28.75-31.78)	
5	Rice husk	0-0.2 wt%	Fixed bed reactor	450(180 min)	10	7.0 (53.0-60.0)	n.r.	n.r.	[96]
6	Rice husk (RH)	OS/RH:2/1-1/2	Fixed bed reactor	600(20 min)	n.r.	10.8(59.8-49.0)	8.8(18.9-27.7)	2.0**(21.3-23.3)	[95]
7	Fly Ash	0.0-16.7 wt%	Fixed bed reactor	600(90 min)	20	3.91(16.58-20.49)	0.16**(74.09-73.93)	3.75(9.33-5.58)	[14]
		16.7-50.0 wt%				9.94(20.49-30.43)	15.92**(73.93-58.01)	5.98(5.58-11.56)	
8	Steam Oil sludge ash (OSA)	0-1.6 ml/min	Stainless steel stirred tank reactor	450(60 min)	20	5.88(12.45-18.33)	4.10(5.82-1.72)	1.23(3.08-1.85)	[128]
		OS/OSA: 1/0-1/2				5.37(12.45-17.82)	4.52(5.82-1.30)	1.13(3.08-1.95)	
9	Granular Activated Carbon (GAC)	0-10 wt%	Microwave reactor (1 kW, 2.45 GHz)	up to 900	n.r.	21.2(56.3-77.5)	24.0(32.3-8.3)	2.8(11.4-14.2**)	[129]
		10-15 wt%				8.9(77.5-68.6)	6.6(8.3-14.9)	2.3(14.2**-16.5)	
10	Side wall waste tire (SWWT)	OS/SWWT = 100/0-0/100	Fixed bed reactor	500(n.r.)	15	8.1(64.9-56.8)	13.2*(20.2-33.3)	5.1**(14.9-9.9)	[130]
11	Steel slag (SS)	0-15wt%	Rotary kiln reactor	550(n.r.)	n.r.	3.40(10.63-14.03)	6.70*(58.38-51.68)	2.69**(22.51-25.20)	[72]

The remaining part up to 100% is water

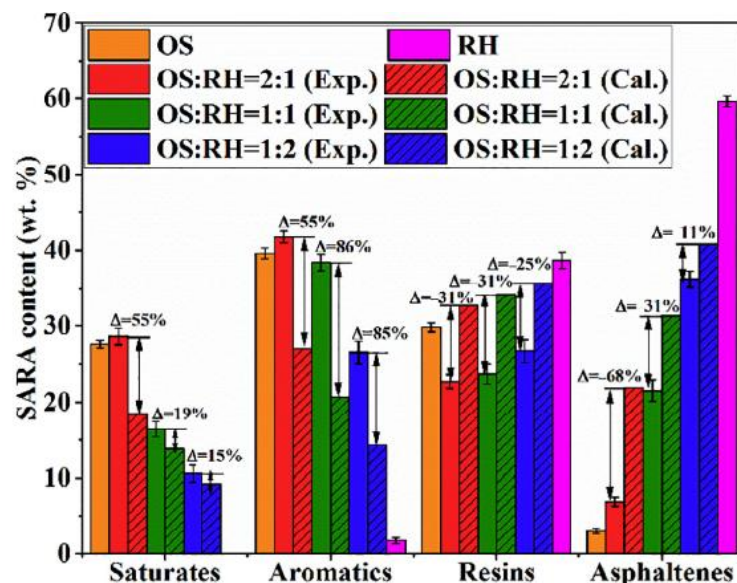


Fig. 4: SARA contents of oil products from co-pyrolysis of oily sludge and rice husk. Reproduced from.^[80] Fig. 3.

The quality of pyrolysis oil is also improved by the torrefaction (200 to 300°C) of rice straw and its co-pyrolysis with OS in a thermogravimetric analyzer and a fixed-bed reactor. This also led to a gradual reduction in volatiles, an increase in ash content, low crystallinity, and an increase in surface aromaticity.^[78] Co-pyrolysis significantly increased the formation of alkanes (11.22-23.84%) and olefins (2.33-4.48%), while suppressing the formation of oxygenates (13.71-26.54%) in the oil product.

The synergistic effect of co-pyrolysis of sawdust and oil sludge resulted in improved oil quality.^[91] This is confirmed by the increased H/C ratio (from 1.5 to 2.0) at a sawdust-to-oil sludge ratio of 3:1, as well as an increase in calorific value (from 19.5 to 24.5 MJ/kg) compared to pyrolysis of sawdust alone. A high percentage of sawdust in the feedstock increased the carbon content in the char product.

