

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

**HIGH TEMPERATURE PYROLYSIS OF COMPOSITE WASTES FOR
SYNGAS PRODUCTION**



M.Sc. THESIS

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Department of Chemical Engineering

Chemical Engineering Programme

JANUARY 2023

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**KOMPOZİT ATIKLARDAN YÜKSEK SICAKLIK PİROLİZİ İLE SENTEZ
GAZI ÜRETİMİ**

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To dream of a better World,



FOREWORD

This thesis was written with the motivation of contributing to the idea of creating a sustainable world. As a chemical engineer, I have been always keen on developing sustainable processes for waste to energy applications since my B.Sc. study. This thesis can be designated as the first concrete work that I have done in terms of the goals I want to achieve.

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December 2022

Yusuf Tolunay KILIÇ
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ABBREVIATIONS

EC	: European Comission
EGD	: European Green Deal
EU	: European Union
EJ	: Exajoule
IEA	: International Energy Agency
GHG	: Green House Gas
Gt	: Giga Tonne
Hz	: Hertz
LNG	: Liquefied Natural Gas
MSW	: Municipal Solid Waste
MWh	: Mega Watt per Hour
Mt	: Millione Tonne
rpm	: Rotate per Minute
SNG	: Synhetic Natural Gas
WB	: World Bank
WtE	: Waste to Energy



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HIGH TEMPERATURE PYROLYSIS OF COMPOSITE WASTES FOR SYNGAS PRODUCTION

SUMMARY

The increasing demand for energy on a global scale has led to the need for alternative energy sources and alternative energy production methods becoming even more important. Among alternative energy sources, waste is one of the most important sources that have come to the fore in recent years. Evaluating wastes with appropriate technologies and obtaining products with high added value are of great importance in terms of sustainability and circular economy. In this study, it was aimed to evaluate composite label wastes and commercial waste pellets in similar content with pyrolysis technology towards syngas generation rich in hydrogen and methane. Composite label wastes were supplied from Frimpeks A.Ş. in rolls. These rolls were cellulosic or plastic materials. The rolls were shredded and pelleted in mixtures with different cellulose-plastic proportions. Secondly, commercial pellets in similar composition were supplied from USA for comparison. Commercial and in-house prepared pellets were characterized with the well-known techniques such as proximate and ultimate analysis, calorimetry, thermal gravimetric analysis, X-ray fluorescence, inductively coupled plasma atomic emission spectroscopy. Pyrolysis tests were performed in both the batch reactor and continuous reactor at pilot scale. Experimental results have shown that that syngas yield was improved at increasing plastic content of the pellets and also with pyrolysis temperature. Moreover, wax formation was observed for plastic containing pellets in batch reactor unit but in a less amount at comparatively high temperatures. On the other hand, wax formation was disappeared for the same pellets pyrolyzed in continuous reactor unit, possibly due to the more extended secondary cracking reactions. When the pellets contained some portion of plastics, higher yields of pyrolysis oil and waxes were obtained depending on the pyrolysis temperature, reactor configuration and reaction mode, batch or continuous. Since the objective of study was to obtain high syngas yields rich in hydrogen and methane, studies were continued over continuous pyrolysis reactor at high pyrolysis temperature, namely at 900 °C. Thanks to the secondary thermal cracking reactions under these conditions, 66% to 76% of the feedstock was converted into pyrolysis gases. Hydrogen and methane contents of the gas were in the ranges of 32-35% and of 21-32%, respectively. Quite low pyrolysis liquids were obtained, namely at around 10 %, together with the char as the remaining part.



KOMPOZİT ATIKLARDAN YÜKSEK SICAKLIK PİROLİZİ İLE SENTEZ GAZI ÜRETİMİ

ÖZET

Küresel ölçekte enerjiye olan talebin hızlı bir şekilde artması, alternatif enerji kaynaklarına ve enerji üretim yöntemlerine olan ihtiyacın daha da önemli hale gelmesine sebep olmaktadır. Mevcut enerji arzında fosil yakıtların sahip olduğu yüksek orandaki pay göz önüne alındığında, alternatif enerji kaynaklarının enerji arzına dahil edilmesi sürdürülebilirlik noktasında büyük önem arz etmektedir. Alternatif enerji kaynakları arasında atıklar son yıllarda öne çıkan en önemli kaynaklardan birisidir. Avrupa Birliği Yeşil Mutabakat'ta da bahsedildiği üzere atık yönetimi sisteminin yeniden ele alınması, başta evsel ve endüstriyel olmak üzere, atıkların uygun teknolojiler ile değerlendirilmesi ve katma değeri yüksek ürünler elde edilmesi sürdürülebilir kalkınma ve döngüsel ekonomi açısından büyük öneme sahiptir.

Atıkların enerji üretiminde değerlendirilmesi konusunda öne çıkan seçenekler arasında termal dönüşüm yöntemleri bulunmaktadır. Yakma, gazlaştırma ve piroliz termal dönüşüm yöntemleri olarak adlandırılmaktadır. Bu üç farklı yöntem arasındaki temel fark reksiyon ortamında oksijenin bulunma durumudur. Günümüzde atıklar yaygın olarak yakma teknolojisi ile değerlendirilmekte ve elektrik/ısı enerjisi üretilmektedir. Mevcut emisyon seviyeleri göz önüne alındığında, yakma teknolojisi atıkların enerji arzına dahil edilmesi noktasında sürdürülebilir bir yöntem olarak değerlendirilmemektedir. Diğer termal dönüşüm yöntemleri olan gazlaştırma ve piroliz ise yakma ile kıyaslandığında daha sürdürülebilir ve çok yönlü teknolojiler olarak değerlendirilmektedir. Gazlaştırma ve piroliz teknolojileri yardımıyla atıklardan ikincil enerji taşıyıcıları elde edilebilmektedir. Gaz, sıvı veya katı formda olabilen bu ikincil enerji taşıyıcılarından farklı sıvı yakıtlar, kimyasallar ve elektrik enerjisi üretilebilmektedir. İkincil enerji taşıyıcılarından biri olan sentez gazı, içeriğinde yüksek oranda karbon monoksit, metan ve hidrojen bulunan bir gaz karışımıdır. Gazlaştırma ve piroliz teknolojilerinin gaz ürünü olan sentez gazı, doğrudan elektrik enerjisi üretiminde kullanılabildiği gibi, farklı teknolojiler yardımıyla sıvı ve gaz yakıtlara dönüştürülebilmektedir.

Bu çalışmada hidrojen ve metanca zengin sentez gazı üretimine yönelik olarak piroliz teknolojisi ile kompozit etiket atıkları ve benzer bileşimine sahip ticari peletlerin değerlendirilmesi amaçlanmıştır. Kompozit etiket atıkları Frimpeks A.Ş.'den rulolar halinde temin edilmiştir. Yapılarında boya, kaplama maddesi ve tutkal gibi katkıları bulunan bu atıklar, kompozit atık olarak sınıflandırılmaktadır. Selüloz ve plastik olmak üzere iki farklı türde bulunan kompozit etiket atıkları çeşitli ön işlemlere tabi tutulmuştur. Ön işlem amacıyla rulolar önce parçalanmış ve daha sonrasında peletleme makinası yardımıyla peletlenmiştir. İhtiva ettikleri tutkal ve sebebiyle peletleme işleminde herhangi bir katkı maddesi ilave edilmemiştir. İkinci olarak karşılaştırma için ABD'den benzer bileşimdeki ticari peletler temin edilmiştir. ABD'den temin edilen ticari pelet örneği için herhangi bir ön işlem uygulanmamıştır.

Yerli olarak temin edilen kompozit etiket atıklarına ait peletler ve ticari pelet örneği çeşitli karakterizasyon işlemlerine tabi tutulmuştur. Karakterizasyon amacıyla pelet örnekleri ile kısa analiz, elementel analiz, kalorifik değer tayini, termal gravimetrik analiz, X-ışını floresansı ve endüktif olarak eşleşmiş plazma atomik emisyon spektroskopisi gibi iyi bilinen tekniklerle işlemler gerçekleştirilmiştir. Karakterizasyon işlemlerinin ardından bu atıklar ile piroliz testleri gerçekleştirilmiştir. Piroliz testlerinde sisteme beslenecek kompozit atıklara ait karışım oranları için Frimpeks A.Ş.'den bu atıklara ait yıllık oluşum miktarı bilgisi temin edilmiştir. Yıllık oluşum miktarları göz önüne alınarak dört farklı hammadde reçetesi hazırlanmıştır. Farklı oranlarda selüloz ve plastik içeren bu reçetelere ilave olarak sadece ticari pelet örneğini içeren bir reçete de çalışmalarda kullanılmıştır.

Kompozit atıkların piroliz davranımlarının tespit edilmesi amacıyla bir dizi piroliz testi gerçekleştirilmiştir. Bu piroliz testleri için hem kesikli reaktör hem de pilot ölçek sürekli reaktör sistemleri kullanılmıştır. Kesikli reaktörde dört farklı reçete için elde edilen sonuçlar sentez gazı veriminin peletlerin plastik içeriği ve piroliz sıcaklığı ile arttığını göstermiştir. Kesikli reaktörde plastik içeren reçeteler ile gerçekleştirilen çalışmalarda vaks oluşumu gözlemlenmiştir. Öte yandan, kesikli reaktör ünitesinde plastik içeren peletler için nispeten yüksek piroliz sıcaklıklarında vaks oluşum miktarının azaldığı da tespit edilmiştir.

Aynı reçeteler ile pilot ölçek sürekli reaktör sisteminde gerçekleştirilen piroliz testlerinde ise vaks oluşumu gözlemlenmemiştir. Vaks oluşumu noktasında sürekli sistemde elde edilen bu sonucun daha uzun ikincil parçalanma reaksiyonları ve sistemde bulunan ikincil termal parçalama ünitesi ile bağlantılı olduğu sonucuna varılmıştır. Ek olarak, pilot ölçek sürekli piroliz sistemi bünyesinde bulunan Auger tipi piroliz reaktörünün sahip olduğu konfigürasyonun daha etkin bir ısı transfer mekanizması sağladığı ve bu sayede piroliz işlemi esnasında meydana gelen parçalanma reaksiyonlarının veriminin arttığı sonucuna varılmıştır.

Farklı oranlarda selüloz ve plastik içeriğine sahip reçeteler ile gerçekleştirilen piroliz testlerinde elde edilen sonuçlar, piroliz sıcaklığına, reaktör konfigürasyonuna ve reaksiyon moduna (kesikli veya sürekli) bağlı olarak piroliz ürünlerine ait verimlerin değiştiğini göstermiştir. Çalışmanın amacı yüksek verim ile hidrojen ve metan zengin sentez gazı elde etmek olduğundan, yüksek piroliz sıcaklığında yani 900 °C'de sürekli piroliz reaktörü üzerinden çalışmalara devam edilmiştir. Bu koşullar altında ikincil termal parçalanma reaksiyonları sayesinde hammaddenin %66 ila %76'sı piroliz gazlarına dönüştürülmüştür. Hidrojen ve metan içerikleri sırasıyla %32-35 ve %21-32 aralığında olan bir gaz ürün elde edilmiştir. Oldukça düşük miktarda pirolitik sıvı ürün (yaklaşık ağırlıkça %10) ile birlikte bakiye çar oluşumu gözlemlenmiştir. Çar miktar ve verimleri ile ilgili elde edilen deneysel sonuçlar ve kısa analiz ile hesaplanan teorik sonuçlar karşılaştırılmıştır. Sürekli sistemde elde edilen çar miktarının, teorik miktardan ortalama %30 daha fazla olduğu gözlemlenmiştir. Bu sonucun, meydana gelen ikincil piroliz reaksiyonlarındaki artıştan kaynaklandığı sonucuna varılmıştır.

Kesikli piroliz reaktöründe elde edilen sonuçlar ile karşılaştırıldığında, sürekli sistemde pirolitik yağ oluşumu minimize edilerek sentez gazı verimi olabildiğince yüksek değerlere ulaştırılmıştır. Piroliz işlemi esnasında oluşan sıvı buharlarının termal parçalanma ünitesi yardımıyla ikincil bir termal işleme tabi tutulmasının sentez gazı verimini arttırdığı sonucuna varılmıştır. Öte yandan, sisteme beslenen reçete içerisindeki plastik oranı artışının sentez gazı içerisindeki hidrojen ve metan gazlarına ait hacimsel konsantrasyonlar üzerinde pozitif etkiye sahip olduğu tespit edilmiştir.

Sürekli reaktörde 900°C’de gerçekleştirilen piroliz testlerinde, besleme içeriğindeki plastik oranı artışı ile birlikte sentez gazı içeriğindeki CO gazına ait konsantrasyonun azaldığı, hidrojen ve metan gazlarına ait konsantrasyonların ise arttığı gözlemlenmiştir. Ticari pelet örneği ile gerçekleştirilen piroliz testlerinde elde edilen sonuçların, yerli kompozit etiket atıklarını içeren ve %30 plastik %70 selüloz içeriğine sahip reçeteye ait sonuçlar ile sentez gazı içeriği ve verimi noktasında benzerlik gösterdiği tespit edilmiştir.





1. INTRODUCTION

Energy demand is tremendously increasing with a continuous progress and changes in modern life. Contingencies on a global scale such as pandemic have temporarily slowed down energy demand but continuation of the upward trend is expected in the long term. Anthropologic greenhouse gas emissions are the major concern in terms of climate change and its social, environmental and economic effects. According to the 2022 report of the International Energy Agency (IEA), increasing economic activities on a global scale after the pandemic have caused emissions to reach an annual value of 36.9 Gt, quadrupling the 9 Gt value in 2020. On the other hand, the amount of industrial, domestic, and hazardous waste formed globally reached 7-9 billion tons as of 2022 (Uday et al., 2022; IEA, 2022). Increasing emissions create serious concerns about climate change, which is an inevitable fact of our time. The greenhouse gases, which occurs as a result of the release of CH₄, CO₂, and N₂O into the atmosphere causes the acceleration of the climate change phenomena and catastrophic effects on Earth. Despite taking various measures on global scale, GHGs does not seem to be reduced below the target levels, namely 450 ppm CO₂ in the atmosphere. Kyoto Protocol of 1997 was the first initiative to agree on the reduction of GHG emissions on a global scale and then the Paris Agreement was signed in 2015 with the signatures of 180 countries to act to keep the global temperature increase below 2°C (Oreggioni et al., 2021).

After the Kyoto Protocol and the Paris Agreement, the world's leading economies have reached a consensus on a target of reducing emissions to net zero by 2050. The net-zero emission target includes many different elements and variables. The goal of reducing emissions to net-zero will ensure not only a shift from existing to green technologies but also will bring a change in habits and trends on both an economic, social, and industrial scale. All these will change the world from fossil-based economy to renewables in a sustainable perspective. Today, while the approach of societies to renewable energy is extremely positive, the current cost issues and energy supply security still make it difficult to fully transition to renewable energy (Obobisa, 2022).

Regarding sustainability, another important issue is undoubtedly the circular economy. A circular economy is a multifaceted approach that can bring about many different positive results such as reaching the net zero emission target and minimizing the consumption of existing raw material resources in the world. The concept of circular economy, which is a suitable business model for creating added value from waste, has been one of the most important basics inspiring the thesis objective.

Current studies on the circular economy are concentrated on minimizing the negative effects of the waste problem on a global scale and bringing these wastes to the economy through green technologies. The linear economy model was established on the disposal of wastes generated as a result of industrial processes and this model was adopted for many years. The fact that this model cannot be survived for a long time, since it is not sustainable. It has been well understood in recent years that alternative models have to be focused on (Felix et al., 2022).

There are different methods and strategies for evaluating waste and creating added value. The waste-to-energy (WtE) strategy, which is one of these methods, is one of the most critical and important issues when the current energy crisis and the limitation of fossil fuel use are considered. The WtE strategy involves the production of gas or liquid fuels from different types of waste (such as biomass, and plastic) that come out of different sources (industrial or domestic). There are different methods and technologies in this regard. Wastes can be converted into energy in different forms by thermal, chemical, or physical conversion methods (Lee et al., 2023). For thermochemical conversion, pyrolysis technology has become one of the prominent technologies among waste-to-energy. Pyrolysis, which allows the production of different types of raw fuels from biomass and waste without the need for additional chemical pretreatment, can be defined as the thermal degradation of materials at different temperatures (300-1200°C) in an oxygen-free environment (Kwon et al., 2019).

As of 2022, when fossil fuel consumption is still very common, there are different scenarios and research on the inclusion of waste to the energy mix. One of the most prominent alternative fuels in future scenarios is undoubtedly hydrogen. The reason why hydrogen has the potential to lead the transformation in the energy economy is that it is a clean energy carrier and its utilization gives zero CO₂ emissions. There are several constraints to the rapid incorporation of hydrogen into the energy supply.

These constraints include current hydrogen production costs, storage, and transportation issues (Kovač et al., 2021). One of the feedstocks for hydrogen production is organic wastes. With a decrease in the effects of the pandemic, the increasing industrial productions and concurrent consumptions gave rise in both municipal and industrial wastes. It may be cost-advantageous to use these wastes in hydrogen production through various processes. Thermochemical processes were among the promising technologies for hydrogen production. There are researches efforts on handling the sustainability aspects and cost issues for hydrogen production via pyrolysis or gasification of waste (Wijayasekera, Hewage, Hettiaratchi, et al., 2022; Wijayasekera, Hewage, Siddiqui, et al., 2022).

Another alternative fuel for reducing dependence on fossil fuel is methane from waste. Methane from waste, which has the potential to substitute natural gas, has opportunity to be produced in an integrated way and can be mixed to the existing natural gas distribution grid. Another advantage of methane from waste comes from the sustainability within the scope of the circular economy (Jaffar et al., 2019).

1.1 Aim of the Study

There are different types of industrial wastes that arise from various processes. With varying origin and forms. The annual amount of waste is an important criterion for their utilization. Composite label wastes, which are the subject of this study, can be defined as the roll-shaped, self-adhesive wastes of the labels printed on different consumer products (packaging/bottle etc.). These wastes are of two different types, cellulose-based (paper origin) and plastic-based (polyethylene, polypropylene, and polyethylene terephthalate). Label wastes are considered be in composite nature since their content includes some inks, adhesives, laminating additives and so on besides its main cellulosic or plastic matrix.

In this study, cellulose-based and plastic-based label wastes in rolls were supplied from Frimpeks A.Ş., one of the largest label manufacturers in Türkiye. The rolls were shredded and pelleted in mixtures with different cellulose-plastic proportions. Secondly, commercial pellets in similar composition were supplied from Convergen Energy LLC U.S.A. for comparison. Then these wastes were characterized with the well-known techniques such as proximate and ultimate analysis, calorimetry, thermal gravimetric analysis, X-ray fluorescence, inductively coupled plasma atomic emission

spectroscopy. Pyrolysis tests were performed in both the batch reactor and continuous reactor at pilot scale. The results were compared in terms of gas yield, hydrogen and methane selectivity and processability of the wastes in two different types of pyrolysis units.



2. LITERATURE SURVEY

2.1 World Energy Outlook

When today's energy trends are examined, an increase in energy prices is apparent due to the limited supply of energy sources and an upward trend in the energy demand of consumers. In this regard, the climate change issues direct the governments to develop and implement the necessary policies in spite of the trends towards less energy efficient electrification in heating. Figure 2.1 shows the share of different energy sources in the total demand for the year 2021. As noticed from the figure, the total energy demand of 564.01 EJ in 2020 has been increased to 595.14 EJ in 2021. The share of fossil fuels is still too high in total demand portfolio on global basis. Oil, coal, natural gas, hydropower, renewable and nuclear are the primary energy sources taking place in the first five rank, respectively. This order has remained the same from 2020 to 2021 (BP, 2022; IEA, 2022).

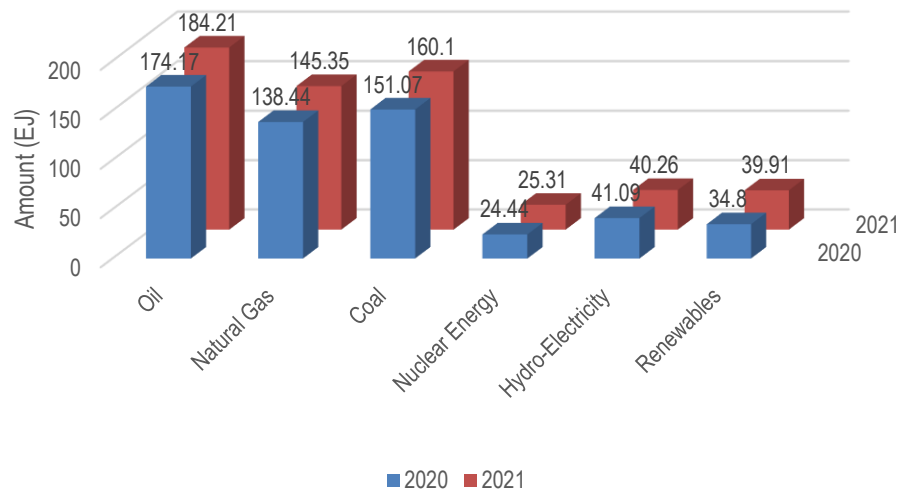


Figure 2.1: Primary energy demand by fuel in 2020 and 2021 (BP, 2022).

With the Russian-Ukrainian war as started in 2021, a new energy crisis has broken out, especially in European countries. Many European and American energy companies have suspended existing investments in Russia and cancelled long-term investments. While the United States and Canada banned oil imports from Russia, Europe's high

dependence on Russian natural gas and oil prevented the prohibition of energy imports from Russia. This crisis in natural gas has pushed European countries to search for new energy sources that can be substituted to natural gas (Foss, 2022).