Co-pyrolysis of oil sludge with other biomasses (rice husk, sawdust, walnut shells, apricot pits) resulted in oil consisting of more aliphatic hydrocarbons C₁₃-C₁₉ and fewer heterocyclic compounds than original oil sludge, pointing towards its suitability as a fuel, such as diesel fuel.^[96]

In the study,^[92] it was confirmed that co-pyrolysis of three fractions of biomass (hemicellulose - Hemi, cellulose - Cel, and lignin - Lig) with OS produced less vigorous gas release (CH₄, H₂O, CO, and CO₂) and lower apparent activation energies than pyrolysis of individual biomass fractions. Co-pyrolysis of OS/Hemi and OS/Cel promoted the formation of char and gas, as well as the generation of oxygenates in the oil products. On the other hand, co-pyrolysis of OS/Lig increased gas production and promoted the formation of long straight-chain alkanes with less oxygenate formation. Moreover, co-pyrolysis with OS made the product profiles more predictable and increased the comprehensive pyrolysis index compared to pyrolysis of OS alone.

The addition of fly ash (a product of wastewater sludge gasification) to oil sludge reduces the content of aromatic

hydrocarbons and non-hydrocarbons (resins and heterocycles), while the molecular weight of straight-chain alkanes decreased as the ash content increased (16.7-50.0 wt%) (Fig. 5(a)).^[14] The carbon distribution range of the pyrolysis oil mostly lies in the C₁₅-C₂₅ range. Fly ash facilitated the cracking of long-chain alkanes into smaller molecules (Fig. 5(b)). Ash promoted the reduction of H₂ and C₂-C₃, but increased the content of CH₄ and CO. The lower heating value (LHV) of the gas was between 16.62 and 19.88 MJ/Nm³. High concentrations of Fe, Ba, Si, and Ca in the pyrolysis char, and heavy metals in oil sludge (Pb, Zn, Cr, Cu, Ni, Cd, As, and Hg), fly ash, and pyrolysis char can be considered as moderate risk.

Another type of fly ash, derived from the incineration of municipal solid waste (incineration fly ash - IFA), was used for co-pyrolysis with OS to increase H₂ production, improve pyrolysis oil quality, and reduce CO₂ emissions. This also led to the immobilization of heavy metals in stable fractions with lower environmental risks.^[133] At an optimal temperature of 600°C and with the addition of 20 wt% IFA, the highest selectivity for aromatic hydrocarbons (30.72%) and the lowest coke yield (106.13 mg/g) were observed, while the peak ratio of light to heavy oil reached 179.42%. Adding 50 wt% IFA significantly increased H₂ yield (from 21.02 L/kg OS to 60.95 L/kg OS).

IFA was also used in another study,^[134] where individual pure inorganic compounds (present in IFA from the incineration of municipal solid waste) were added to co-pyrolysis with OS in a fixed-bed reactor at 600°C to study the contributions of inorganic compounds to the overall catalytic activity of IFA. The results showed that compared to IFA, CaCl₂ and KCl significantly improved the processing of pyrolysis oil, while IFA components together had a positive catalytic effect on pyrolysis gas and coke production. CaCl₂ and KCl also promoted the breakdown of heavy compounds and aromatization of alkanes, reducing coke formation and

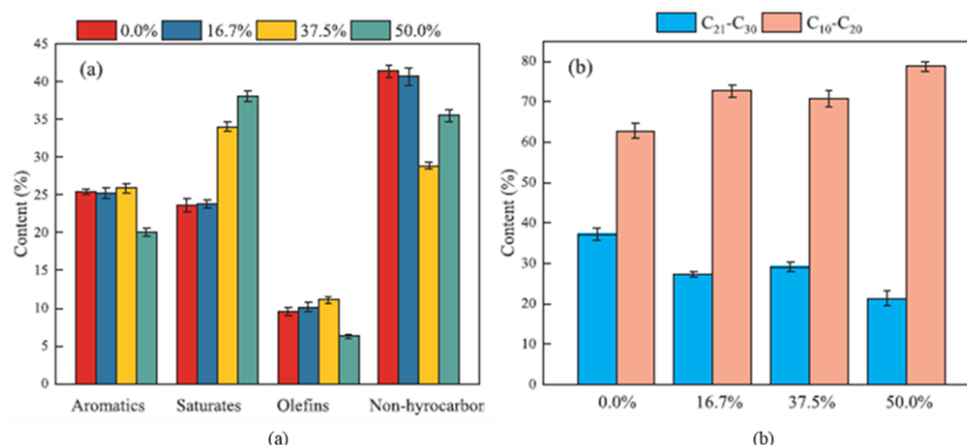


Fig. 5: (a) Chemical composition of the oil from pyrolysis of oily sludge with different rate of fly ash additive. (b) The straight-chain alkanes content of the pyrolysis oil with different rate of fly ash.

increasing the production of light aromatic compounds. In contrast, NaCl increased the alkane fraction, while CaSO₄ and CaCO₃ inhibited catalytic reactions, promoting carbon conversion into coke. Ca(OH)₂ increased H₂ yield by 137.16%, while alkaline metal chlorides converted oxygenates into CO and CO₂.

Oil sludge ash (Al₂O₃, Fe₂O₃, CaO, and SiO₂) was used in co-pyrolysis with OS under inert conditions in a stirred reactor to study the catalytic effect of metal oxides on oil product quality.^[128] The pyrolysis conditions were determined as 450°C at 5 rpm. Adding OS ash led to a reduction in carbon residue and the migration of S, N, and O from the oil sludge to the oil product. The authors suggested that this improvement in oil quality was due to the catalytic effect of Al₂O₃, Fe₂O₃, and CaO (in the OS ash) and their corresponding compositions in the oil sludge ash. The Lewis acid catalytic action of Al₂O₃ led to an increase in the saturate fraction of the oil product.

The results of using OS ash as a solid heat carrier in the OS pyrolysis process showed that the addition of OS ash could increase oil yield and lower the optimal reaction temperature from 500°C to 450°C.^[75] It was found that OS ash could: promote the cracking of the heavy fraction into a light fraction and the isomerization of oil, reduce coke and carbon residue yields in the oil product, increase the ratio of light to heavy oil, and reduce the number of heteroatoms and aromatic carbon, as well as the total number of rings in the oil product. The authors concluded that OS ash is a potential alternative to silica sand as a solid heat carrier in the OS pyrolysis process for oil production.

Co-pyrolysis of OS with steam and OS ash showed that increasing the additions of steam and OS ash could inhibit the secondary cracking reaction, as evidenced by a decrease in the olefin/paraffin ratio.^[128] The steam injection effect on inhibiting the secondary cracking reaction was greater than that of adding OS ash. Adding OS ash could also contribute to the conversion of the heavy fraction into lighter fractions. Steam injection led to an increase in the proportion of heavy

and medium fractions in the oil product and prevented further cracking of the oil products into gas.

The results of co-pyrolysis of OS and steel slag (SS) showed that adding SS: 1) significantly increased the content of short alkanes and the C₅-C₁₀ fraction (by decomposing the C₁₅-C₂₀ fraction); 2) promoted the formation of H₂ and CH₄ (yields of H₂ and CH₄ increased in the ranges of 26.43-30.41% and 34.65-43.38%, respectively) (Fig. 6).^[72] Adding SS also increased the weight loss rate of oil sludge and led to a decrease in pyrolysis activation energy. The tar from OS and the tar from the mixture of OS and SS (OSS) had the same high calorific value as commercial diesel fuel, while the tar from OSS was lighter than the tar from OS.

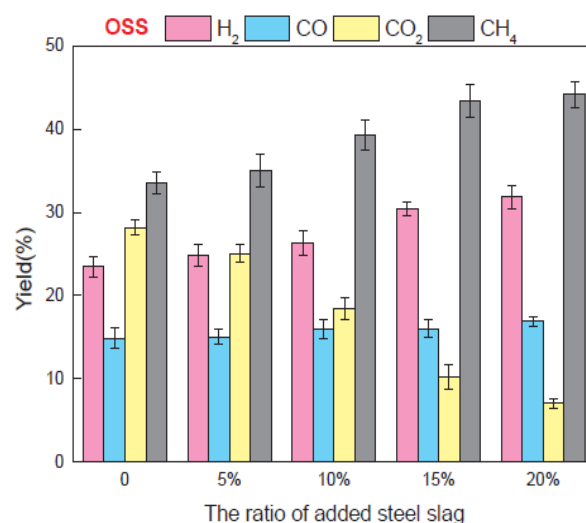


Fig. 6: The pyrolysis products yield and non-condensable gas of OS and OSS in the CP. Reproduced from.^[57] Fig. 4.