According to the commodity markets outlook report published by the World Bank (WB) in 2022, the impact of the Russia-Ukraine war on energy prices has become devastating in addition to the economic problems experienced after the pandemic. The WB energy price index increased by 50% in the two-year period between April 2020 and April 2022. This is the highest increase since the 1973 oil crisis. Following these events, the European Union (EU) has announced that it will completely restrict natural gas imports from Russia and turn to different alternatives. While the import of liquefied natural gas (LNG) from different countries is seen as one of the options, it has also been announced that steps will be taken on biomethane production from renewable sources (World Bank, 2022).

The shift towards alternative fuels and technologies raises the question of the current sustainability and capacity issues in these areas. The complete transition to sustainable resources by leaving oil, natural gas and coal behind in the short term does not seem to be realistic since these are the primary sources having the highest share of the current energy supply. There are some technical and non-technical issues that need to be resolved like high cost, high space requirements etc. While there is a 0.2 m³ space requirement for 1 MWh electricity generation from natural gas and coal, the space requirement to produce the same amount of electricity from wind or solar energy is 5 and 50 times more (Foss, 2022). The quest for low-emission and low-cost fuels has brought hydrogen to the forefront. Production of hydrogen has reached an annual value of 30 Mt by 2022. When the trade volume was examined, it is seen that although the majority of the hydrogen produced was for on-site use, its international trade and fuel market can have a capacity of about 12 Mt (IEA, 2022).

2.2 Circular Economy and Waste to Energy

The basic principle in the circular economy can be explained as reuse, recycling, reduction, and recovery (4R). When we look at Europe in particular, especially in 2015 and later, different steps have been taken to transition from the current linear economy model to the circular economy model. In the action plan announced by the European Commission (EC) on the reorganization of the current waste management within the

scope of the circular economy model, there are headings such as the recovery of municipal solid waste (MSW) and packaging wastes to reach 65% and 75% respectively by 2030, and the reduction of landfill rates to 10% by 2030 (Rada et al., 2018).

The EU Green Deal (EGD), which defines the actions on the emission problem and sustainable development goals was announced by the EC in 2019. According to the EGD, sustainable technologies will be supported investment-wise in the green transition process. One of the ultimate goals of this green transition is to make Europe the first emission-neutral continent. The fact that approximately 75% of the emissions covered by the EGD come from the energy sector. This has led to the community to agree on the decarbonization of the energy sector (Gil, 2022).

There are different studies in the literature on the green transformation of the energy sector in line with circular economy and sustainable development strategies. In these studies, conversion technologies for various types of wastes have been put forward and case studies have been conducted. In case of industrial wastes, the production of heat, electricity, syngas or biogas from industrial wastes by applying thermochemical (gasification and pyrolysis) or biochemical technologies is the significant concern within the framework of the circular economy principle. While waste-to-energy (WtE) practices have sufficient competence in responding to the increase in energy demand, waste management and emission reduction, more legislative regulation and financial support are needed for their further implementation (Pan et al., 2015; Su & Urban, 2021).

The critical points for the incorporation of waste to the energy supply mix are to accurately classify and standardize the wastes and to apply the right technology. Information on the classification of waste or waste-derived fuels according to their type and source is summarized in Table 2.1 (Bosmans et al., 2013).

Table 2.1 : Definition of waste and waste-derived fuels (Bosmans et al., 2013).

Fuel type	Definition
Fuel	Intended for use as an energy carrier.
Municipal Solid Waste (MSW)	Domestically produced waste by households. It can contain paper, plastic, organic, or garden waste.
Commercial&Industrial Waste (C&IW)	Industrially or commercially produced waste. It can contain paper, metals, and plastics.
Refuse Derived Fuel (RDF)	Fuel obtained from MSW or C&IW by separation of non-combustible parts.
Solid Recovered Fuel (SRF)	Similar to RDF. Includes less contamination and has higher specifications.

Today, the conventional technology for WtE is incineration. Incineration technology is often used to generate heat and electricity from MSW type wastes. Steam turbines are preferred for the generation of electricity. Incineration technology is not the choice if the material recovering and chemical production from waste is the main concern. On the other hand, chemicals production, energy and material recovery in thermochemical conversion routes such as pyrolysis and gasification can be achieved via syngas generation, ash and char treatments, oil upgrading, combined energy cycles etc. Therefore, they offer more versatile productions compared to incineration where only heat and electricity can be obtained. These gaseous and liquid products, which can be described as secondary energy carriers, can be used to produce energy and versatile chemicals. Due to these features, pyrolysis and gasification of wastes are called as clean waste treatment technologies. Figure 2.2 summarizes the different WtE technologies and their potential products. As mentioned above, there are different thermal conversion methods currently used to generate energy from waste. In addition to these methods, dark fermentation and anaerobic digestion which are known as biochemical methods may be used to produce energy from waste (Bosmans et al., 2013).

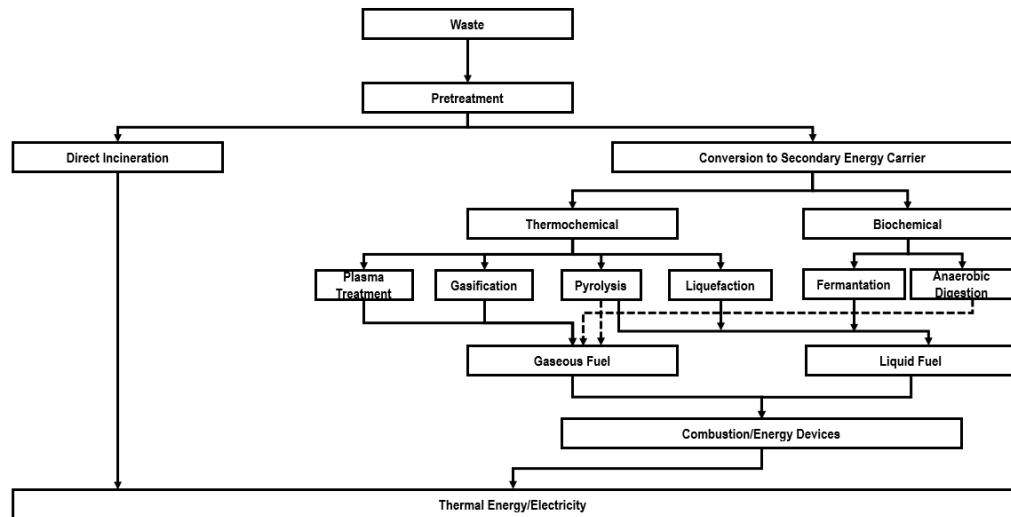


Figure 2.2: WtE technologies for thermal energy and electricity production (Bosmans et al., 2013).

Apart from the technological routes related to heat and electricity generation from wastes, the production of different chemicals and end-use gaseous products can be viable as gaseous and liquid products. From the circular economy perspective and the current energy crisis, the concept of hydrogen and methane production becomes quite important.

2.3 Waste-to-Energy Applications for Hydrogen and Methane Productions

Gasification and anaerobic digestion are the most common ways of gas generation routes from waste. In anaerobic digestion technology, biogas, a mixture of CH_4 and CO_2 , is produced by the digestion of wastes with the help of a microbiological process. In gasification technology, syngas is produced from wastes thermochemically by using different gasification agents such as air, carbon dioxide and water vapor. Gaseous product, biogas or syngas, can be directly used in electricity generation or converted into valuable chemicals with the subsequent catalytic processes. High temperature pyrolysis is the alternative route yielding high pyrolysis gas with more or less syngas composition. However, it is a route less subject to research. Syngas or pyrolysis gas can be rich in hydrogen or methane depending on the operating conditions of the thermochemical conversion process. If economical production of pure hydrogen and/or methane can be achieved, both can serve as an alternative fuel in transportation sector, can find use in industrial heat and steam supply or can be significant

intermediate commodities for chemical sectors such as fertilizers, iron ore reduction, hydrogenation products etc.

Hydrogen production can be carried out with diverse processes and energy sources and their nomenclature with color codes is common. For example, steam methane reforming (SMR) or coal gasification produces grey hydrogen entailing substantial CO₂ emissions, which makes these technologies unsuitable towards net-zero emission economy. In spite of this, approximately 96% of hydrogen production is carried out through using fossil fuels today (Wijayasekera, Hewage, Siddiqui, et al., 2022).

According to World Energy Outlook statistics, since natural gas ranks second in total primary energy demand on a global scale, sustainable production of synthetic methane is outmost importance in terms of circular carbon economy. Compared to other fossil fuels, natural gas has the highest H/C ratio and releases less CO₂ per fuel compared to other hydrocarbon fuels. Moreover, it's steam reforming is the most mature hydrogen production route (Bolt et al., 2020).

Although the ultimate goal is to produce green hydrogen from renewables, advanced utilization of hydrocarbon sources for hydrogen production can serve as the intermediate solution. Turquoise hydrogen is one of them. Its production is based on natural gas pyrolysis technology with no CO₂ production. Turquoise hydrogen can be obtained via the pyrolysis of methane leaving a valuable byproduct, carbon black. However, turquoise hydrogen via pyrolysis of methane is still at the pilot stage. As an alternative to pyrolysis of methane for turquoise hydrogen, high temperature pyrolysis of composite wastes is another option worth researching.

2.4 Pyrolysis Technology

The pyrolysis is composed of a series of reactions that occurs in the absence of oxygen and leads decomposition via cracking and/or depolymerisation induced by heat (Basu, 2018). Pyrolysis technology has been used for years for the production of charcoal. Today its use extends to the production of many valuable chemicals. Three main products can be obtained in the pyrolysis process. These are char, pyrolytic oil and pyrolytic gas (syngas). Pyrolysis products can be considered as renewable or sustainable energy carriers depending on the feedstock. The pyrolysis process can be carried out at different temperature ranges and heating rates. In general, pyrolysis occurs in the range of 300-1200°C and the yields of the products depend on the

pyrolysis temperature, heating rate, feedstock characteristics and vapor residence time (Lee et al., 2023). Pyrolysis is also the first step in other thermal conversion routes such as gasification and combustion. The fuel particle undergoing thermal degradation is then subject to partial oxidation in gasification and total oxidation in combustion. Depending on the temperature, heating rates and vapor residence time, pyrolysis is divided into four main classes as given in Table 2.2. As noticed from the Table, high temperature pyrolysis is called as gasification (T. Bridgwater, 2006). However, this might be confusing regarding the well-known gasification technology using the oxidants. Therefore, high temperature pyrolysis will be the preferred terminology instead of using gasification in this thesis.

Table 2.2: Product yields and conditions of different type of pyrolysis (T. Bridgwater, 2006).

Type	Conditions	%Char	%Liquid	%Gas
Fast	Temperature: ~500°C Hot vapor residence time: ~1 s	12	75	13
Intermediate	Temperature: ~500°C Hot vapor residence time: 10-20 s	20	50	30
Slow	Temperature: ~400°C Hot vapor residence time: Long	35	30	35
Gasification	Temperature: ~800°C Hot vapor residence time: Long	10	5	85

In the literature, studies differentiating from each other according to the target product, aiming increasing the yields of solid, liquid or gas products. For example, low temperature and slow heating rates during pyrolysis were applied for biochar while fast heating rates at moderate temperatures and fast quenching when the aim was to increase the bio-oil yield. As seen, high gas yields can be achieved only at high pyrolysis temperatures whatever the heating rates at long residence times. Tsai et al examined the current biochar production methods and suggested that slow pyrolysis is the most appropriate method of production among the existing technologies (Tsai et al., 2022).

Heating rate or fast quenching determines the gaseous or liquids yield. For example, when the pyrolysis process carried out at high temperature but with short residence times of below 1 second as in the case of flash pyrolysis, condensable pyrolysis

vapours do not have enough time to react secondarily. Therefore, the pyrolytic oil is not expended to give gaseous ones. Applications related to this subject include bio-oil production. The yield of bio-oil can be increased by fast or flash pyrolysis applications and various chemicals can be produced with further upgrading processes (A. v. Bridgwater et al., 1999).

2.4.1 Auger type pyrolysis reactor

The pyrolysis process can be carried out in a variety of reactor types, including with those with high heat and mass transfer rates. Fluidized bed (FB), both bubbling and circulating types, rotating cone, ablative and Auger reactors are the most commonly used reactors in pyrolysis. Regarding with the technical and economic parameters, these reactors have advantages and disadvantages (Campuzano et al., 2019). Overview of the different type reactors are shown in Table 2.3.

Table 2.3: Key features of the reactors used in pyrolysis process (Campuzano et al., 2019).

Type	Status	Complexity	Inert Gas Requirement	Reactor Size
Bubbling FB	Commercial	Medium	High	Medium
Circulating FB	Commercial	High	High	Medium
Entrained Flow	Laboratory	Medium	High	Medium
Auger	Pilot	Medium	Low	Low

Auger reactors typically have an enclosed shell with a helical screw inside it. This helical screw allows feedstock to be moving forward inside the reactor. Also, this screw conveys char to the end of the reactor. The Auger reactors can have a single or double-screw system. The pyrolysis reactor used in this study has a single screw Auger type. Campuzano et al summarize the strengths of the Auger reactor in pyrolysis as follow:

- Being capable to be used for a wide range of feedstock with different particle sizes and typologies.
- Allowing to be used in fast, intermediate, and slow pyrolysis since it has a strong capability of controlling the feedstock residence time and mass flow rate.
- Ensuring the sufficient mixing of feedstock inside the reactor.

2.4.2 High-temperature pyrolysis technology (HTP)

Studies to increase the yield of the gaseous product as a result of pyrolysis requires high temperatures and long residence times. Although there is no consensus in the literature on the nomenclature of this gaseous product, in this study the gas will be named as syngas instead of pyrolysis gas. High-temperature pyrolysis (HTP) is in general carried out in the ranges of 800-1300°C and with different types of wastes such as biomass, sewage sludge and plastics in order to increase the gas yield at the expense of liquid products (Al-Asadi & Miskolczi, 2020; Efika et al., 2015; Jiang et al., 2023; Mastral et al., 2002; Yang et al., 2021). In case of HTP process for plastics, the amount of primary wax products with aliphatic hydrocarbons up to C₃₀ decrease with an increase in pyrolysis temperature. Mastral et al observed that pyrolytic oil and wax yields decreased with an increase in temperature for the pyrolysis of high-density polyethylene (HDPE) in the temperature ranges of 645-850°C. Any wax products were not observed at the pyrolysis temperatures of 750°C and above. In their study, gas yields were increased at the expense of wax and pyrolytic oil (Mastral et al., 2002)

2.4.3 Secondary cracking of tar and volatiles

The liquid pyrolysis product is known as pyrolytic oil and this product is in quite heterogeneous nature. Its chemical structure varies depending on the feedstock subjected to pyrolysis. Many consecutive and parallel pyrolysis reactions take place. These reactions can be simply classified as primary and secondary pyrolysis reactions. During primary reactions, char, light gases, water and condensable organic vapour (like tar) fractions are mainly formed. In the second stage, condensable organic vapours undergo secondary reactions such as cracking or charring to give non-condensable gases and additional char. The overall reaction mechanisms for pyrolysis of the pure cellulose structure are shown in Figure 2.3 (Fagbemi et al., 2001).

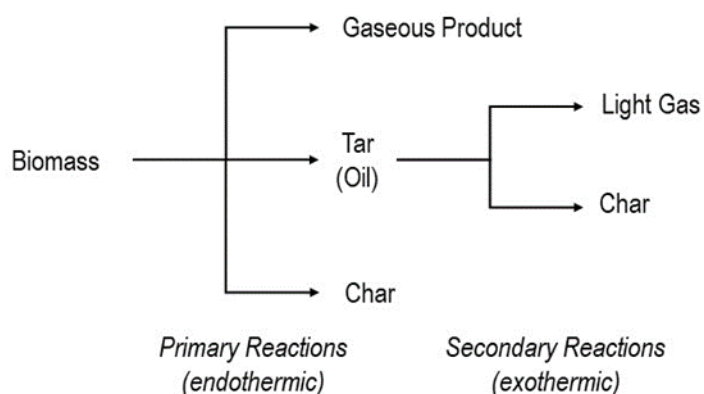


Figure 2.3: Primary and secondary pyrolysis reactions of pure cellulose (Fagbemi et al, 2001).

Pyrolytic oil is a mixture of condensable hydrocarbons. There is no clear definition of tar in the literature. However, tar can be defined as aromatic hydrocarbons with molecular weights higher than benzene and formed by tar precursors like acetylene at high temperature. The vast majority of tar compounds are in polyaromatic hydrocarbons (PAH) and benzene-based structures. The tar formed in the pyrolysis process can have negative effects on the gas yield and the syngas needs to be cleaned afterwards. There are various applications to reduce tar formation during pyrolysis. These applications include performing pyrolysis at high temperatures or subjecting the gas and liquid vapor to secondary thermal cracking (Zhai et al., 2015).

Yang et al. examined the changes on vapor phase products upon secondary pyrolysis reactions at different temperatures and residence times. In their study, as the condensable vapour phase hydrocarbons being heavier, these hydrocarbons degrade more easily even at low temperatures, namely at 500°C. Secondary cracking reactions extend more when the temperature was increased from 500°C to 700°C. Depending on the degree of secondary cracking, oxygen content of the pyrolytic oil decreases as well (Yang et al., 2021).

It is apparent that secondary cracking in the pyrolysis process will reduce tar yield and give less dense pyrolytic oil. In summary, secondary pyrolysis reactions has a certain effect on gas yield and composition. Syngas yield increases by subjecting condensable hydrocarbon vapours to the thermal cracking more via secondary pyrolysis reactions. Another important to remark here that the concentration of CH₄ and H₂ in syngas increase proportionally depending on the secondary cracking temperatures (Serio et al., 2012; Zhai et al., 2015).

2.4.4 Co-pyrolysis of biomass and plastics

Considering the waste problem on a global scale, the use of plastic wastes in energy production through the pyrolysis technology well coincides with the principle of the circular economy. According to the current statistics, only 10% of plastic waste in Europe can be recycled. Although the pyrolysis process does not allow the mechanical recycling of plastic wastes, it allows these wastes to be converted into valuable products by thermochemical and subsequent catalytic routes (Qureshi et al., 2020).

The high H/C ratio of plastics enables them to act as hydrogen donor in the process of co-pyrolysis of plastic & biomass mixtures. Thus, this feature ensures deoxygenation of pyrolysis oil. With an increase in the plastic ratio, H₂ concentration in syngas increase and pyrolytic oil density decreases. The addition of plastic improves the quality of pyrolysis products and reduces the activation energy required for the thermal degradation of biomass (Bober et al., 2011; Sophonrat et al., 2017).

Current studies in the literature have focused on the effect of plastics on oil yield and content in co-pyrolysis with biomass. Studies on the effect of plastics on syngas and char yields and contents are more limited. When the effect of the addition of plastic on syngas was examined, it was observed that the yield and heating value of syngas increased, although it varied depending on the type of plastic. Plastics, which have a hydrogen donor effect in the co-pyrolysis process, also increase the H₂ ratio in syngas. The effect on char is present in the literature as an increase in the heating value and the expansion of the surface area (Uzoejinwa et al., 2018).

In their pyrolysis-gasification study with biomass and plastic mixtures, Alvarez et al. examined the effect of the plastic ratio in the feed mixture on the H₂ ratio in syngas. Their findings suggest that with the addition of plastic to the feed mixture, the ratio of H₂ in syngas increases, while the proportions of CO and CO₂ gases decrease. On the other hand, in different studies, it has been found that the addition of plastic increases the yield of H₂ while reducing the yield of syngas. In these studies, the temperature values at which the pyrolysis process is performed vary in the range of 500-700°C (Alvarez et al., 2014; Wang et al., 2021).

2.4.5 Thermal degradation kinetics of cellulose and plastics

Determining the thermal behaviour of the wastes to be utilized with pyrolysis technology has a great importance. The thermal gravimetric analysis is commonly used for determining the degradation profiles of the wastes. Basic principle of TGA is determining of the weight loss versus temperature curve of the sample. Thermal gravimetric data can be obtained by two different methods. These methods are named as isothermal and non-isothermal. Non-isothermal method is the commonly used one for determining the thermal degradation profile of waste samples. In this method, sample was heated with a ramp value to a final temperature. During the analysis, nitrogen flow is used for obtaining the inert condition. With the help of TGA, pyrolysis process can be simulated for desired final temperature and heating rate (Hillier et al., 2010).

There are several efforts available in the literature for determining the pyrolysis behaviours of cellulosic and plastic wastes. In these studies, thermal gravimetric curves of the wastes were obtained in the pyrolysis conditions. In one of these studies, the thermal degradation kinetics of paper industry wastes were investigated in pyrolysis conditions (900°C final temperature, 20°C/min heating ramp) . According the results in the relevant study, thermal degradation of the reject paper (containing ink) took place in two distinct steps. The first stage of degradation occurs between 250°C and 450°C with a peak for cellulose at 350°C. The secondary degradation step occurs between 700°C and 850°C with the peak value at 750°C (Arenales Rivera et al., 2016).

Unlike the cellulosic wastes, plastics typically have a single degradation profile. For example, PET has a single profile between 360°C and 460°C and. These profiles are specified in the literature as 370-570°C for HDPE and 330-590°C for PP. Since the plastics have single degradation profile, they lose most of their weights at these temperature ranges (Mortezaeikia et al., 2021).

3. EXPERIMENTAL STUDIES

In this study, pyrolysis tests were performed with composite label wastes and commercial waste pellets obtained from two different sources in order to examine their pyrolysis behaviors and syngas compositions. Detailed information on the wastes used in experimental studies is given in Sections 3.1.1 and 3.1.2. The wastes used in the studies and their origins are as follows:

- a.** Composite label waste (domestic).
 - i.** Composite label waste of cellulose origin.
 - ii.** Composite label waste of plastic origin.
- b.** Commercial composite waste pellets (imported, a mixture of cellulosic and plastic materials).

Within the scope of experimental studies, preliminary preparation processes were done for composite waste samples at the beginning to obtain proper samples for characterization and pyrolysis studies. Several characterization techniques were performed for determining the chemical compositions and thermal behaviors of the composite waste samples. After the characterization, pyrolysis tests were performed in the laboratory, and pilot scales. In pyrolysis tests, four different recipes that contained plastics in different ratios were used as feedstock. The findings of the pyrolysis tests were examined in terms of both syngas contents and characterization results of char and pyrolytic oil samples. Experimental studies are summarized as a workflow diagram and shown in Figure 3.1.

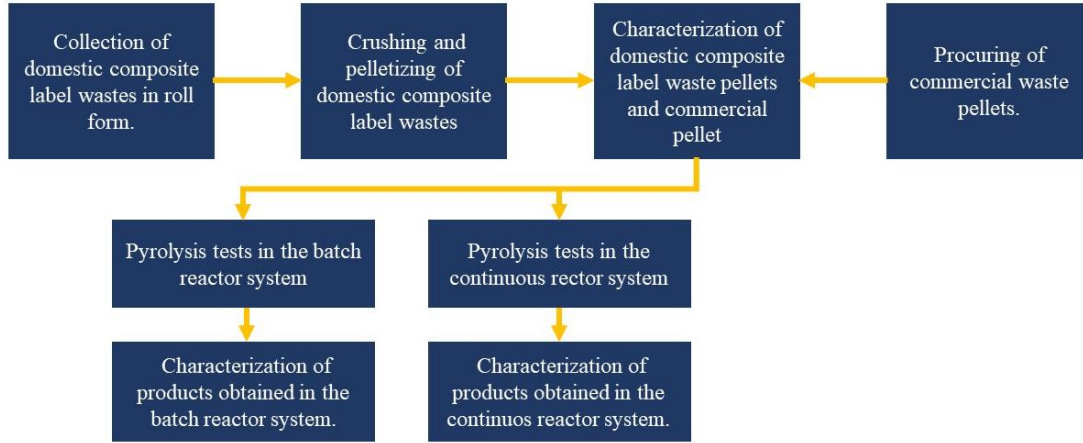


Figure 3.1: Workflow diagram of the experimental studies carried out.

3.1 Materials

As mentioned before, two different types of composite waste were used in this study to observe the pyrolysis behaviors of composite wastes. One of these composite wastes is domestically produced composite label waste procured from the company in Türkiye. The other composite waste is commercial waste pellets which are used as fuel in different energy plants. Commercial waste pellets were procured from a producer company located in the U.S.A.

Within the scope of experimental studies, preliminary preparation processes were performed to obtain proper samples for characterization and pyrolysis tests. These preparation studies were only performed for the domestically procured composite label wastes since the original form of the commercial waste pellet is suitable for characterization studies and pyrolysis tests. For the sample preparation, the infrastructure in the ITU-SENTEK (İstanbul Technical University Synthetic Fuels and Chemicals Technology Center) Solid Fuel, Biomass, and Waste Sample Preparation Laboratory was used.

After the preliminary preparation of composite waste samples, they were characterized both chemically and thermally. Since the original waste samples have a heterogeneous structure, samples in pellet form were used in the characterization studies for avoiding any deviation in the results. The techniques used for the characterization of composite waste samples as follows: Proximate analysis, ultimate analysis, calorific value determination, ash chemical content determination, and atmospheric thermal

gravimetric analysis. Instruments in ITU-SENTEK Characterization and Thermal Analysis Laboratories were used in studies.

Pyrolysis tests of composite waste samples were done in the final step of the experimental studies. In these tests, two different reactors with two different scales were used. One of the pyrolysis reactors used is a batch-type laboratory-scale pyrolysis reactor. In addition to laboratory-scale tests, a pilot-scale continuous pyrolysis reactor was also used to observe composite waste samples' high-temperature pyrolysis behaviors in a continuous process. Both laboratory-scale and pilot-scale reactor systems used in pyrolysis tests are located in the ITU-SENTEK Pyrolysis and Gas Cleanup Laboratory.

3.1.1 Composite label wastes

Label wastes, which have a composite nature since the additives (glue, paint, etc.) they include, form in different labeling processes. The glue they contain gives a self-adhesive property to composite label waste samples. In this study composite label waste samples were procured from Frimpeks A.Ş., one of the label producers in Türkiye. There is no current data or research available in the literature on label waste. The statistics and necessary information about the label wastes subject to this study were obtained from Frimpeks A.Ş. as well.

Labels, which have two different types (cellulose-based and plastic-based), leave behind waste in rolls after being labeled on different materials in the industry. Figure 3.2 shows the original form of the label roll before use and the waste left after labeling. Label waste contains paint, glue, and various coating materials. Composite label wastes are classified as industrial waste and their annual occurrence in Türkiye amounts to 15-20,000 tons. In Europe, statistics show that these wastes amount to 200-250.000 tons per year. Currently, there are no recycling or reusing applications for these wastes in Europe.



Figure 3.2: Original and the used forms of label rolls.

As mentioned before, composite label wastes are classified on the basis of the material they are produced from. There are three different types of cellulosic materials in the structures of cellulose-based composite label wastes: cardboard, coated paper, and paper. A total of six different types of cellulose-based composite label waste, which have one of three different types of cellulosic materials in their structure, were used in this study. Similarly, plastic-based composite label wastes are also classified according to the type of plastic. In this study, three different types of plastic-based composite label waste, polypropylene (PP), polyethylene (PE), and polyethylene terephthalate (PET), were used in experimental studies.

3.1.2 Commercial waste pellets (CWP)

Commercial waste pellets can be briefly described as a composite waste mixture that contains different types of packaging materials and labels. Approximately 200 kilograms of commercial waste in the form of pellets was purchased from the relevant company (Convergen Energy, GreenBay, Wisconsin U.S.A.) to be used in this study. The image of pellets imported from the U.S.A. is shown in Figure 3.3. The information obtained from the company is that these composite waste pellets contain 60-65% paper, cellulosic fiber, and cardboard, and 35-40% plastic. Since the composition of commercial waste pellets includes both cellulose-based and plastic-based wastes, it was aimed to observe its characteristics and pyrolysis behavior to examine domestically produced wastes' potential for commercial usage.



Figure 3.3: Commercial waste pellet procured from the U.S.A.

3.2 Sample Preparation

Composite label waste samples were collected from different facilities in the roll form. In the first step, rolls were crushed via a specially designed industrial-size crusher to reduce particle size which is suitable for use in the pelleting machine. Sample preparation steps are shown in Figure 3.4. Commercial waste pellets procured from the U.S.A. have not undergone any preliminary preparation process because they have a pellet form.

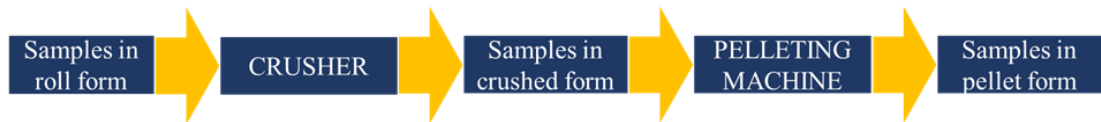


Figure 3.4: Sample preparation steps.

Samples were reduced to a particle size of approximately 1-5 mm in the crushing/shredding machine (special design) shown in Figure 3.5 (a). After crushing, samples in crushed form were pelletized by pelleting machine (Kürelsan) shown in Figure 3.5 (b). Since the samples contain additives such as glue, etc., no additives need to be used during pelletizing. The samples milled to a particle size of <5 mm were shaped into cylindrical pellets with the dimensions of $L = 22 \text{ mm} \times D = 4 \text{ mm}$ in the pellet machine.

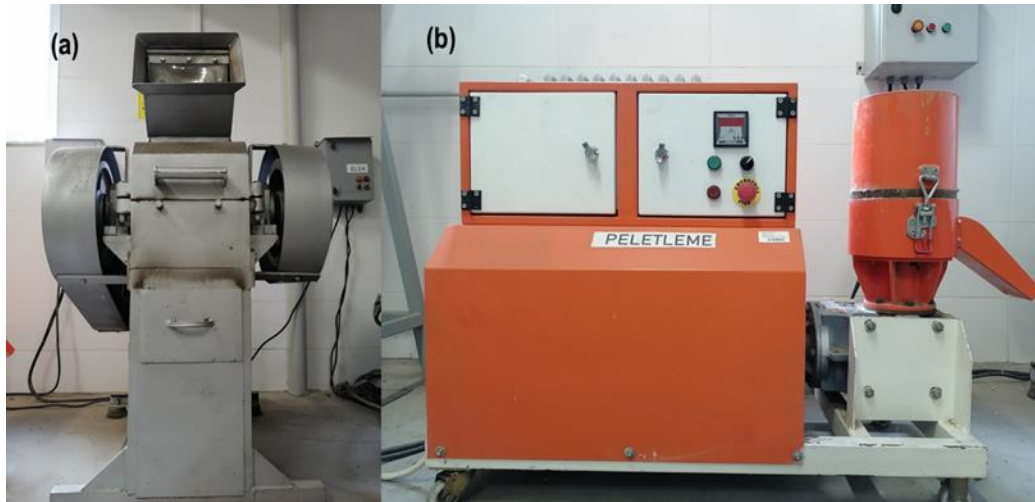


Figure 3.5: Machines used for crushing and pelletizing of samples.

Characterization studies of the composite label wastes and commercial waste pellets were carried out on parts that were ground and cut from pellets. The original, shredded/milled, and pelletized photographs of the characterized composite label waste samples are shown in Table 3.1. Composite waste samples are coded according to their types in order to make it easy and understandable to present the results in the continuation of the study. Cellulose-based composite label wastes will be submitted with the “C” code, plastic-based composite label wastes will be presented with a “P” code and commercial waste pellets will be submitted with the “CWP” code.

Table 3.1: Original, shredded/milled, and pelletized photographs of the samples.

Sample	Original Form	Crushed/Milled	Pellet Form
Cellulose-Based (1) Coated Paper C(1)			
Cellulose-Based (2) Paper C(2)			
Cellulose-Based (3) Coated Paper C(3)			
Cellulose-Based (4) Paper C(4)			
Cellulose-Based (5) Coated Paper C(5)			

Table 3.1 (continued): Original, shredded/milled, and pelletized photographs of the samples.

Sample	Original Form	Crushed/Milled	Pellet Form
Cellulose-Based (6) Cardboard C(6)			Pelletizing was not performed as the existing fragmented form was suitable for use in analyses.
Plastic-Based (1) Polypropylene P(1)			
Plastic-Based (2) Polyethylene P(2)			
Plastic-Based (3) PET P(3)			Pelletizing was not performed as the existing fragmented form was suitable for use in analyses.
Commercial Waste Pellets CWP		Crushing was not performed as the existing fragmented form was suitable for use in analyses.	Pelletizing was not performed as the existing fragmented form was suitable for use in analyses.

3.3 Characterization of Composite Waste Samples

Characterization studies of the composite label waste samples and CWP were performed via different instruments to obtain the samples' thermal behaviors, calorific values, and elemental compositions. The thermal behaviors of composite label waste samples and CWP were determined for the pre-specified conditions with thermal gravimetric analysis (TGA). Proximate analysis was used to obtain percentage amounts of samples' moisture, volatile matter, ash, and fixed carbon contents. In addition to thermal analyses, percentage amounts of carbon, hydrogen, nitrogen, and sulfur elements were obtained via ultimate analysis. Calorific values of the composite waste samples were determined by an automatic calorimeter. In order to determine the chemical content of the ashes of the samples, the samples were burned in an oxygenated environment in the ash oven. Inductively coupled plasma optical emission spectroscopy (ICP-OES) and X-ray Fluorescence Spectrometer (XRF) analysis were performed to determine the chemical contents of the ash samples.

3.3.1 Proximate analysis

The proximate analysis process, which has been used for many years in the characterization of different types of fuels such as biomass and coal, is an analysis carried out to determine the amounts of volatile matter and moisture in the gas phase and inorganic ash and fixed carbon in the solid phase in the structure of the fuel. In addition, there is a direct correlation between the amount of fixed carbon obtained as a result of proximate analysis and the amount of char formed as a result of pyrolysis (Nunes et al., 2018). In this study, proximate analysis of composite waste samples was done with the Macro TGA instrument (LECO TGA 701). Pellet samples were placed in the alumina crucibles in the first place and their initial weights were determined by the device. During the analysis, the mass loss experienced by the samples due to temperature increase was automatically monitored. The amounts of moisture and volatile component are determined by checking at the mass loss up to 107°C and 950°C respectively under the N₂ flow. The amount of ash is determined by the mass loss up to 750°C under the oxygen flow. The fixed carbon was calculated by subtracting the amounts of moisture, volatile matter, and ash components from the initial mass. This method is specified in ASTM D7582-15. The device and alumina crucibles used in the analysis are shown in Figure 3.6.

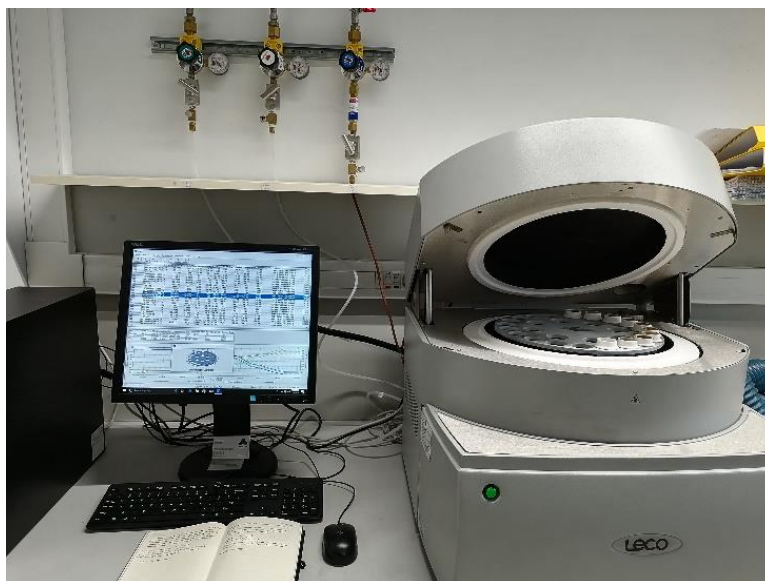


Figure 3.6: Macro TGA used in the proximate analysis of composite wastes.

3.3.2 Ultimate analysis

Ultimate analysis was completed to assess how much carbon, hydrogen, nitrogen, sulfur, and oxygen gave an account of dry material or dry, ash-free basis. Elemental analyzers are used for the study of combustion processes, in which a weighed quantity of material is combusted in a controlled atmosphere. The gaseous products are identified by analyzers (Tuli et al., n.d.). In this study, an elemental analyzer (Elementar Vario Macro) was used to determine the C, H, N, and S content of composite waste samples on the basis of percentage. Oxygen amounts were calculated by hand from the equation proposed in the ASTM standard. According to ASTM D3176-15, oxygen amount can be calculated with the values from ultimate and proximate analysis (Equation 3.1). The instrument used in the ultimate analysis is shown in Figure 3.7.

$$O\% = 100 - (C\% + H\% + N\% + S\% + Ash\%) \quad (3.1)$$



Figure 3.7: The elemental analyzer used in the ultimate analysis of composite wastes.

3.3.3 Calorific value determination

Calorific values of composite waste samples were realized with the LECO AC600 automatic calorimeter device shown in Figure 3.8 with the method of ISO 1928:1995. For the analysis, around 1 gram of each pellet sample was weighed and placed in the crucible. After the weighting, the crucible was installed into the vessel (calorimeter bomb) and the cap of the vessel was fixed. The vessel was filled with oxygen to obtain complete oxidation during the analysis. At the beginning of the analysis, the sample was ignited with the help of a firing wire. The calorific value of the sample was determined by measuring the temperature change of the water in which the vessel was submerged into it.

In the analyzes performed with the automatic calorimeter, lower heating values (LHV) were obtained. The higher heating values (HHV) of the waste samples were calculated in kcal/kg by using the LHV values obtained by the calorimeter device, the moisture contents from the proximate analysis, and H% and O% contents from the ultimate analysis (Equation 3.2).

$$HHV = LHV + 0.212 * H\% + 0.0245 * Moisture\% + 0.008 * O\% \quad (3.2)$$



Figure 3.8: Automatic calorimeter used to determine samples' calorific values.

3.3.4 Chemical composition of ash

Ashing for cellulose-based composite label waste samples was carried out in the oxidative atmosphere in a high-temperature furnace. A sample of 10 grams from pellets belonging to cellulose-based samples was placed in ceramic crucibles and ash was obtained in the high-temperature furnace (Magma Therm) under the conditions of the heating rate of 10°C/min, the final temperature of 900°C and isothermal standby for 30 minutes.

Since the ash content of composite label wastes of plastic origin is very low, no studies have been conducted on the ash analysis of these samples. The mineral contents of the cellulose-based samples (C(1)-C(6)) were performed by inductively coupled plasma optical emission spectroscopy (Perkin Elmer Optima 2100DV) and X-ray Fluorescence Spectrometer (Philips PW-2404).

The sample solution for quantitative analysis by ICP was prepared as follows: Samples subjected to digestion were weighed 0.3 g and dissolved by microwave at 1400 W by adding 2 ml of HF (%99.99), 1 ml HCl (%99.99), 6 ml HNO₃ (%99.99) in a teflon container. As a result of the procedure, 12 ml of 5% boric acid was added and the fluorine ions were complexed again with the microwave oven program. After dissolving with a microwave oven, the solutions are diluted to 50 ml. The elements Ca, Si, Al, Mg, Fe, Ti, P, Na, K, and Zn in solutions were analyzed by Perkin Elmer Optima 2100 DV inductively coupled plasma-optical emission spectroscopy.

3.3.5 Thermal gravimetric analysis

Thermal behaviors of composite waste samples in an inert atmosphere (pyrolysis conditions) were obtained via a thermal gravimetric analyzer (TA TGA 55) for a pre-specified heating ramp and final temperature. These analyses were aiming to simulate the pyrolysis behaviors of samples. The heating ramp and final temperature were chosen as 10°C/min and 900°C respectively. Isothermal standby time at 900°C is set to 15 minutes. Nitrogen flow was set to 100 ml/min during the whole analysis. Inert atmosphere conditions were ensured with this nitrogen flow. The instrument used in the ultimate analysis is shown in Figure 3.9.

In addition to simulating pyrolysis behaviors, derivatives of the TGA curves (DTG) were used to obtain approximate amounts of cellulose and hemicellulose contents of the composite waste samples. For this purpose, DTG peaks of pure cellulose and hemicellulose acquired from literature for different heating rates under pyrolysis conditions were compared with the peaks obtained from composite waste samples DTG peaks (Ding et al., 2020).

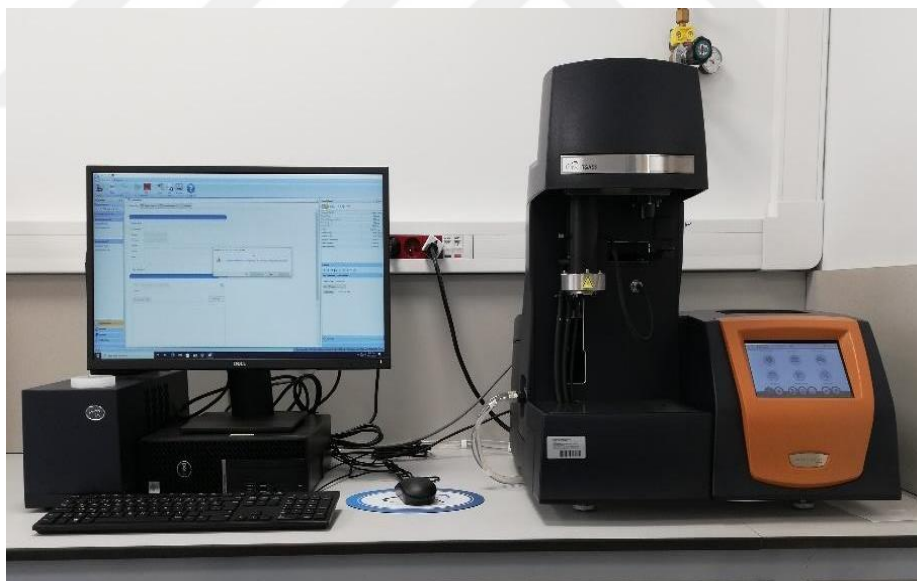


Figure 3.9: Atmospheric TGA device used in the analyses.

3.4 Pyrolysis Tests of Composite Waste Samples

Following the characterization studies, a series of pyrolysis tests were carried out to examine the pyrolysis behaviors and to observe product yields/distributions of composite waste samples. These tests were carried out in a laboratory-scale batch pyrolysis reactor with a feeding capacity of approximately 1 kg and a pilot-scale

continuous pyrolysis reactor with a feeding capacity of approximately 5 kg/hour. In order to examine the pyrolysis behaviors of composite waste pellets, experiments were first carried out for different pyrolysis temperatures, different recipes in the batch pyrolysis reactor, and the effects of temperature and plastic rate in the feedstock on syngas content and product yields were observed. In light of the findings obtained from the studies carried out with the batch pyrolysis system, pilot-scale test procedures and process conditions were designated.

Pyrolysis tests in the batch reactor were carried out with pellets of cellulose-based and plastic-based composite label waste samples and CWP. In these studies, different recipes were obtained by considering the annual formation amount of these composite wastes in the industry. Information about the amount of formation in the industry was obtained from Frimpeks A.Ş. On the basis of these amounts, it has been determined how the cellulose-based and plastic-based label wastes will be proportioned within themselves. According to Frimpeks A.Ş, the proportion of cellulose-based composite wastes formed in the industry is 55.0% C(1), 18.0% C(2), 14.0% C(3), 7.0% C(4), 4.0% C(5), 2.0% C(6), and the formation rate of plastic-based composite wastes are 70.0% P(1), 26.0% P(2), 4.0% P(3). In the feeding mixture, different experiments were carried out on which the cellulose-based and plastic-based composite wastes distributed according to these ratios could have in the total feed, and the recipes given in Table 3.2 were established. In order to determine the pyrolysis behavior and product yields of CWP and to compare them with domestic composite wastes, testing was carried out with recipe number 4 in the batch and continuous pyrolysis reactors.