Co-pyrolysis of OS with steel slag (SS) or red mud (RM) at a 30 wt% addition can improve oil quality, reduce activation energy, and promote H₂ production.^[131] RM and SS facilitated the cracking of macromolecular compounds into micromolecular compounds (non-condensable gases). Adding

RM reduced the olefin content (from 5.85 to 3.68 wt%) and increased the alkane content (from 91.38 to 94.08 wt%), indicating an improvement in the saturation level. The addition of RM and SS: 1) slightly increased the content of C_{20+} (by 4.77 and 1.01 wt%, respectively); 2) reduced the contents of $C_6\sim C_{12}$ and $C_{13}\sim C_{19}$ by 1.52 and 3.27 wt% for RM, and by 0.65 and 2.15 wt% for SS. RM, which contains more Fe_2O_3 , showed more pronounced catalytic effects on pyrolysis compared to SS. RM produced significantly more combustible gas, especially a higher yield of H_2 (about 41.91 L/kg). Fe_2O_3 promoted H_2 generation and heavy oil upgrading to light fuels, while CaO , SiO_2 , and Al_2O_3 lowered the oxygen content of pyrolytic oil due to their acid-base characteristics, improving oil quality.

In co-pyrolysis of oily residues and polyethylene waste, liquid and gas products were obtained with calorific values of 44-47 MJ/kg and 27-32 MJ/kg, respectively.^[135] The liquid products from the co-pyrolysis also exhibited other characteristics similar to those of conventional fuels, such as diesel fuel, and thus have a very good potential for use as transportation fuel and other chemical feedstocks for further processing.

These findings demonstrate that co-pyrolysis not only improves oil yield but also enhances the fuel properties of the pyrolytic oil. The resulting oils show higher hydrogen content and calorific values ranging from 38 to 45 MJ/kg, depending on the feedstock composition and temperature. The reduction in heteroatoms and oxygenates improves thermal stability and reduces corrosiveness, making these oils suitable for use as transportation fuels or chemical feedstocks. Additionally, the gas fraction produced during co-pyrolysis exhibits a lower heating value (LHV) of 16.5–20 MJ/Nm³, allowing its utilization as a clean energy source.

5.3 Influence of additives on other factors

Co-pyrolysis of various types of biomass (such as walnut shell, coconut shell, or cottonwood sawdust) with OS (carbon-enriched oil sludge) was carried out to produce adsorbent materials for sulfamethoxazole (SMZ) in the aqueous phase.^[136] The resulting char was activated using K_2CO_3 to modify its microstructure and functional groups. The results showed that activated carbon materials (ACs) made from the mixture contained more mesopores than ACs made from biomass alone and were more porous with higher yields compared to ACs made from OS. ACs prepared from the walnut shell and oil sludge mixture exhibited the highest values for BET surface area (1342 m²/g), SMZ adsorption capacity (361.9 mg/g), and microporosity (85.1%).

In the co-pyrolysis of OS and waste tires (WT), a waste tire-sludge adsorbent (WTSA) was produced, and its efficiency in crude oil adsorption was investigated^[7] The WTSA showed a high carbon content (89.95%), with mesopores and macropores as the dominant pore structures. The BET surface area, pore volume, and average pore size were 686.81 m²/g, 0.74 cm³/g, and 5.91 nm, respectively. In

adsorption tests of crude oil, WTSA had comparable adsorption capacity to activated carbon (AC) but with a better initial adsorption rate. WTSA is more superior to AC in that WTSA is recyclable and reusable multiple times, hence it is environmentally and economically friendly.

Furthermore, the carbon-rich char produced during co-pyrolysis can serve as a long-term carbon sink. Its application in asphalt mixtures and cement composites enables partial replacement of traditional fillers and promotes carbon fixation in the built environment. Similarly, when applied as biochar to soil, it not only enhances soil fertility but also contributes to long-term carbon sequestration, improving the sustainability of agricultural systems.

The addition of agricultural waste, such as wheat straw (WS), peanut straw (PS), and coconut shell (CS), in the pyrolysis process with OS had a stimulating effect, improving overall pyrolysis properties and reducing the energy barrier for reactions when WS content was 40%, PS 40%, and CS 50%.^[137] The addition of these three additives helped reduce the formation of CH_4 and CO and increased CO_2 precipitation.