Table 3.2: Feedstock recipes used in pyrolysis tests.

Recipe No	Composition		
	Cellulose - Based	Plastic - Based	CWP
1	%100	0%	0%
2	%85.0	%15.0	0%
3	%70.0	%30.0	0%
4	0%	0%	%100

3.4.1 Pyrolysis tests in the batch system

A series of experiments were initially carried out in the batch pyrolysis system in order to investigate the pyrolysis behavior of composite label wastes and CWP. For this purpose, pyrolysis tests were carried out with Recipe 1, 2, 3, and 4 at three different pyrolysis temperatures. The ultimate goal of these studies is to examine the effect of temperature and the addition of plastic to the feedstock on the distribution and content of pyrolysis products. These temperature values were determined based on the temperatures tested for cellulose-plastic mixtures in the literature and the limitations of the system. Temperature values of 450°C, 650°C and, 850°C were selected as pyrolysis temperatures. For the pyrolysis tests at 450°C and, 650°C it was expected to obtain wax formation according to the information mentioned in Section 2. In this respect, 850°C was chosen to examine the effect of high-temperature pyrolysis conditions on wax yield in cellulose-based and plastic-based composite waste mixtures' pyrolysis.

The system, in which experiments were carried out, has a batch reactor. The reactor vessel contains a mixer inside itself and the reactor has an average feed capacity of 1 kg. The system has an oil trap, a gas cooling column, and a scrubber. The heat is provided by electric resistances in the oven. The syngas produced in the system can be analyzed with the online syngas analyzer (MRU SWG 200) and the syngas composition can be monitored throughout the experiment. Including the analyzed syngas, the entire syngas produced in the system can be disposed of with the help of a propane pilot flame in the flare system and sent to the chimney. Photographs and block diagram of the batch pyrolysis system are shown in Figure 3.10 and 3.11 respectively.

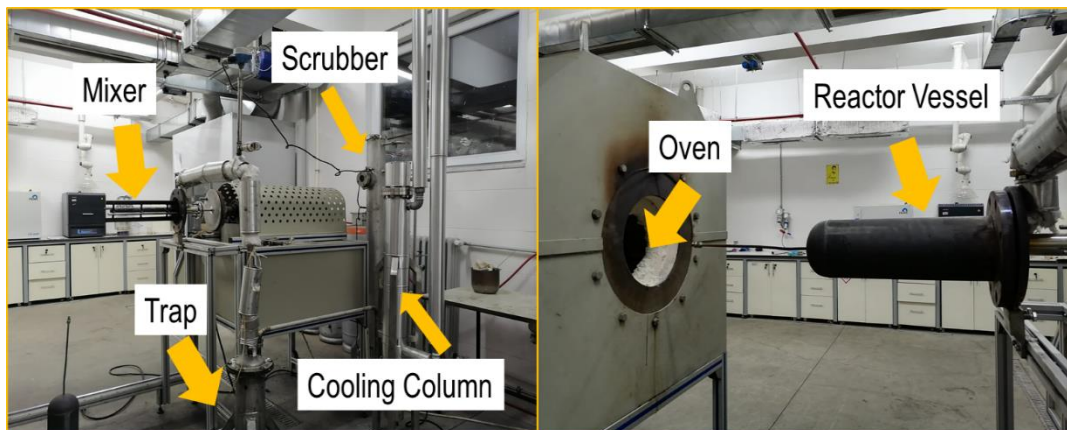


Figure 3.10: Batch pyrolysis system.

The trap shown in the block diagram of the system was used to collect aliphatic structures (wax). The wax structure, which can be frozen at room temperature, can be formed in experiments where plastic-based composite wastes are found in the feed mixture. As mentioned in Section 2.5.1, the wax formation can be seen in plastic pyrolysis processes performed at temperatures of approximately 700°C and below. The trap was used to collect this creamy wax structure at ambient temperature. In addition to the aliphatic structures, pyrolytic oil was collected by condensing liquid vapors in the cooling column with cooling water. The water has a temperature value of 5 °C and it is provided by an industrial chiller. The cooling column is a shell-tube type of heat exchanger. The cooling water passing through the tube part ensures that the liquid vapors in contact with the shell part condense. Pyrolytic oil condensed in the column is collected in the lower chamber of the column. A scrubber is available in the system in order to remove dust, particles, and similar structures that the gas that is free from liquid vapor and heavy structures can carry. In the scrubber, washing is carried out with the help of water. Wash water is sprayed into the column from the upper point with the help of an electric pump and retracted from the lower chamber. Some amount of the washed gas is fed into the online syngas analyzer (Figure 3.12). The volumetric concentrations of O₂, CO₂, CO, H₂, and CH₄ gases in the analyzed syngas were recorded in certain periods, and graphs were prepared. The analyzed syngas and the syngas coming out of the system are then fed into the flare system. In the flare system, with the help of a pilot flame provided by propane gas, the synthesis gas is disposed of by burning and sent to the chimney.

The char formed in the pyrolysis process was taken from the system after the reactor vessel reached room temperature. Char samples were preserved under appropriate storage conditions for characterization studies.

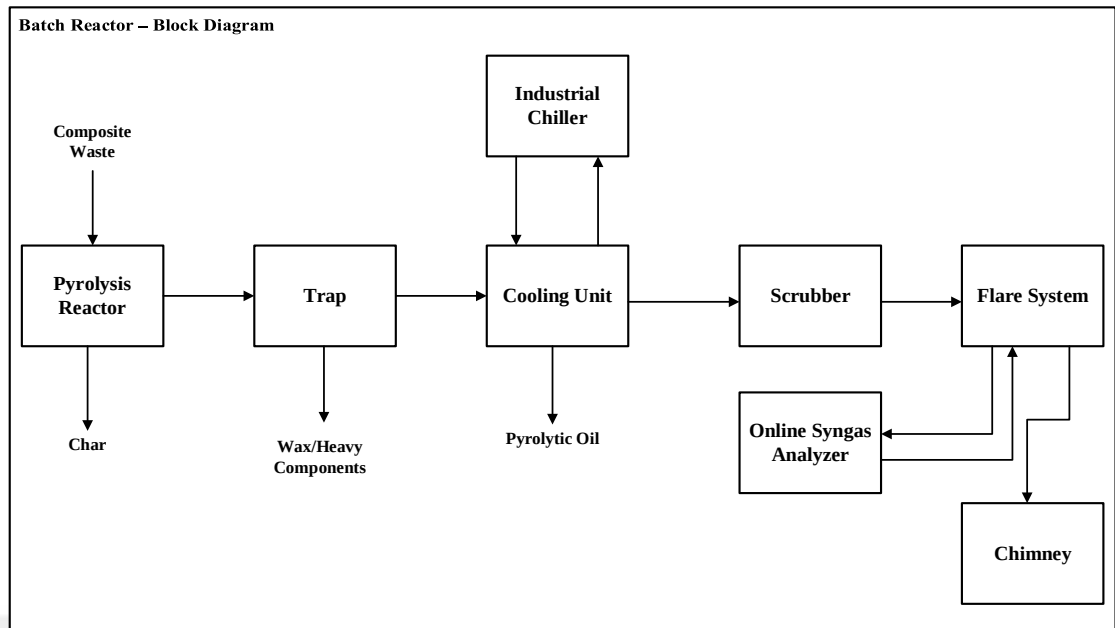


Figure 3.11: Block diagram of the batch pyrolysis system.



Figure 3.12: Online syngas analyzer used in pyrolysis test.

3.4.1.1 Process operating conditions

The operating conditions of the experiments performed in the batch pyrolysis system are summarized in Table 3.3. In the experiments to be carried out in the batch pyrolysis system, the amount of 500 grams of pellet mixture (recipe) given in Table 3.2 was fed to the reactor vessel shown in Figure 3.10, and the system was fixed with the help of a bolt. The oven shown in Figure 3.10 was set to the temperature value at which the experiment will be carried out through the system's control panel and is expected to

reach the desired temperature. After the oven reached the set temperature, the pyrolysis process was started by pushing forward the oven towards the reactor vessel with the help of the rail system.

During the period when the pyrolysis process continued, the temperature of the gas coming out of the reactor was monitored instantaneously with the help of the thermocouple in the reactor output line. During the experiment, the cooling column and scrubber actively worked. At the reactor's rotational rate of 5 Hz, the reactor's feed mixture is mixed homogeneously throughout the pyrolysis. The pyrolytic oil is collected in glass containers at certain intervals and removed from the system to be stored in a proper environment. During the pyrolysis process, the syngas analyzer took measurements instantaneously and these measurement values were recorded. After the gas product and liquid product formation was finished, the electric resistances in the system were turned off and the system was put into cooling. After sufficient cooling was achieved, the reactor vessel was dismantled and the char was removed from the system.

Table 3.3: Process operating conditions of experiments carried out in batch pyrolysis system.

Process Operating Conditions	
Feed Ratio	500 grams
Pyrolysis Temperature	450°C, 650°C, 850°C
Rotation Speed (Mixer)	5 Hz
Cooling Water	5°C
Scrubber	Active

3.4.2 Pyrolysis tests in the pilot scale continuous system

In light of the results obtained from the studies carried out in the batch pyrolysis reactor for composite label waste samples, a series of pyrolysis tests were carried out using the continuous pyrolysis reactor system for recipes given in Table 3.2. Images of the continuous system in which pyrolysis tests were carried out are shown in Figures 3.13, 3.14, 3.15, and 3.16. These tests aimed to reach the composition and quantity information of the syngas obtained in continuous feeding and steady-state conditions for different recipes. The experiments carried out on the continuous pyrolysis reactor, which is designed to operate at high temperatures, were based on the temperature value

at which maximum syngas and H₂ yields were obtained in the batch pyrolysis reactor. In addition, as stated in the literature, it is aimed to reach the maximum amount of syngas efficiency by reaching HTP conditions (>800°C) in this system. The block diagram of the continuous system is shown in Figure 3.17.

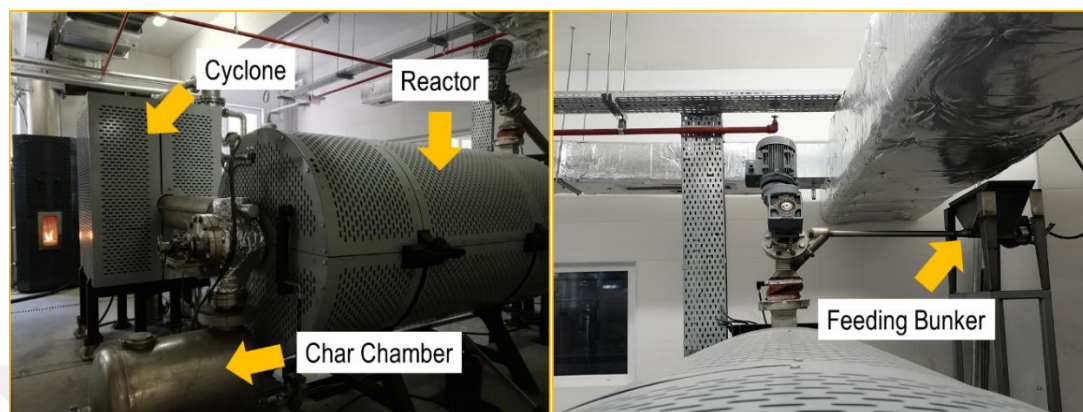


Figure 3.13: Reactor, char chamber, cyclone, and the feeding bunker units of the continuous pyrolysis tests system.

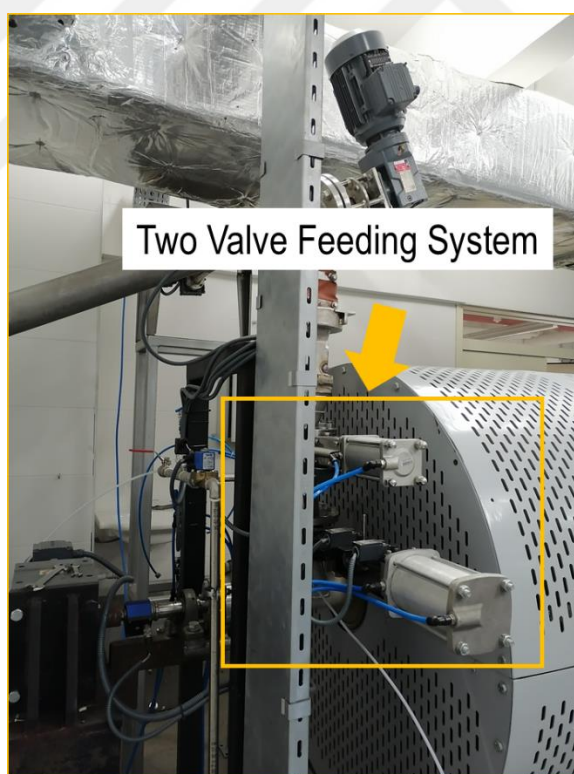


Figure 3.14: Two valve feeding system on the reactor entrance.

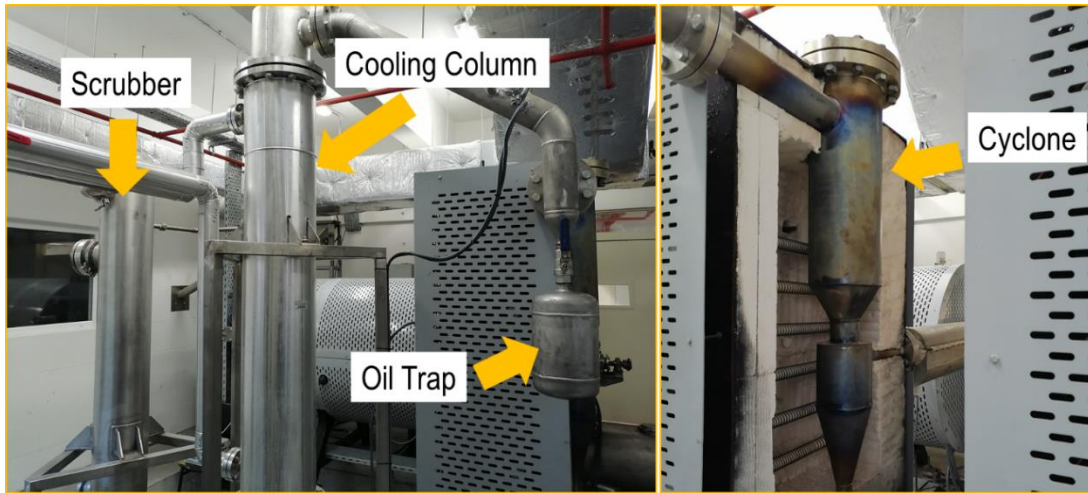


Figure 3.15: Cyclone (inside), oil trap, cooling column, and the scrubber units of the continuous pyrolysis tests system.

The units of the system used in continuous pyrolysis tests can be summarized as follows; feeding bunker, pyrolysis reactor, charcollecting chamber, thermal cracking unit/cyclone, gas cooling unit, industrial chiller, scrubber, online syngas analyzer, and flare system. The type of reactor can be classified as an Auger reactor according to pyrolysis reactor types in the literature mentioned in Section 2. As a typical Auger reactor, the reactor used in this study has an enclosed shell with an endless screw inside. The feeding system (Figure 3.13) supplies feedstock into the reactor from the bunker and the feedstock moves forward inside the reactor with the help of an endless screw. The char formed during the pyrolysis drops down to the char chamber (Figure 3.13) at the end of the reactor.



Figure 3.16: Flare system that disposes of the syngas obtained during pyrolysis tests.

The Auger reactor used in this study has a diameter of 30 cm and a length of 230 cm (Figure 3.18). The outside of the reactor is surrounded by an insulation material that ensures the system avoids any heat loss from the enclosed shell.

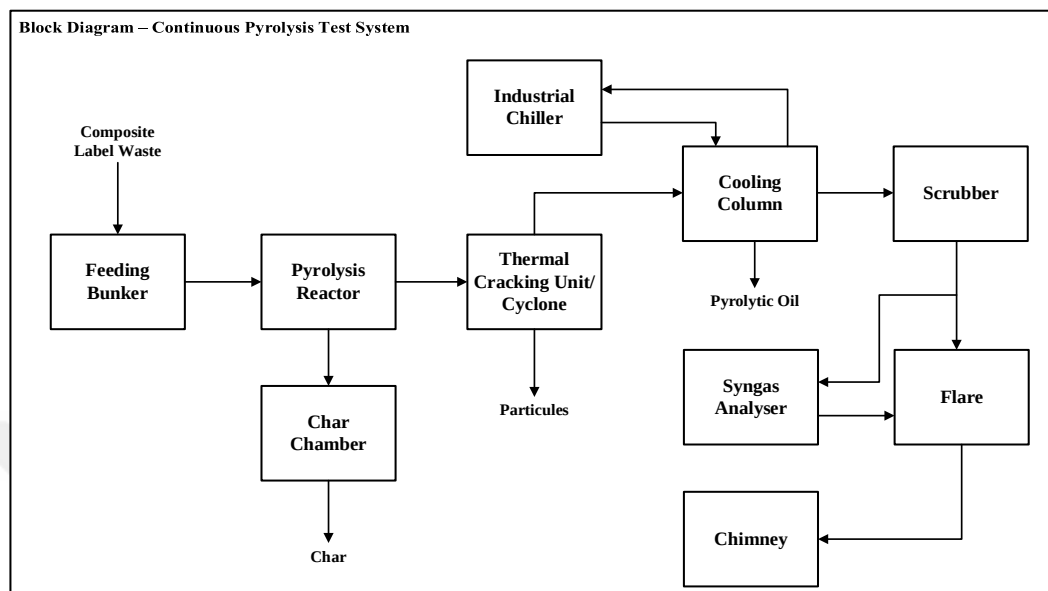


Figure 3.17: Block diagram of the continuous pyrolysis test system.

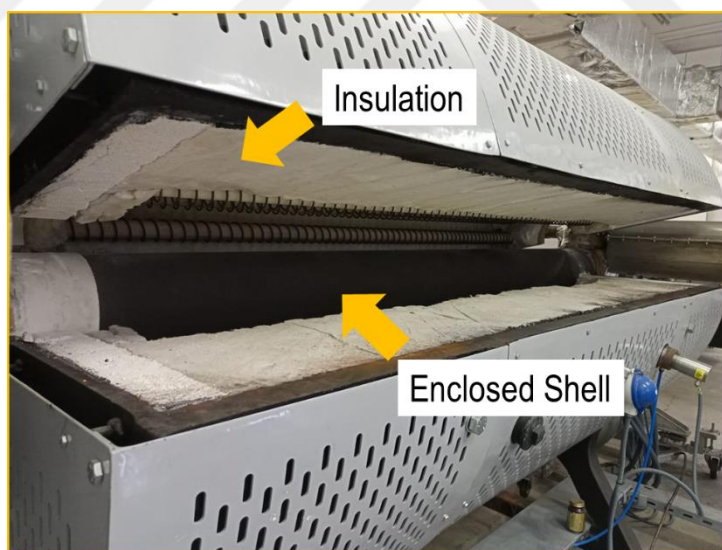


Figure 3.18: Enclosed shell which has an endless screw inside and its insulation.

The continuous pyrolysis test system has an average hourly feed capacity of 5 kg. The reactor within the system has an electric resistance heating that can reach a temperature value of approximately 1000 °C. Similarly, the thermal cracking unit/cyclone (Figure 3.15) has an electric heating system and is capable of heating up to a temperature value of 700 °C. The gas cooling unit in the system (Figure 3.15) works integrated into an industrial chiller and the cooling process is carried out with cooling water with a

temperature value of 5 °C. This column, in which the cooling process is carried out, has a shell and tube-type design. The pyrolytic oil formed in pyrolysis is condensed in this column. The scrubber unit in the system (Figure 3.15) recirculates the wash water in the column with the help of a pump and performs the washing of the raw syngas with the help of the sprinkler at the top of the column.

Some portion of the cooled and cleaned syngas is fed to the syngas analyzer (MRU SWG 200 Figure 3.12), which works integrated into the system and performs online analysis, and the volumetric ratios of O₂, CO₂, CO, H₂, and CH₄ gases in the syngas content are obtained instantly. The remaining amount of the cooled and cleaned syngas and analyzed gas is disposed of by the flare system (Figure 3.15) with the help of the propane pilot flame. The disposed of gas first passes through a cooling tower and its temperature is lowered. The cooled combustion gases are finally fed into the chimney.

The char formed during the pyrolysis process accumulates in the char chamber at the reactor outlet. The accumulated char was removed from the system after the completion of the experiment and preserved under appropriate conditions.

3.4.2.1 Process operating conditions

In the pyrolysis of four different recipes in the continuous pyrolysis system, parameters that must be controlled were adjusted and monitored with PLC-SCADA (Programmable Logic Controller – Supervisory Control and Data Acquisition) system on a computer. Setting the operating temperatures of the units within the system, adjusting the rotational speed of the endless screw, and monitoring the pressure/temperature values were carried out over the computer with the help of the PLC-SCADA (Figure 3.19).

The process flow diagram in the continuous pyrolysis system, including the points where temperature values are measured and set, is shown in Figure 3.20. In the pyrolysis experiments carried out with four different recipes, the pyrolysis temperature is assumed to be the temperature where the T1 thermocouple takes measurements. This temperature shows the temperature value of the enclosed reactor. The temperature of T2 indicates the temperature of the gap between the insulation material surrounding the reactor exterior and the reactor wall. The operating temperature of the pyrolysis reactor, coded as R101, was set to 900°C before starting the pyrolysis and the system was expected to reach the desired temperature. In addition to the reactor, where

secondary thermal cracking reactions will take place, the cyclone unit coded C101 is set to the operating temperature of 600°C, and the temperature in the unit is regularly checked with the help of the thermocouple coded T3. Before the pyrolysis process, in addition to R101 and C101, the gas washing unit coded C102 and the industrial chiller with the code U101 were switched on. In this way, it is ensured that the cooling water reaches the desired 5°C temperature value before the pyrolysis. After the T1 and T3 temperature values reached the desired values of 900°C and 600°C, the pilot flame was activated with the help of the air and propane mixture provided by P102 in the U102 coded flare.

After the pyrolysis system reached the set temperature values, the mixture of the desired recipe was filled into the bunker (Figure 3.13). The bunker is activated and adjusted for a 2.5 kg per hour feeding rate. In order to provide the desired feed amount, calibration tests were performed for four different recipes while the system was cold and the required bunker operating speeds were determined for 2.5 kg per hour. The feedstock which starts to be loaded into the system from the bunker (stream 2), first falls on the two-valve system at the reactor entrance (Figure 3.14). The two-valve system is designed to prevent air entrance to the reactor during pyrolysis. The feedstock poured over the first valve is poured over the second valve by opening the first valve when the second valve is closed.

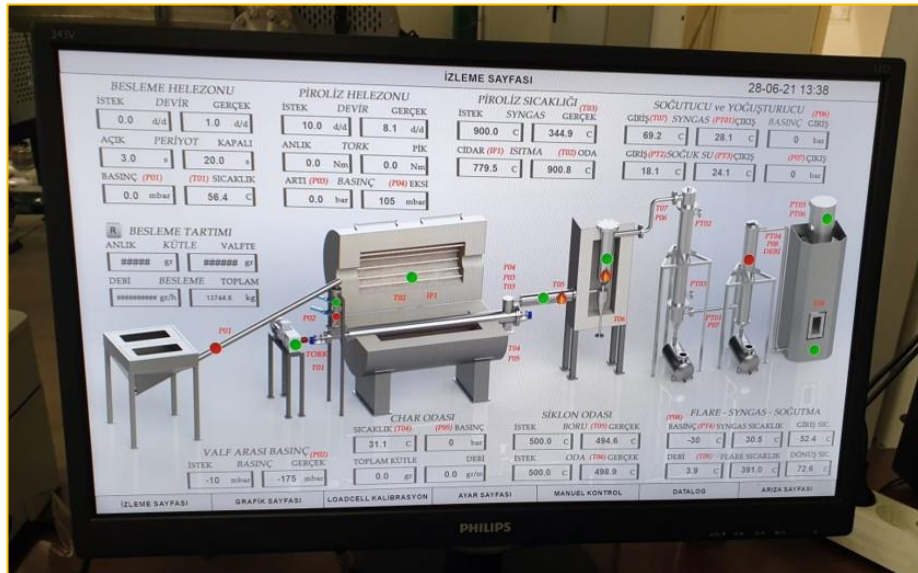


Figure 3.17: PLC-SCADA interface of the continuous pyrolysis system.

The feedstock entering the reactor is pyrolyzed by moving through the reactor with the help of an endless screw. The rotation speed of the screw was set to 10 rpm for all four different recipes. This value was determined in line with the information and experience obtained in previous pyrolysis studies carried out in the same system. The char formed as a result of pyrolysis in R101 is poured into the char chamber T101 by stream number 4. The liquid vapors and gaseous products formed as a result of pyrolysis are fed to the C101 unit with stream number 3 to the secondary thermal cracking process. Another function of the C101 unit is to clean the gaseous product and liquid vapors from the particles with the help of the cyclone inside. The solid particles separated in the cyclone are collected in the T102 tank with stream 5 and are removed from the system at the end of the experiment.

Liquid vapors and gaseous products, which are exposed to thermal cracking at 600°C in the C101 unit, are fed to the C102 coded gas cooling unit by following stream 6. Before entering C102, the T103 tank is located on the line in order to collect the structures that can condense at room temperature. In addition, the temperature of the hot stream coming out of C101 is measured with the T3 thermocouple. The liquid vapors and gaseous product entering C102 are cooled with 5°C cooling water and the pyrolytic oil is collected in the T104 tank located under the column (stream 8). Cooling water at 5°C temperature is supplied from U101 coded industrial chiller. The cooled gas product is fed to the scrubber unit with code C103 through stream 9. The temperature of the cold gas is monitored with the T4-coded thermocouple on line 9. With the help of the P101 coded pump, the wash water is fed to the upper part of the C103, where it is sprayed homogeneously into the scrubber and comes into contact with the gas. The cooled and cleaned gas (syngas) follows stream 10 to the flare system. With the additional connection on stream 10, some of the syngas is fed to the online syngas analyzer, and the rest is fed to the flare unit coded U102, following stream 10. Here, the syngas mixed with the air provided by the P103-coded blower is burned with the help of the pilot flame and disposed of. Pilot flame is obtained by mixing the propane gas supplied from the cylinder with the air supplied by the P102-coded blower. Gases formed as a result of the combustion of the syngas in U102 are fed to the cooling tower with the code U103, following stream 11. The temperature of the combustion gases is monitored with a T5-coded thermocouple before entering the

cooling tower. The combustion gases cooled by the water supplied from the water main in U103 are finally sent to the chimney with stream 12.

The process operating conditions of the studies performed with four different recipes in the continuous pyrolysis system, the controlled parameters, and the set values of the units are summarized in Table 3.4. After the completion of the pyrolysis process and the cooling of the system, the char and pyrolytic oil samples were collected from the relevant tanks and stored under suitable conditions. Details of the characterization of these products are given in the relevant sections.

Table 3.4: Operating conditions and controlled parameters of the continuous pyrolysis test system.

Process Operating Conditions		
Feed Ratio	2.5 kg per hour	
Equipment	Controlled Parameter	Set Value
R101 – Pyrolysis Reactor	Temperature	900°C
R101 – Pyrolysis Reactor	Screw Rotation Speed	10 rpm
C101 – Thermal Cracking	Temperature	600°C
Unit		
C102 – Cooling Column	Active/Inactive	Active
C103-Scrubber	Active/Inactive	Active
U102 - Flare	Active/Inactive	Active
U101 - Chiller	Cooling Water Temperature	5°C

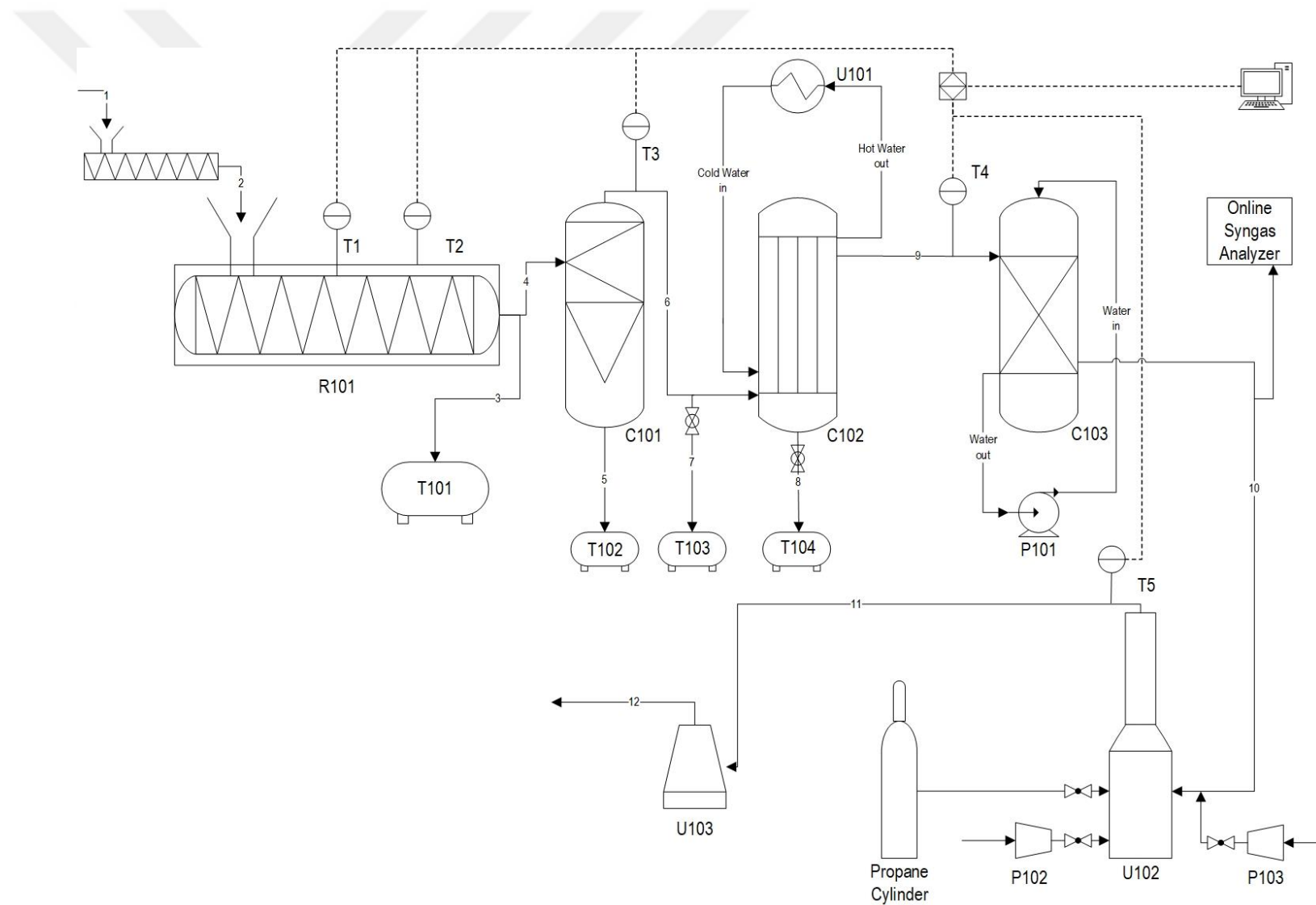


Figure 3.18: Process flow diagram of the continuous pyrolysis test system.

3.5 Characterization of Pyrolysis Products

Characteristics of char and pyrolytic oil were used to observe whether the experiment was archive desired pyrolysis conditions or not. For the char, proximate analysis results on the basis of volatile matter content show the efficiency of the thermal decomposition during the pyrolysis. In addition to proximate analysis, ultimate analysis was done for char samples to determine the C, H, N, S, and O content of the char samples. By comparing the fixed carbon amount of char from proximate analysis and the total carbon amount from the ultimate analysis it was examined that the volatile carbon content of char. As mentioned before, the percentage of the volatile content of char was aimed to keep reduced with an efficient thermal degradation during the pyrolysis experiments. Also, the calorific values of the char samples were determined for establishing a relation between the calorific value of char and feedstock characteristics. As mentioned in Section 2, the calorific value of char is directly affected by the plastic amount in the feedstock. This effect was examined for the pyrolysis of composite waste samples in this study. The same procedures and instruments in the sub-sections 3.3.1, 3.3.2, and 3.3.3 were used in the char characterization.

Due to the high heterogeneity of pyrolytic oil, calorific value determination and ultimate analysis procedures were only performed for selected pyrolytic oil samples. In addition to these analyses, water contents of the aqueous phases were also determined. For the water content determination, pyrolytic oil samples were filtered by a filtering system that includes a quantitative filter paper (grade 391), a Buchner funnel, a flask, and a vacuum pump. The amount of water in the filtered pyrolytic oil sample (aqueous phase) was determined according to ASTM E203-16 standard in an automatic titration device (Methrom KF 915) by the Volumetric KF (Karl-Fischer) Titration Method. The instrument used in water content determination is shown in Figure 3.21.



Figure 3.19: Automatic titration instrument used for Volumetric KF Titration.

4. RESULTS AND DISCUSSION

In this section, the results and discussions of the experimental studies mentioned in Section 3 will be included. The results obtained in characterization studies of composite waste samples, findings of pyrolysis tests performed with composite waste samples in both laboratory and pilot scales, and the characteristics of pyrolysis products were examined in the relevant sub-sections.

4.1 Characterization Results of Composite Waste Samples

Following the sample preparation process, which was discussed in detail in Section 3.2, characterization studies were carried out for cellulose-based composite label wastes, plastic-based composite label wastes, and CWP. First of all, proximate analysis was performed with the samples in the pellet form, and moisture, volatile content, ash, and fixed carbon amounts were investigated. Then, ultimate analysis was performed for the same samples, and carbon, hydrogen, nitrogen, and sulfur amounts were determined. The amount of oxygen was calculated with Equation 3.1 using the ash percentage from the proximate analysis and the result of the ultimate analysis. The calorific values of the samples were determined with the help of an automatic calorimeter device and the HHV values were calculated from Equation 3.2 by using the moisture, hydrogen, and oxygen contents of the samples. ICP-OES and XRF analyzes were performed to determine the chemical structure of the ash. Finally, a TGA study was carried out in order to examine the pyrolysis behavior of the pellet samples and to determine the DTG peaks of samples.

4.1.1 Proximate analysis results

Preliminary information about the composite wastes was obtained by determining the quantities of moisture (M), volatile matter (VM), ash (A), and fixed carbon (FC) as percentages in the original samples. Results obtained in the proximate analysis of ten different samples are shown in Table 4.1.

For the cellulose-based composite label wastes, moisture and volatile matter contents show similarities between them. The ash content of the C(1) sample is remarkably

different from other cellulose-based composite waste samples. On the other hand, the ash contents of cellulose-based waste samples except for C(1) have similar ash contents. For the fixed carbon, percentages are changing between the range of 2.80% and 4.90% for the cellulose-based composite waste samples. Sample C(6) has a great difference for the fixed carbon amount which has a value of 10.35%. For the volatile matter, amounts are changed in the range between 75.10-82.50%. Since the proximate analysis results of cellulose and hemicellulose in the literature do not match with the cellulose-based waste samples' results, it can be asserted that the difference originated from the additives that consist in the samples.

Table 4.1: Proximate analysis results of composite label waste samples and CWP.

Waste	M (%)	VM (%)	A (%)	FC (%)
C(1)	4.65	75.10	17.45	2.80
C(2)	4.78	80.10	10.92	4.20
C(3)	4.70	79.40	11.37	4.55
C(4)	5.35	82.50	9.55	2.51
C(5)	5.25	80.90	8.95	4.90
C(6)	8.17	81.19	8.46	10.35
P(1)	0.20	98.40	1.30	0.10
P(2)	0.20	99.20	0.59	0.01
P(3)	0.50	87.45	11.78	0.27
CWP	2.10	85.52	4.98	7.40

For the plastic-based waste samples, low moisture, ash, and fixed carbon contents are the general characteristics of these ones. However, sample P(3) has a higher amount of ash and a lower amount of volatile matter content. Lastly, CWP has its own characteristic that is similar to the average of the cellulose and plastic-based waste samples' proximate analysis results. This similarity was an expected result on the basis of information got from the company that the CWP's content includes both cellulose-based and plastic-based wastes.

4.1.2 Ultimate analysis results

Elemental compositions of composite waste samples are shown in Table 4.2. The ultimate analysis results of cellulose-based samples show that the elemental composition of these waste samples is close to each other. When the elemental carbon content was examined, it was seen that the carbon content of the samples were in the ranges between 36.77-43.83%. Considering the fixed carbon determined in the proximate analysis, it is seen that the majority of the carbon in the samples comes from its volatile matter. When the pyrolysis process is considered, it can be said that the high carbon in the volatile matter will increase the hydrocarbon yield in the vapor phases. In addition, cellulose-based waste samples were found to have low nitrogen and sulfur but high oxygen contents.

The results obtained for plastic-based waste samples show that the samples had a high carbon and hydrogen content, as expected. Given the chemical nature of plastics, the results obtained were within the expected range. The fact that the P(3) sample contained less carbon and hydrogen and more oxygen than P(1) and P(2) was due to its high ash content.

The results show that the CWP contained more carbon and hydrogen than cellulose-based wastes. In contrast, CWP had less carbon and hydrogen and more oxygen than P(1) and P(2) and were within the expected ranges for the cellulose-plastic mixture. On the other hand, it has been found to have less sulfur content than composite label waste samples.

Table 4.2: Elemental compositions of composite waste samples.

Waste	C (%)	H (%)	N (%)	S (%)	O (%)
C(1)	40.16	5.37	0.03	0.22	54.22
C(2)	43.73	6.27	0.07	0.53	49.40
C(3)	43.83	6.25	0.09	0.45	49.38
C(4)	43.17	6.33	0.05	0.28	50.17
C(5)	40.82	5.93	0.06	0.22	52.97
C(6)	36.77	5.33	0.16	0.32	57.42
P(1)	78.24	11.96	0.11	0.25	9.44
P(2)	80.76	12.95	0.05	0.27	5.97
P(3)	62.09	4.14	0.03	0.18	33.56
CWP	59.13	8.50	0.52	0.05	31.80

4.1.3 Calorific values

The HHV values of the composite waste samples calculated with the help of Equation 3.2 are given in Table 4.3. While the HHV values of cellulose-based samples vary in the range of 14.34-18.95 MJ/kg, the HHV values of plastic-based samples with ash and oxygen content much higher than cellulose-based samples. HHV values for plastic samples vary in the range of 23.02- 43.21 MJ/kg. The HHV value of the P(3) sample was 23.02 MJ/kg, comparably lower than the other plastic samples and this was due to its high ash content. Although the HHV of the CWP sample was higher than the cellulose-based wastes but lower than the plastic-based P(1) and P(2) ones. The HHV of CWP, which is a mixture of cellulose-based and plastic-based wastes, was in the expected range.

Table 4.3: Calorific values of composite waste samples.

Waste	HHV MJ/kg	HHV kcal/kg
C(1)	15.23	3636.86
C(2)	18.87	4507.84
C(3)	18.95	4524.83
C(4)	18.81	4491.87
C(5)	16.68	3982.81
C(6)	14.34	3424.79
P(1)	39.94	9539.62
P(2)	43.21	10320.80
P(3)	23.02	5497.67
CWP	27.12	6477.10

Following the proximate analysis, ultimate analysis, and calorific value determination performed for composite wastes, the average values for the recipes to be fed to the reactors in the pyrolysis tests were calculated. These values were calculated by using analysis results of each waste and the ratio of that waste in the feed mixture. Results are shown in Table 4.4 for different recipes (please refer to Table 3.2 for the recipes).

Table 4.4: Average amounts of analysis results for different feed mixtures.

Recipe	M	VM	A	FC	C	H	N	S	O	HHV
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	MJ/kg
1	4.87	74.81	14.22	3.37	35.59	4.95	0.04	0.26	44.94	16.69
2	4.17	78.31	12.32	2.88	41.82	5.97	0.05	0.26	39.58	20.20
3	3.47	81.82	10.42	2.38	48.05	6.99	0.06	0.26	34.23	23.71
4	2.10	85.52	4.98	7.40	56.19	8.08	0.49	0.05	30.22	27.12

The sum of fixed carbon and ash content of the recipes shown in Table 4.4 were used to determine theoretical char amounts that should be obtained in pyrolysis experiments. Calculations used in the determination and comparison of theoretical and obtained chars in experiments are shown in section 4.2.

4.1.4 Chemical compositions of ash samples

XRF analysis results are given in Table 4.5 in comparison with ICP results. As can be seen in Table 4.5, all cellulose-based samples are shown to contain calcium oxide, silicon oxide, and aluminum oxide. The mineral substance with the predominantly highest content is calcium oxide, which is thought to be caused by additives such as calcium carbonate and precipitate calcium carbonate, which are known to be used in label coatings. It is seen that the total inorganic matter content calculation results made using the ICP analysis results are in line with the proximate analysis results given in Table 4.1.

Table 4.5 provides XRF and ICP results comparatively. Since XRF analyses were performed on ash, ICP analyses were also normalized to 100% as the amount of inorganic matter in the ash. The comparison study shows that the ICP results are compatible with the XRF results. The amount of zinc oxide detected by both methods in the C(2) sample indicates that zinc oxide may have been used as the pigment in this sample.

Table 4.5: Results of ash analyses performed in ICP and comparison with XRF results.

The results of the analysis performed by inductively coupled plasma optical emission spectroscopy (ICP).											
Sample,% Weight	CaO	SiO ₂	Al ₂ O ₃	Na ₂ O	MgO	TiO ₂	Fe ₂ O ₃	P ₂ O ₅	K ₂ O	ZnO	Total
C(1)	14,2	2,2	1,9	0,10	0,18	0,03	0,07	0,016	0,016	0,003	18,70
C(2)	6,2	2,9	2,4	0,14	0,15	0,07	0,05	0,028	0,014	0,021	12,10
C(3)	4,2	4,5	3,6	0,05	0,15	0,11	0,16	0,019	0,019	0,000	12,70
C(4)	7,8	0,3	0,2	0,12	0,09	0,01	0,02	0,035	0,008	0,008	8,60
C(5)	7,5	3,2	1,8	0,15	0,38	0,05	0,08	0,027	0,017	0,004	13,20
C(6)	11,6	2,1	1,5	0,18	0,52	0,07	0,12	0,039	0,000	0,009	16,20
Comparison of analyses performed on ash with XRF with analyses performed with ICP.											
Sample, %Weight		CaO	SiO ₂	Al ₂ O ₃	Na ₂ O	MgO	TiO ₂	Fe ₂ O ₃	P ₂ O ₅	K ₂ O	ZnO
C(1)	ICP	75,87	11,75	10,15	0,53	0,96	0,16	0,37	0,08	0,11	0,00
	XRF	78,00	10,98	8,49	0,68	1,00	0,19	0,45	0,1	0,1	0,00
C(2)	ICP	51,76	24,21	20,04	1,17	1,34	0,58	0,42	0,24	0,08	0,17
	XRF	55,15	21,81	18,23	1,51	1,34	0,71	0,67	0,25	0,14	0,19
C(3)	ICP	32,76	35,10	28,08	0,39	1,25	0,86	1,25	0,15	0,16	0,00
	XRF	32,07	35,84	28,20	0,99	1,02	0,93	0,65	0,09	0,13	0,07
C(4)	ICP	90,75	3,49	2,33	1,40	1,05	0,12	0,23	0,4	0,12	0,12
	XRF	91,58	3,62	2,04	1,20	0,93	0,08	0,32	0,11	0,11	0,00
C(5)	ICP	56,79	24,23	13,63	1,14	2,88	0,38	0,61	0,2	0,15	0,00
	XRF	61,19	20,65	12,65	1,30	2,66	0,37	0,9	0,21	0,07	0,00

4.1.5 Thermal behaviors of composite waste samples

The temperature-dependent weight loss graph and derivative thermogravimetric curve (DTG) of the cellulose-based waste samples are shown in Figures 4.1 and 4.2, respectively. When the degradation profiles detected in the thermogravimetric analyzes of the samples under nitrogen flow are examined, it is seen that all cellulose-based samples go through three basic degradation processes after moisture loss. These decays are around 350°C, 400°C, and 700°C respectively. From this point of view, it is concluded that the basic degradation behavior of materials under pyrolysis conditions under nitrogen flow is the same. However, both due to the differences in the additives, ash and fixed-carbon contents of the samples, their thermal degradation rates and degradation peak areas change. When the amount of residue was examined from TGA profiles, it was determined that the highest residue was found for the C(6) sample and the least for the C(5) sample (Figure 4.1). In Figure 4.2, it is seen that the DTG of the cellulose-based composite waste samples has two peaks between 250-450°C. According to the weight loss profiles of cellulose-based samples, their weight changes were calculated as 63.64%, 64.55%, 66.31%, 66.17%, 68.45%, and 55.43% respectively. These results show that the cellulose-based samples might have an average pure cellulose content of 64.09%.