The addition of wood waste in co-pyrolysis with OS positively influenced the immobilization of heavy metals in the solid residue by converting loosely bound metals into more strongly bound complexes.^[11] Another study showed that co-pyrolysis of OS with sawdust (SD) reduced activation energy. Fe_3O_4 in the solid residue was reduced to iron by carbon at 700°C, producing CO and CO_2 .^[126] Sawdust was also used in co-pyrolysis with oil sludge to reduce the physical viscosity of OS.^[15] Pyrolysis, assisted by steel slag, provided sufficient waste heat to replace external heat sources. Adding 20 wt% sawdust reduced the average viscosity of oil sludge from 24.19 to 19.37 Pa·s.

The solid residue (char) from co-pyrolysis often contains stable mineral phases and aromatic carbon structures, with BET surface areas ranging from 300 to over 1300 m²/g. These characteristics enable its use in a variety of applications, including as a precursor for activated carbon, as a sorbent for water purification, and as a stabilizing filler in construction materials like asphalt and concrete. Furthermore, the low leaching toxicity of heavy metals in the residue confirms its environmental safety when properly treated or immobilized.

6. Conclusion

In recent years, with the continuous expansion of the oil industry, the production of unconventional oil and gas reserves has been increasing, resulting in the generation of high viscous, toxic and acidic oil sludge. When selecting a treatment method for oil sludge, it should be considered that oil sludge contains high levels of heavy metals, heteroatomic compounds and other harmful and toxic pollutants. As a result, a number of methods have been developed, among which pyrolysis is a promising technology for the treatment of various OS since it provides a dual advantage of energy recovery and safe disposal. Since OS contains high content of total petroleum hydrocarbons, which is both environmentally

toxic and non-biodegradable, pyrolysis distributes these toxic elements and heavy metals among the pyrolysis products, particularly in the pyrolytic oil and gas. This negatively impacts the quality of the pyrolysis oil and also aggravates the pollutant emission requirements due to stringent gas emission standards. Therefore, the necessity of co-pyrolysis with various additives is directly linked with overcoming the main problems of pyrolysis oil, *i.e.*, its quality, oil content in the solid residue and mobility of toxic elements and heavy metals. Besides, to increase the economic value of OS pyrolysis products, valuable additives added in the pyrolysis cracking process yield some advantages compared to additive-free pyrolysis. Co-pyrolysis can reduce the reaction temperature, decrease the reaction time, and narrow the range of product distribution.

In addition to enhancing fuel production efficiency, co-pyrolysis presents a viable strategy for mitigating environmental issues. The immobilization of heavy metals, reduction of volatile pollutants, and potential for carbon fixation in solid residues (*e.g.*, biochar and mineral char) align this process with global carbon neutrality goals. The environmentally friendly nature of pyrolytic gas and upgraded oils further underscores the relevance of this technology in sustainable waste management.

Analysis of a series of studies of the co-pyrolysis of oil sludge with different additives has shown that the technological conditions of the pyrolysis process (*e.g.*, reactor type, temperature, reaction duration, etc.) are no less important for increasing the pyrolysis products yield and quality than the physico-chemical characteristics of the additives themselves. The co-pyrolysis of OS with different types of feedstock (waste) is mainly regulated by the composition of the feedstock (*i.e.* the H/C ratio), which has a direct impact on the efficiency of co-pyrolysis. For instance, feedstocks having a larger molar H/C ratio improve the quality of pyrolysis oil, *e.g.* biomass. However, different biomass components play a role, making synergistic effects more complex during co-pyrolysis. It is therefore essential to understand how different biomass types affect co-pyrolysis efficiency with OS, keeping in mind that both biomass (hemicellulose, cellulose and lignin) and OS have a composite character. This makes it extremely difficult to quantify co-pyrolysis efficiency as well as oil product quality. Alternatively, hydrocarbon fuels may be employed as feedstocks for co-pyrolysis with OS in order to produce hydrogen-rich gas, liquid streams and carbon-rich solid streams by the facilitatory action of hydrogen diffusion. When other organic residues are considered, account must be taken of thermal degradative behavior and chemical composition of the feedstock. If they are identical to those of OS, either the synergistic effect will be missing or much weaker.

Though pyrolysis and co-pyrolysis of OS provided irrefutable results, the complex composition of the components and additives of oil sludge, as well as excessive energy consumption, call for further research and development in this area. This will provide a better

understanding of the influence of feedstock chemical structure on the investigated process and the co-pyrolysis process of OS and additives. It will also provide a more distinct view of the mechanism of the synergistic effect to further improve the efficiency of co-pyrolysis.

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Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

CRedit Statement

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