In addition to the degradation profile of cellulose, decay obtained at 700°C is a significant finding for cellulose-based composite wastes. When the pyrolysis behavior of waste paper is examined, it is seen that the thermal degradation of cellulose is followed by the degradation of inorganic compounds including ink compounds. Since the weight loss at 700°C was observed for all samples with or without ink, it was concluded that the thermal degradation at this temperature can be caused by the presence of other additives in addition to ink.

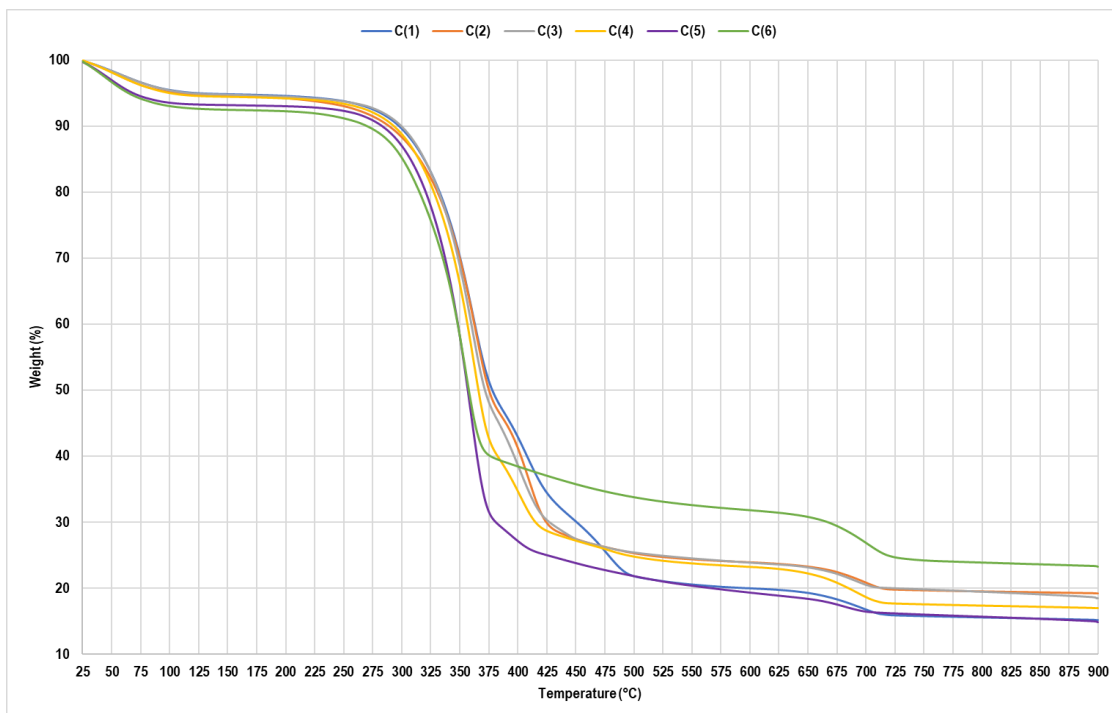


Figure 4.1: Temperature-dependent mass loss curves of cellulose-based samples.

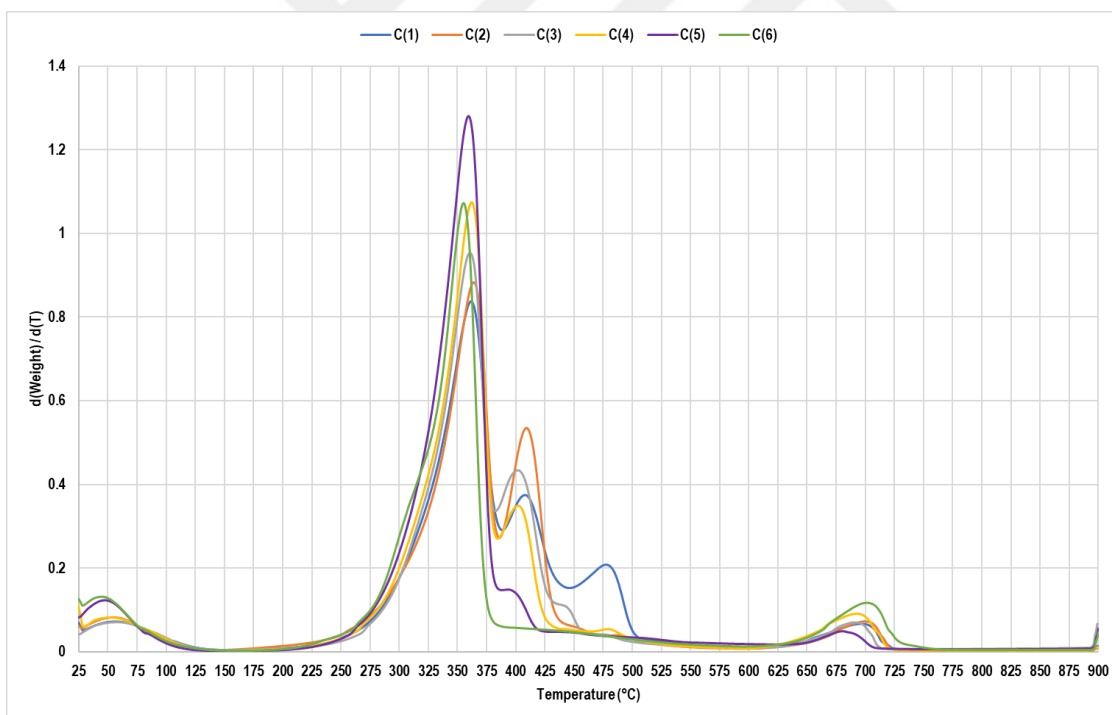


Figure 4.2: DTG curves of cellulose-based samples.

The curves of the temperature-dependent mass loss of plastic-based wastes are shown in Figure 4.3. It was found that three different types of plastic-based waste began to lose mass at 350°C. Samples P(1) and P(2) lost almost all of their mass, and P(3) had a residue of about 10%. Hence, it can be asserted that findings on the residue amounts

are parallel with the ash contents obtained from proximate analysis of plastic-based samples. When the DTG of plastic wastes was examined (Figure 4.4), it was determined that three wastes experienced degradation in the range of 300-500°C. For P(1) and P(2), samples have two peaks at temperature values varying between 300-500°C. However, the P(3) sample has only one peak at the same temperature range. The curve of the temperature-dependent weight loss of CWP is shown in Figure 4.5. When the curve was examined, it was seen that the CWP began to lose mass around 300°C. The mass loss occurred rapidly up to 500°C, after which the sample began to lose mass again at 700°C. After reaching a temperature of 900°C, the sample retained close to 10% of its total mass. It was observed that the thermal degradation profile of CWP has significant similarities with cellulose and plastic-based composite waste samples. These similarities can be seen in the DTG curve shown in Figure 4.6. The peaks which were obtained between 275-400°C and at 700°C overlapped with the DTG of cellulose-based composite waste samples. Also, the same peak between 400°C and 500°C was observed for both CWP and plastic-based composite waste samples. As mentioned before, the peak obtained between 250°C and 450°C rely on the thermal degradation of cellulose. However, the plastic content of the CWP makes it difficult to predict the cellulose content by using the DTG curve since the plastics have a thermal degradation at nearly the same temperature range.

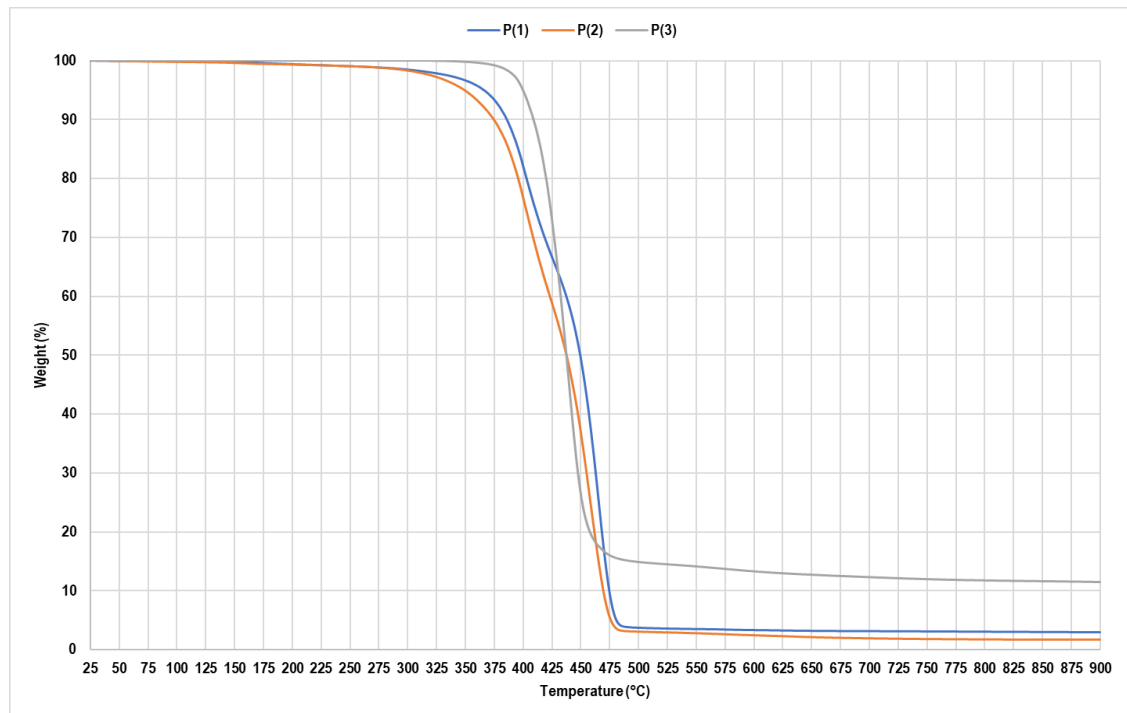


Figure 4.3: Temperature-dependent mass loss curves of plastic-based samples.

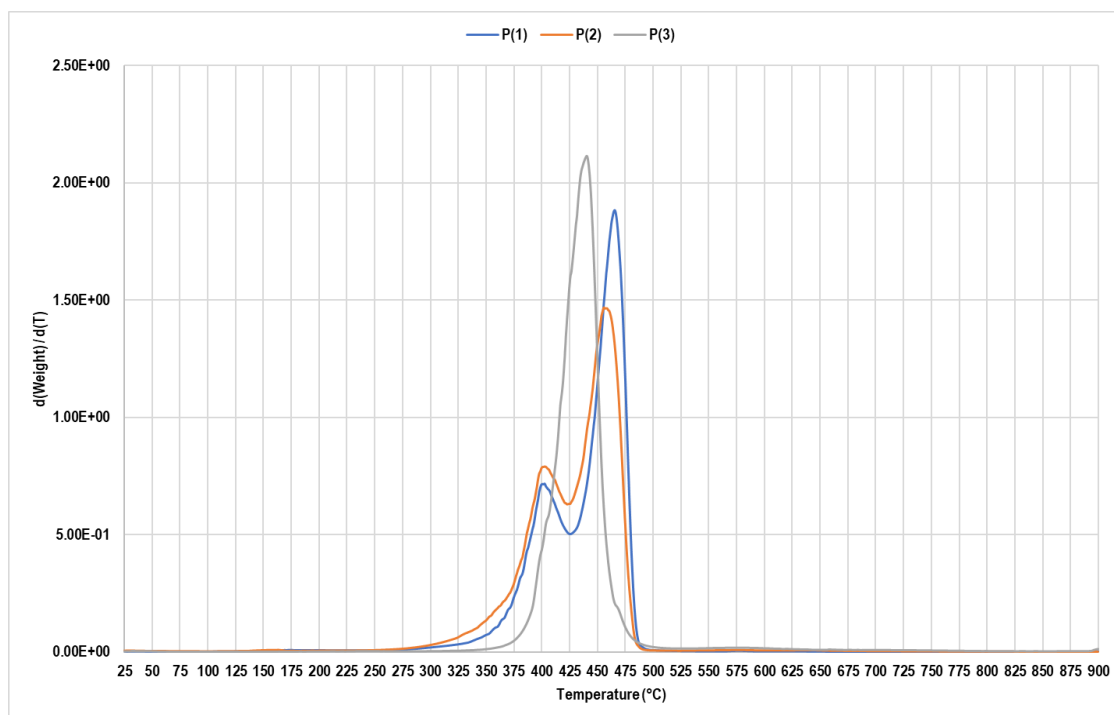


Figure 4.4: DTG curves of plastic-based samples.

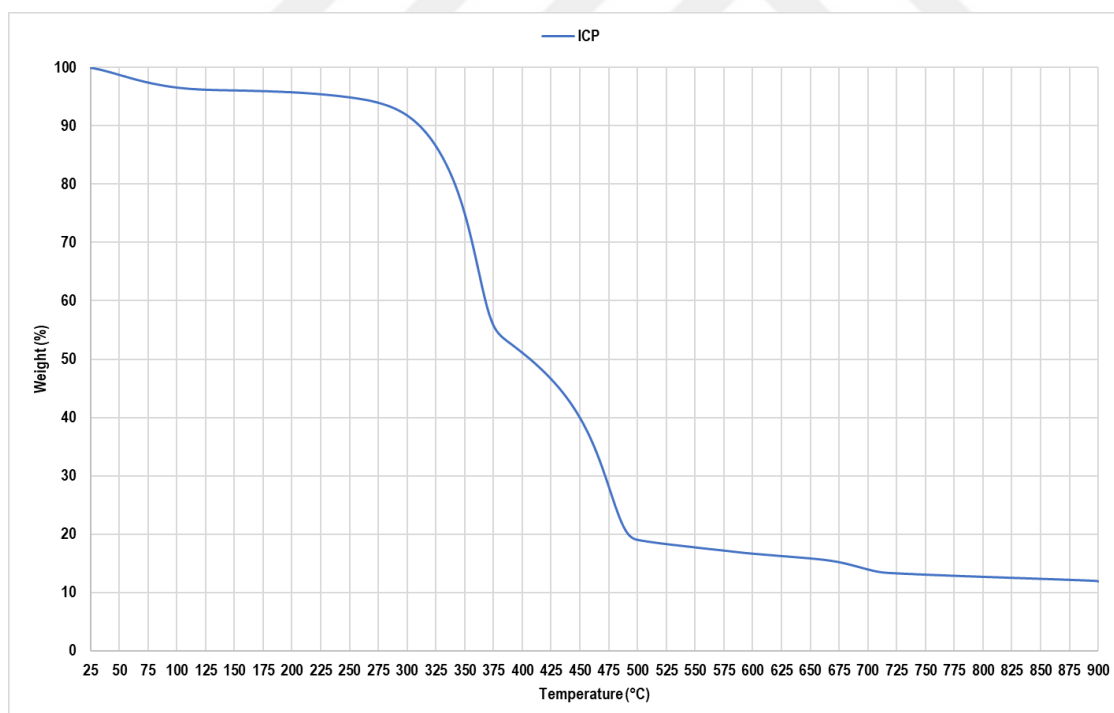


Figure 4.5: Temperature-dependent mass loss curve of CWP.

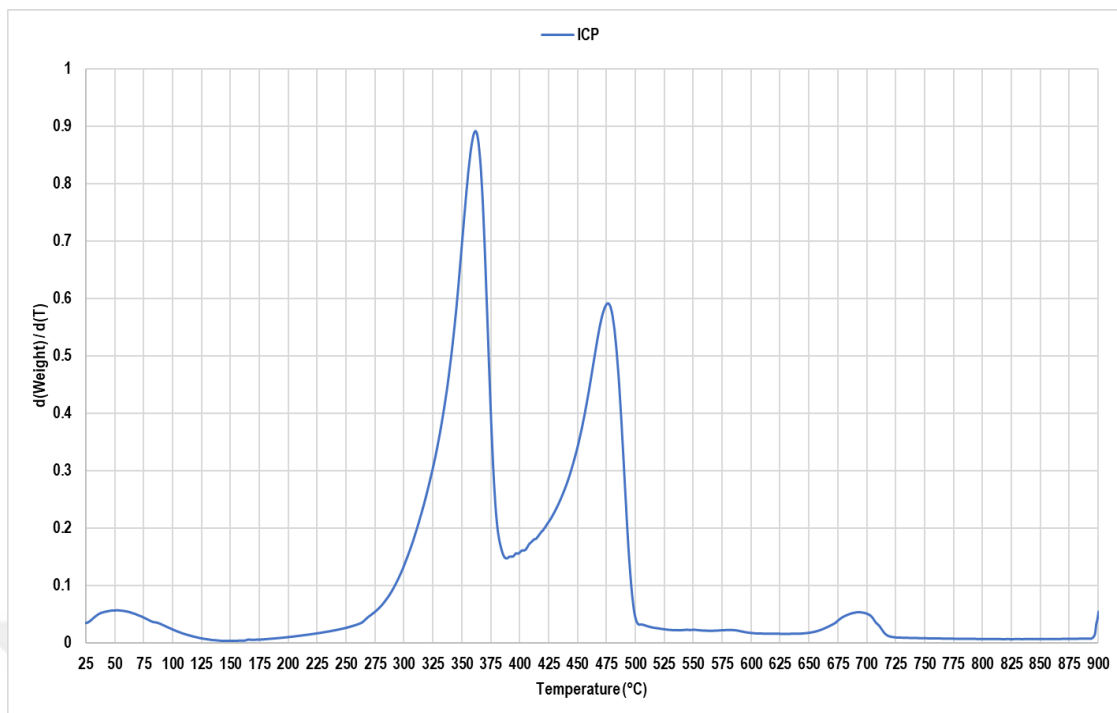


Figure 4.6: DTG curve of CWP.

4.2 Results of Pyrolysis Tests

Pyrolysis tests were performed in batch reactor and continuous reactor test systems with four different recipes. The results of the product distribution of pyrolysis, syngas compositions, and characterization results of the products are given in section 4.2.2 for the batch reactor system and section 4.2.3 for the continuous reactor system.

4.2.1 Determination of amount and composition of syngas

As a result of the pyrolysis tests carried out in two different systems, first of all, the amount and distribution of the products were determined, the necessary calculations were made, and then the characterization of the pyrolysis products was carried out. The syngas obtained in the studies contains high levels of H_2 , CH_4 , CO , and CO_2 . The volumetric ratios of these components were measured with an online syngas analyzer. Especially since the syngas content obtained in the continuous pyrolysis reactor contains an average of 97-98% mixture of H_2 , CH_4 , CO , and CO_2 , no other analysis was performed for other gaseous components with another instrument.

The amount of syngas, one of the critical parameters in the studies, was calculated in the same way in two different systems. The syngas amounts (m_{syngas}) obtained in both batch and continuous systems were calculated according to the principle of mass

balance (Equation 4.1). The yields ($Yield_i$) of char, pyrolytic oil, and syngas were calculated by dividing the mass of the product (m_i) by the total feed of the composite waste mixture (m_{feed}) (Equation 4.2).

$$m_{syngas} = m_{feed} (g) - (m_{char} (g) + m_{oil} (g)) \quad (4.1)$$

$$\%Yield_i = \frac{m_i (g)}{m_{feed} (g)} \times 100 \quad (4.2)$$

4.2.2 Results obtained in the batch system

In the studies carried out in the batch pyrolysis system, the pyrolysis behavior of composite wastes at different temperature values was examined. The main purpose of these studies is to determine yields and contents of char, pyrolytic oil, and syngas that will be formed in the pyrolysis of composite waste samples and to examine their potential for the evaluation of these wastes with pyrolysis technology. Another of the findings obtained in this system is to observe the effect of plastic-based wastes on the yield and content of pyrolysis products, especially in the syngas composition.

4.2.2.1 Product yields obtained in the batch system

In the studies carried out, firstly, the effect of temperature on pyrolysis product yields and syngas contents was examined. For this purpose, tests were carried out for Recipe 1 in the batch pyrolysis system at different temperatures. The distribution of product yields of the pyrolysis tests performed at 450°C, 650°C, and 850°C temperature values for Recipe 1 is shown in Figure 4.7.

As shown in Figure 4.7, Recipe 1 which contains only cellulose-based composite label wastes (100% cellulose based), an increment in the product yield of the syngas produced was observed with an increase in temperature to 850°C. However, the increase in gas yield was not significant for the pyrolysis studies from 450°C to 650°C. The syngas yield increased by 10.50% and reached 40.50% at a pyrolysis temperature of 850°C. This finding shows that the syngas yield is remarkably affected in the high-temperature pyrolysis process. On the other hand, while the syngas yield increased, the char yield decreased and the pyrolytic oil yield remained constant in the experiment at 850°C. It was concluded that as a result of temperature increase in the pyrolysis of cellulose-based label wastes, the feedstock undergoes more sufficient thermal degradation in comparison to the pyrolysis up to 650°C.

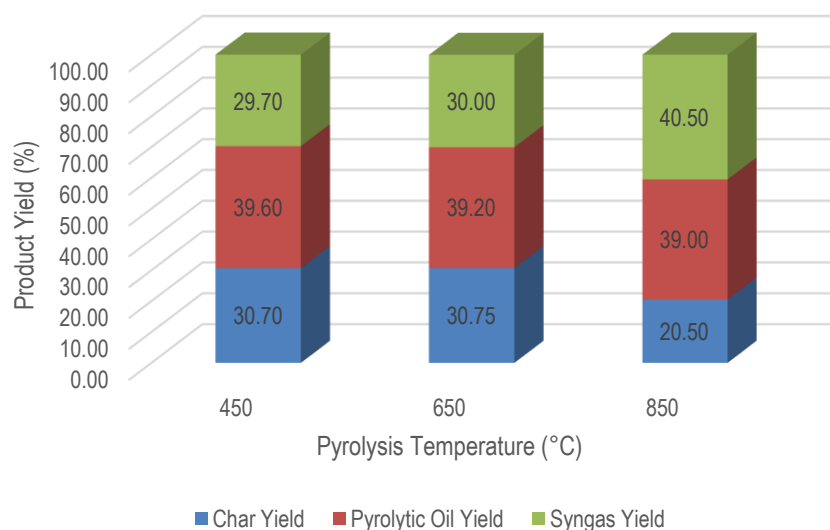


Figure 4.7: Yields obtained at different temperatures for pyrolysis of Recipe 1.

A series of pyrolysis tests were carried out to observe how the product yields and syngas composition would change with the addition of plastic-based wastes to the feed mixture. In these studies, pyrolysis processes were carried out with Recipe 2 (85% cellulosic and 15% plastic waste mixtures) at pyrolysis temperatures of 650°C and 850°C. The graph of the product yields obtained in the studies carried out with Recipe 2 is shown in Figure 4.8. In addition to 650°C and 850°C, a pyrolysis test at 450 °C with Recipe 2 (85% cellulosic and 15% plastic waste mixtures) was performed. Due to the intense wax formation that prevents to keep experiment safely, the experiment at 450°C was not continued till collecting reliable product sampling and the results were not quantitatively reported.

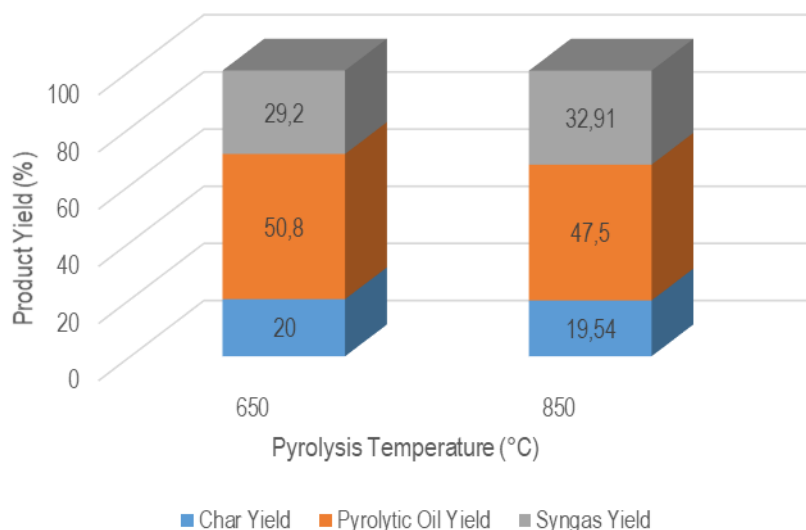


Figure 4.8: Yields obtained at different temperatures for pyrolysis of Recipe 2.

One of the most significant findings in the studies carried out with Recipe 2 was to observe the effect of plastic addition on the products. As a result of the plastic-based composite waste pyrolysis, wax formation was observed. In this study, although the amount of wax was included in the total percentage of pyrolytic oil, it was observed that the obtained oil product and wax structure did not mix with each other, and phase separation was experienced. One of the main reasons for this situation is that the waxy structure passes into the solid phase as a soft creamy form at room temperature. In the study carried out with Recipe 2 at 850°C, the pyrolytic oil obtained in the cooling column and the wax obtained in the trap are shown in Figure 4.9.

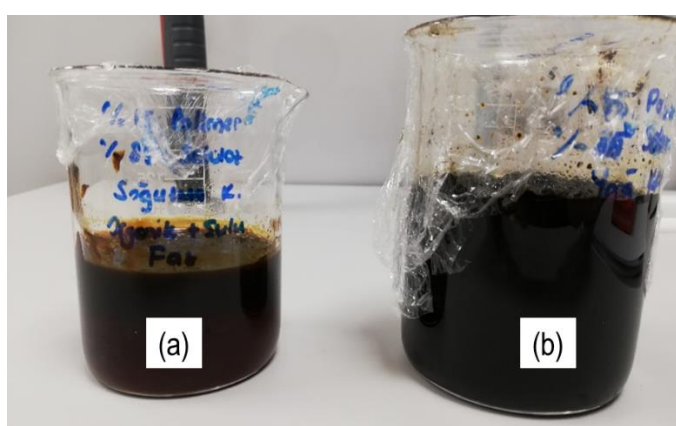


Figure 4.9: Oil (a) and wax (b) products in the pyrolysis of Recipe 2 at 850°C.

The change in the amount of wax formation depending on the temperature is examined. While the ratio of the wax to oil is 0.8:1 at 650°C, this ratio decreases to 0.6:1 when the pyrolysis temperature rises to 850°C. One of the main reasons why the temperature

increase reduces the amount of wax formation might be the increase in the thermal degradation efficiency of the plastics in the pyrolysis process and the cracking of aliphatic structures into smaller molecules. Findings obtained on the product yields support this conclusion. As shown in Figure 4.8, it was observed that the pyrolytic oil yield decreased with the temperature increase while the syngas yield increased at the same temperature.

The formation of wax in pyrolysis processes for plastic containing composite wastes created adverse situations in terms of conducting experiments and safely operating of the batch pyrolysis system. For this reason, for Recipe 3 (70% cellulosic and 30% plastic waste mixtures), pyrolysis was carried out at temperatures of only 650°C and 850°C, and product distributions were determined (Figure 4.10). When the product distributions of the studies carried out with Recipe 2 at the same temperature are examined, it is seen that there is an increase in syngas yield and a decrease in char and pyrolytic oil yields as compared to Recipe 2 (85% cellulosic and 15% plastic waste mixtures).

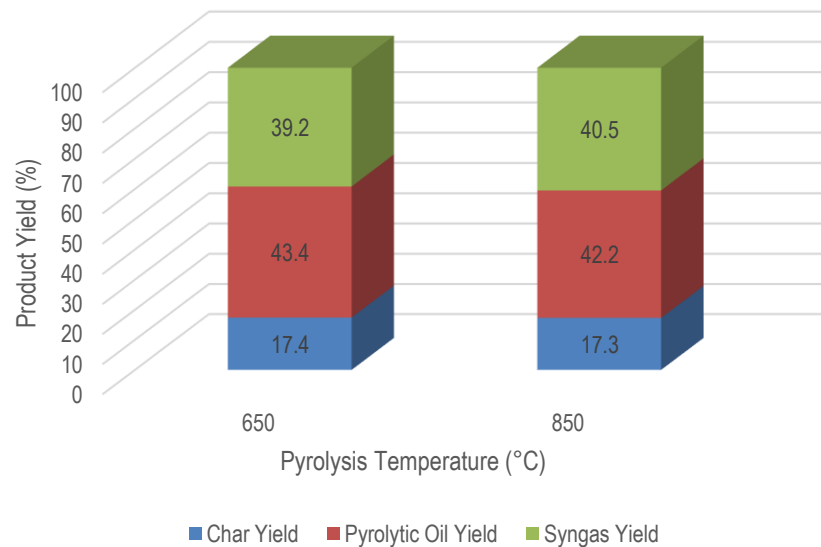


Figure 4.10: Yields obtained at different temperatures for pyrolysis of Recipe 3.

Following the studies carried out with Recipes 1, 2, and 3, which consist of a mixture of composite label wastes, a pyrolysis study was also carried out with Recipe 4 (commercial composite pellets) which contains only CWP. Product distributions in the experiments carried out at 650°C and 850°C are given in Figure 4.11. As a result of the characterization processes where the plastic content was similar to Recipe 3 (70%

cellulosic and 30% plastic waste mixtures), a high amount of wax formation was observed in the pyrolysis of the CWP as in the case of Recipe 3. The photographs of the mixture of wax and oil structures obtained at 850°C are shown in Figure 4.12. In the study, wax condensation was obtained in both the cooling column and the oil trap. This was due to the fact that the high content of plastic in the structure of CWP. It was observed that the product distributions of the pyrolysis of the CWP were in parallel with the results obtained in the studies conducted with Recipe 3 (70% cellulosic and 30% plastic waste mixtures).

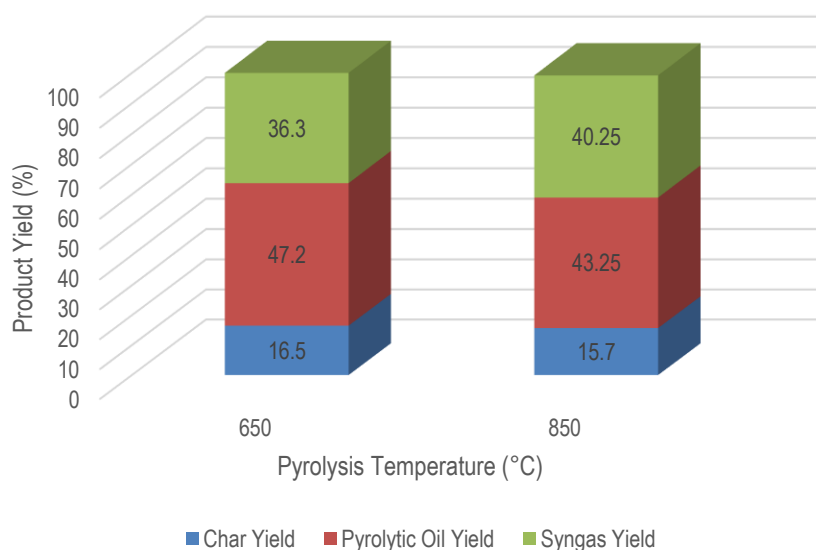


Figure 4.11: Yields obtained at different temperatures for pyrolysis of Recipe 4.

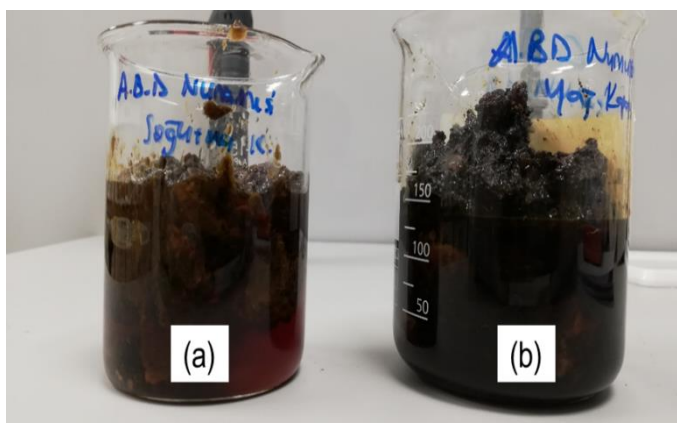


Figure 4.12: Wax and oil obtained in cooling column (a) and trap (b) for Recipe 4 at 850°C.

The product yield distributions obtained in the studies carried out in the batch pyrolysis system with four different recipes are summarized in Table 4.6 and 4.7 for the pyrolysis tests at 650°C and 850°C. Although the results obtained for Recipe 2 and

Recipe 3 showed that the syngas yield increased with an increase in their plastic content in the mixture. The formation of wax in the pyrolysis processes at low temperature, namely at 450- 650°C in which the plastic-based wastes were present in the feed mixture created difficulties in conducting experiments and collecting the products. Since the batch pyrolysis system shown in Figure 3.10 does not have an additional heated line at the reactor outlet, the wax structure easily condensed and accumulated at room temperature during the experiment. These findings showed that in pyrolysis processes for plastic-containing waste mixtures, the pyrolysis temperature should be kept at 850°C and above for smooth operation, and in addition, there should be a heated line to prevent condensation to the reactor's exit. Also, it was concluded that reported values on product yields has some level of inaccuracy due to the condensation and sampling problems. Therefore, studies continued with continuous pyrolysis reactor where hot traps are available for well condensation of wax products.

Table 4.6: Product yields obtained at 650°C with four different recipes.

Recipe No	% Product Yields at 650°C		
	Char	Pyrolytic Oil	Syngas
1	30.75	39.25	30.00
2	29.20	59.80	29.20
3	17.40	43.40	39.20
4	16.50	47.20	36.30

Table 4.7: Product yields obtained at 850°C with four different recipes.

Recipe No	% Product Yields at 850°C		
	Char	Pyrolytic Oil	Syngas
1	20.50	30.00	40.50
2	17.50	47.50	32.91
3	17.30	42.20	40.50
4	15.70	43.25	40.25

4.2.2.2 Characterization result of the products obtained in the batch system

A series of characterization studies have been carried out for char and pyrolytic oil samples obtained in pyrolysis studies performed at different temperatures with four different recipes in the batch pyrolysis system.

Proximate analysis results and calorific values of char samples obtained in pyrolysis tests performed with four different recipes at different temperatures are given in Table 4.9. Results show that the pyrolysis temperature directly affects the properties of the char. For Recipe 1 (100% cellulosic sample), the char obtained at 450°C contains 44.83% volatile matter. While the pyrolysis temperature increased to 650°C and 850°C, the volatile matter content of the char decreased to 29.07% and 9.40% respectively. In addition to volatile matter, it was concluded that the ash and fixed carbon contents are directly related to the pyrolysis temperature. For the char obtained in the pyrolysis of Recipe 1 at 450°C, the ash, and fixed carbon contents were determined as 31.08% and 23.91% respectively. As a result of the temperature increase to 650°C and 850°C, the ash content rose to 43.46% and 58.52% respectively. Similar to the ash content, the fixed carbon increased to 27.32% and 32.84% for the chars obtained at the same temperatures.

The findings obtained from calorific values indicate that the calorific value of a char sample correlates with pyrolysis temperature. As shown in Table 4.9, as a result of higher thermal degradation, the calorific values of the char samples at 850°C are lower than the calorific values at 650°C for all recipes. For Recipe 1, the char sample obtained at 450°C has a calorific value of 19.17 MJ/kg which is higher than the values of 15.25 MJ/kg at 650°C and 14.36 MJ/kg at 850°C. The calorific values of the char samples obtained in the other three recipes have the same correlation with pyrolysis temperature.

According to the characterization results of feedstocks (Table 4.4) and chars (Table 4.9), it was concluded that the properties of the char are directly affected by the feedstock characteristics. For the char samples obtained at 850°C, calorific values are aligned with higher to low for Recipe 4, Recipe 3, Recipe 2, and Recipe 1 respectively. This result shows that the calorific value of the char has a direct proportion with the calorific value of the feedstock.

Characterization of the pyrolytic oil was performed for the aqueous phase and the wax separately. For obtaining the preliminary information about the aqueous phase, the water contents of the samples were determined. Water contents were determined for Recipe 1(100% cellulosic sample), recipe 2 (85% cellulosic and 15% plastic waste mixtures), recipe 3 (70% cellulosic and 30% plastic waste mixtures), and recipe 4 (CWP) as 60.57%, 62.00%, 62.60%, and 60.0% respectively. Detailed information on the characteristics of pyrolysis oil was performed by obtaining the elemental composition of the samples. The pyrolytic oil samples of Recipe 1 and Recipe 2 were selected for ultimate analysis and aqueous and wax phases were analyzed separately. In the study conducted for the products obtained in the studies carried out with Recipe 1 and Recipe 2 at a temperature of 850°C, it was determined that the aqueous phases had a low carbon content (22.55-24.09%). The wax structure has been observed to have a carbon content of 68.30%. It has been determined that the high amount of carbon in the wax structure content is derived from the high carbon content contained in the plastic-based composite wastes and that the wax structure, which is not exposed to a secondary cracking, directly affects the syngas yield and adversely affects the realization of an effective pyrolysis process. In addition, as a result of the calorific value determination performed for the wax structure and aqueous phases obtained with Recipe 2, it was determined that the calorific values are 38.95 MJ/kg and 15.83 MJ/kg for the wax and aqueous phase respectively. The high amount of volatile components contained in the wax structure causes its calorific value to be high. Results of the characterization studies carried out for the pyrolytic oil of Recipe 1 and Recipe 2 at 850°C are given in Table 4.8.

Table 4.8: Elemental composition and calorific values of pyrolytic oil samples.

Recipe No	Component	Ultimate Analysis					Calorific Value
		C (%)	H (%)	N (%)	S (%)	O (%)	HHV (MJ/kg)
1	Oil	22.55	9.13	0.17	0.18	67.97	15.83
	Wax	68.30	9.80	0.23	0.16	21.51	38.95
2	Oil	24.09	9.44	0.26	0.20	66.01	28.38
	(Aqueous P.)						

As a result of the characterization studies, it was concluded that the aqueous phase and the wax structure have different properties on the basis of elemental composition and calorific values. Since the chemical compositions of these two pyrolytic oil components depend on the feedstock characteristics, it was concluded that the plastic content of the feedstock directly affects the carbon content and the calorific value of the pyrolytic oil.



Table 4.9: Proximate analysis results and calorific values of char samples obtained in the batch system.

Recipe No	450°C				650°C				850°C			
	M (%)	VM (%)	A (%)	FC (%)	M (%)	VM (%)	A (%)	FC (%)	M (%)	VM (%)	A (%)	FC (%)
1	0.25	44.83	31.08	23.91	0.25	29.07	43.46	27.32	0.00	9.40	58.52	32.84
2		N/A			0.00	13.51	56.06	30.43	0.00	9.10	58.91	32.52
3		N/A			0.42	18.48	50.29	30.49	0.00	8.70	58.55	32.86
4		N/A			0.75	17.77	31.40	50.06	0.68	3.32	26.23	69.80

Recipe No	450°C		650°C		850°C	
	HHV (MJ/kg)		HHV (MJ/kg)		HHV (MJ/kg)	
1	19.17		15.25		14.36	
2	N/A		14.33		12.44	
3	N/A		21.23		18.43	
4	N/A		26.03		22.60	

4.2.2.3 Composition of the syngas obtained in the batch system

The syngas contents obtained in the pyrolysis studies performed in the batch system were examined for different temperature values and recipes. Since the batch system cannot achieve steady-state conditions, syngas components were examined by their peak values. Peak values were recorded during the pyrolysis experiment and compared on the basis of pyrolysis temperature and feedstock composition. The recorded syngas graph of the experiment carried out with Recipe 2 at 850°C is given as an example in Figure 4.13.

In the studies carried out in the batch reactor system, syngas formation started approximately 15 minutes after the start of the experiment. As given in Figure 4.13, CO₂ has a dominance in the total concentration rather than the other syngas components at the beginning of the test. After the first 15 minutes, it was observed that while the CO₂ concentration reduced while the concentration of the other syngas components increased. The finding on the CO₂ concentration related to the given graph was obtained for all tests carried out in the batch reactor system.

The syngas compositions were evaluated by the peak values as mentioned above. Peak values of H₂, CH₄, and CO were recorded for all pyrolysis tests. From this point of view, the effect of pyrolysis temperature and feedstock composition on peak values was examined. The graphs which include the peak values were prepared for different recipes. For Recipe 1, the peak values of syngas components in tests at 450°C, 650°C, and 850°C pyrolysis temperatures are shown in Figure 4.14. Together with Recipe 1, the peak values in the pyrolysis tests of Recipe 2, 3, and 4 at 650°C and 850°C were given in Figure 4.15, Figure 4.16, and Figure 4.17 respectively.

The results obtained from the studies carried out with Recipe 1 show that the syngas composition is directly affected by the pyrolysis temperature. As can be seen in Figure 4.14, while the pyrolysis temperature increases, the share of the H₂ in the syngas rises from 1.21% to 13.67%, and 16.62% respectively. The finding on H₂ concentration can be explained by the increase in the thermal degradation efficiency at higher temperatures. On the other side, it was observed that the peak values of CH₄ and CO do not have a direct proportion with pyrolysis temperature. While the pyrolysis temperature increases from 450°C to 650°C, the peak value of the CH₄ rises from 10.65% to 27.98%. However, this uptrend was not observed in the experiment at

850°C. It was concluded that the result obtained for CH₄ and CO peak values is related to the secondary pyrolysis reactions occurring at higher temperatures. As mentioned before, at higher temperatures the H₂ formation increases as a result of secondary pyrolysis reactions that include CH₄ and CO as reactants. From the point of syngas yield, an uptrend was obtained as a result of increasing pyrolysis temperature. The findings on both the syngas yield and peak values show that the temperature increase affects syngas yield and H₂ concentration positively for any increasing rate. However, this uptrend is not valid for CH₄ and CO peak values.



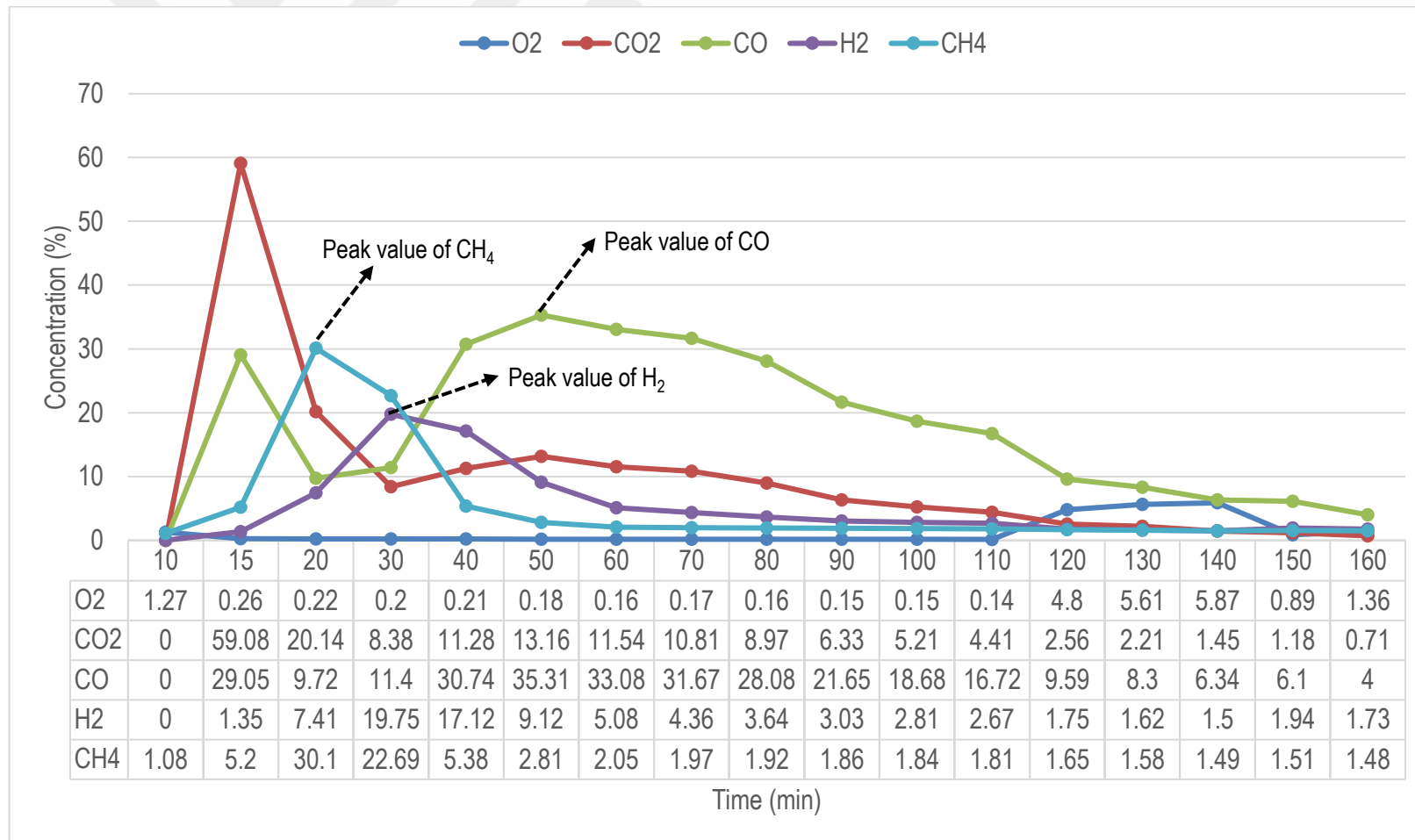


Figure 4.13: The syngas graph used for obtaining the peak values.

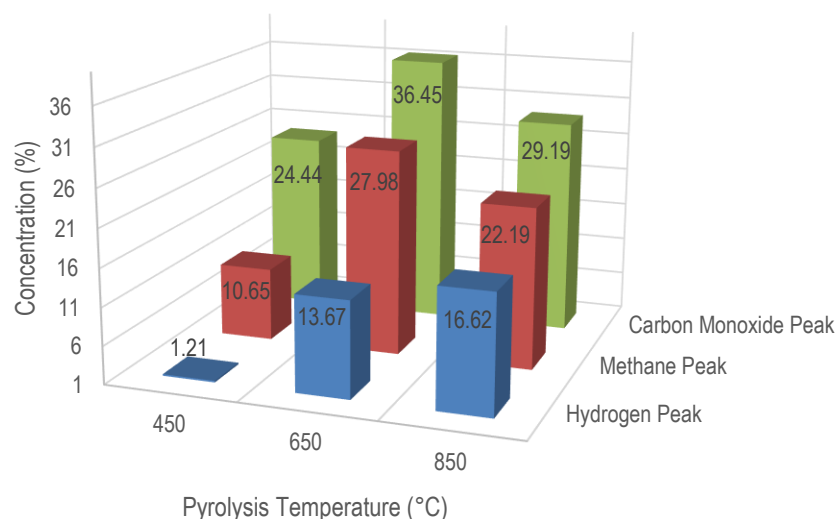


Figure 4.14: Peaks obtained at different pyrolysis tests for Recipe 1.

The effect of plastic-based wastes on syngas composition was determined by results obtained in pyrolysis tests of Recipe 2. While the syngas compositions of Recipe 1 and Recipe 2 were investigated, it was found that the plastic-based waste addition into the feedstock increase the peak values of H_2 , CH_4 , and CO at $850^\circ C$. On the other hand, peak values of the same components at $650^\circ C$ are lower for Recipe 2 than for Recipe 1. In addition to plastic-based waste addition into the feedstock, the effect of the pyrolysis temperature on syngas composition was investigated in tests. For the H_2 concentration, results obtained in tests at $650^\circ C$ and $850^\circ C$ show similarities to Recipe 1. As shown in Figure 4.15, the peak value of H_2 raised from 8.98% to 19.75% while the pyrolysis temperature increased from $650^\circ C$ to $850^\circ C$. In reverse to findings obtained in the temperature increase from $650^\circ C$ to $850^\circ C$ in the tests of Recipe 1, it was observed that peak values of CH_4 and CO raised with the temperature increase. As given in Figure 4.15, it was observed that the peak values of CH_4 and CO raised from 10.21% to 30.31% and from 20.56% to 35.31% respectively.

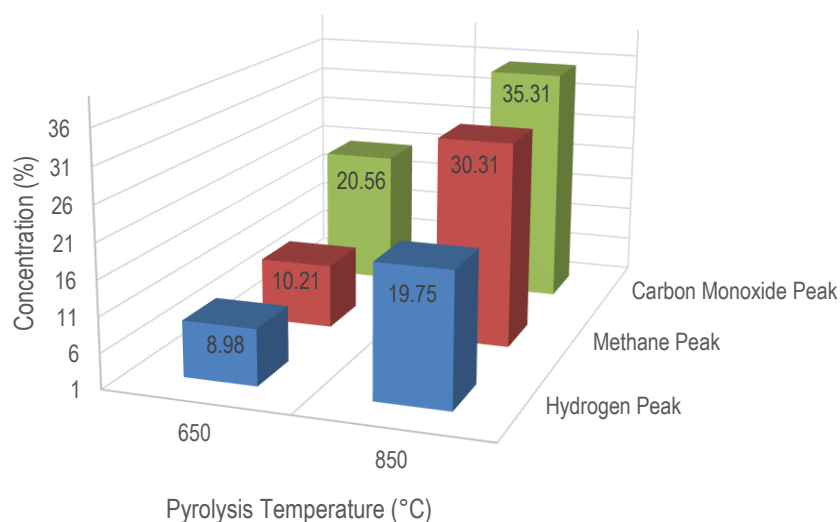


Figure 4.15: Peaks obtained at different pyrolysis tests for Recipe 2.

The effect of plastic-based waste ratio in the feedstock on the syngas composition was observed by results obtained in Recipe 3's pyrolysis tests. When the plastic ratio increased from 15% to 30% in the feedstock, it was obtained that peak values of syngas components decreased. On the contrary of the findings obtained about the syngas yield, it was observed that the increasing plastic ratio in the feedstock causes a decrease in the peak values. However, it was concluded that the increasing amount of syngas yield can be adduced as evidence for a synergetic effect of plastic addition on feedstock. When the peak values shown in Figure 4.16 were investigated, it was seen that the peak value of H₂ raised from 7.28% to 16.99% as a result of a temperature increase from 650°C to 850°C. Similar to H₂, CH₄ and CO peak values were raised from 4.86% and 30.42% to 25.3% and 33.23% respectively.

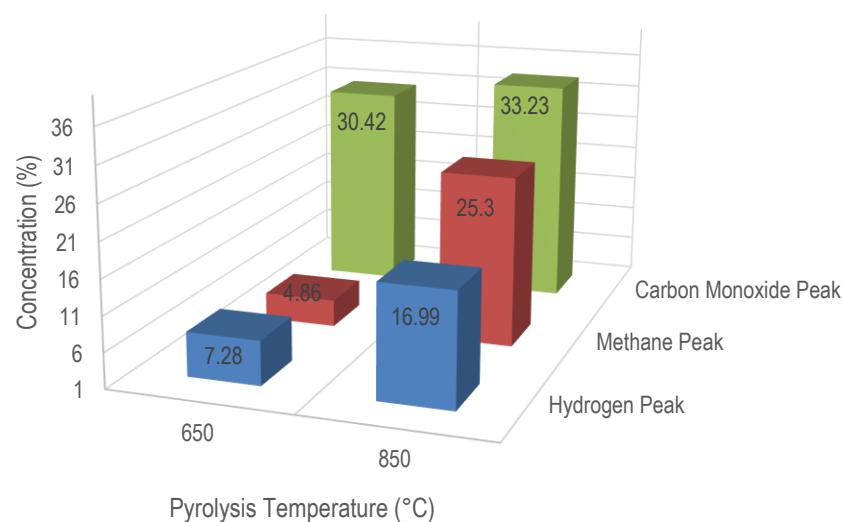


Figure 4.16: Peaks obtained at different pyrolysis tests for Recipe 3.

In the tests carried out with Recipe 4, it was observed that the syngas composition has similarities with the results of Recipe 3 in the aspect of peak values. As obtained in the tests of Recipe 2 and Recipe 4, the peak values of syngas components experienced a rise when the pyrolysis temperature increased. Peak values of H_2 were observed as 7.24% at 650°C and 18.41% at 850°C in tests of Recipe 4. For the CH_4 and CO , in parallel with the H_2 , it was observed that the peak values raised from 6.68% and 24.85% to 28.42% and 29.21% respectively.

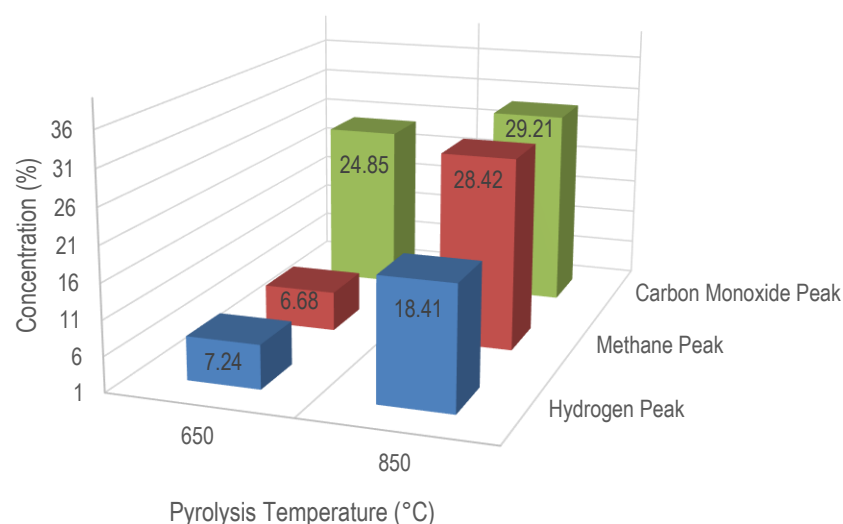


Figure 4.17: Peaks obtained at different pyrolysis tests for Recipe 4.

According to results obtained in the batch pyrolysis system, syngas composition is directly affected by both the pyrolysis temperature and plastic-based waste ratio in the feedstock content. Although the obtained syngas compositions of Recipe 1 at 450°C, 650°C, and 850°C do not have a linear relationship with each other, results of Recipe 2, 3, and 4 show that H₂, CH₄, and CO peaks rise as a result of increasing temperature. As mentioned before, it was observed an intense wax formation in the tests including plastic-based wastes in the feedstock. Therefore, it was concluded that the syngas compositions of these tests do not have a consistent relationship with the plastic-based waste ratio. The lack of efficient thermal degradation of wax components causes this inconsistency.

In summary, it was concluded that temperatures above 850°C can be specified as suitable pyrolysis temperatures for achieving high syngas yields in the pyrolysis of composite waste samples. Additively, the results obtained in the batch system demonstrate the requirement for an efficient secondary cracking unit for minimizing the wax content and observing the effect of plastic-based waste content in the feedstock on syngas composition properly.

4.2.3 Results obtained in the continuous system

Following a series of pyrolysis tests in the batch reactor system, high-temperature pyrolysis tests were performed in the pilot-scale continuous reactor system with the same recipes. The process operating conditions and system information of these tests carried out at 900°C are given in Section 3.4.2. In these studies, it was aimed to increase the efficiency of secondary pyrolysis reactions at a temperature of 600°C in the secondary thermal cracking unit. The studies carried out for composite label wastes were also carried out for CWP under the same conditions, and the pyrolysis behavior and product yields of domestic composite label wastes were compared with CWP. The results of the studies were examined in terms of product yields, product characteristics, and syngas compositions and properties.

4.2.3.1 Product yields obtained in the continuous system

The product yields obtained from pyrolysis tests performed in the continuous reactor system with four different recipes are shown in Figure 4.18. Among the most important findings obtained in the continuous system is the increasing amount of syngas yield.

In tests carried out in the batch reactor system, the syngas efficiency ranged from 32.91-40.50% at a temperature of 850°C (Table 4.7), while in the continuous system this range reached 66.22-75.69% at 900°C. Regarding the pyrolytic oil, its yield vary between 5.78-8.92% in the continuous system which is completely different from the results of the batch system. This finding on the decreasing amount of pyrolytic oil can be explained by the extended thermal degradation of the pyrolytic oil as a result of secondary pyrolysis reactions in the thermal cracking unit. These results showed that, for the same recipe and similar temperatures, the characteristics of the system and the residence of the condensable hydrocarbon vapors have a great effect on the results obtained.

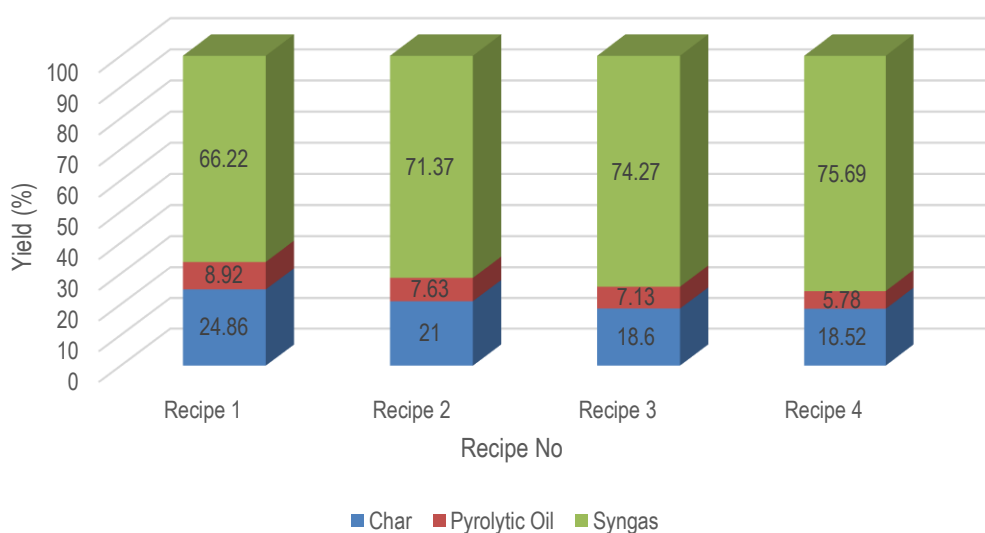


Figure 4.18: Product yields obtained in the continuous pyrolysis test system.

As shown in Figure 4.18, in the test carried out feed Recipe 1 (100% cellulose), the product yields were obtained as 66.22%, 8.92%, and 24.86% for syngas, pyrolytic oil, and char respectively. For Recipe 2 (85% cellulosic and 15% plastic waste mixtures), in which the feedstock consists of 15% plastic-based waste content, yields were obtained as 71.37%, 7.63%, and 21% for syngas, pyrolytic oil, and syngas respectively. Thus, it was concluded that plastic-based waste addition into the feedstock causes an increase in the syngas yield. At the same time, while syngas yield increases, char, and pyrolytic oil yields decrease with the plastic-based waste addition into the feedstock. The yields obtained with Recipe 3 demonstrated this finding. In the tests of Recipe 3 (70% cellulosic and 30% plastic waste mixtures), yields of syngas, pyrolytic oil, and char were obtained as 74.27%, 7.13%, and 5.78% which have the

same increasing and decreasing trends with the results obtained from Recipe 1 and Recipe 2.

The highest syngas yield was obtained in the test of Recipe 4 (CWP). The syngas, pyrolytic oil, and char yields were obtained as 75.69%, 5.78%, and 18.52% respectively. Even if the syngas yield of Recipe 4 is higher than the other recipes it was concluded that the yields of Recipe 3 showed similarities with Recipe 4. This finding, which was also observed in the tests in the batch system, relies on the similarity in feedstock content and characteristic.

Another important finding obtained in the continuous system was the lack of wax formation during the pyrolysis. As mentioned before, it was aimed that the elimination of wax formation with the help of thermal cracking. In the continuous system, the liquid-vapor and gaseous products were fed to the thermal cracking unit with the help of a heated line during after leaving the pyrolysis reactor. Products that were not exposed to ambient temperature were cracked in the form of vapor and gas and reduced to light gases. As a result of efficient thermal cracking, the wax formation was minimized in the test and a higher syngas yield was obtained in the continuous system rather than the batch system.

4.2.3.2 Characterization of chars obtained in the continuous system

Before the characterization process of char samples, theoretical char quantities were calculated for four different recipes based on the results of proximate analysis of the original samples. In the pyrolysis process, the theoretical amount of char was calculated by using the ash and fixed carbon quantities that are expected to form the char structure by remaining quantitatively constant. For four different recipes, it was found that the yield of chars obtained in pyrolysis tests was on average 33% more than the theoretical amount. This situation can be explained by secondary char reactions that occur during the pyrolysis process. These secondary reactions mainly take place during high-temperature pyrolysis and directly affect the active sites of the primary char (Anca-Couce et al., 2017). In order to obtain more detailed information about the char, proximate analysis, ultimate analysis, and calorific value determination were performed.

According to proximate analysis results, it was concluded that the char characteristics depend on the plastic-based waste ratio in the feedstock. As can be seen in Table 4.10,

the percentage of the ash content in the char decreases with the increasing ratio of the plastic-based waste in the feedstock. For Recipe 1, which does not have any plastic-based waste content, the char obtained in the tests has 45.32% ash content. On the other hand, the char of Recipe 3 has an ash content of 38.01%. In addition to the ash, the results showed that the plastic-based waste ratio has a similar effect on the volatile matter content. As a result of increasing the plastic-based waste ratio from %0 to %15, and %30, the volatile matter contents of char samples decreased from %14.52 to %13.23, and %11.44 respectively. The decrease in the volatile matter can be ascribed to the synergistic effect of plastics in the co-pyrolysis process of plastics and biomass. As mentioned before, plastics decrease the activation energy of the biomass during pyrolysis. As a result of decreasing activation energy, biomass undergoes more efficient thermal degradation in pyrolysis.

Table 4.10: Proximate, ultimate analyses results and calorific values of chars obtained in the continuous system.

Recipe No	Proximate Analysis				Ultimate Analysis					
	M	VM	A	FC	C	H	N	S	O	HHV
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	MJ/kg
1	0.81	14.52	45.32	39.33	52.25	0.46	0.78	1.57	0	17.50
2	0.66	13.28	40.48	45.58	53.54	0.14	0.36	0.67	4.81	19.65
3	0.66	11.74	38.01	49.59	56.46	~0	0.33	0.38	4.82	20.10
4	1.28	9.36	33.17	56.19	61.33	0.88	1.31	0.13	3.18	22.42

When the elemental compositions of the char samples were investigated, relevance was found between the chars' and original samples' carbon contents. The results in Table 4.10 shows that the carbon content of the char rises with the increasing ratio of plastic-based wastes in the feedstock. As similar, the average carbon content of the recipes (Table 4.4) rises with the increasing ratio of plastic-based wastes in the feedstock. According to the results obtained in the ultimate analysis, char of the Recipe 4 has the highest carbon and nitrogen contents within the char samples. While the

elemental composition of recipes was investigated, it was obtained that Recipe 4 has the highest carbon and nitrogen contents among the other recipes. In summary, the ultimate analysis results of char samples showed expected results, especially in the aspect of carbon contents.

As a result of the calorific value determination, it was found that the HHV of char was directly proportional to the ratio of plastic-based waste in the feedstock. Char of Recipe 1 which is cellulose-based waste only has an average thermal value of 17.50 MJ/kg, the HHV of char reaches 19.65 and 20.10 MJ/kg respectively when the plastic content in the mixture increases to 15% and 30%. The char in the pyrolysis of Recipe 4 has an HHV value of 22.42 MJ/kg. As expected, it was concluded that the calorific value of the char sample has a direct proportion with the average calorific value of the recipe (Table 4.4).

4.2.3.3 Characterization of pyrolytic oils obtained in the continuous system

Results of KF titration show that pyrolytic oil samples had an average water content of 95-97%. This result shows that the heavy oil structures in the liquid phase are cracked in the high-temperature pyrolysis process with the help of the secondary thermal cracking unit. These samples obtained from the cooling column during the pyrolysis process are light in color and clear, different from the common definition of pyrolytic oil in the literature. Images of pyrolytic oil samples are shown in Figure 4.19.

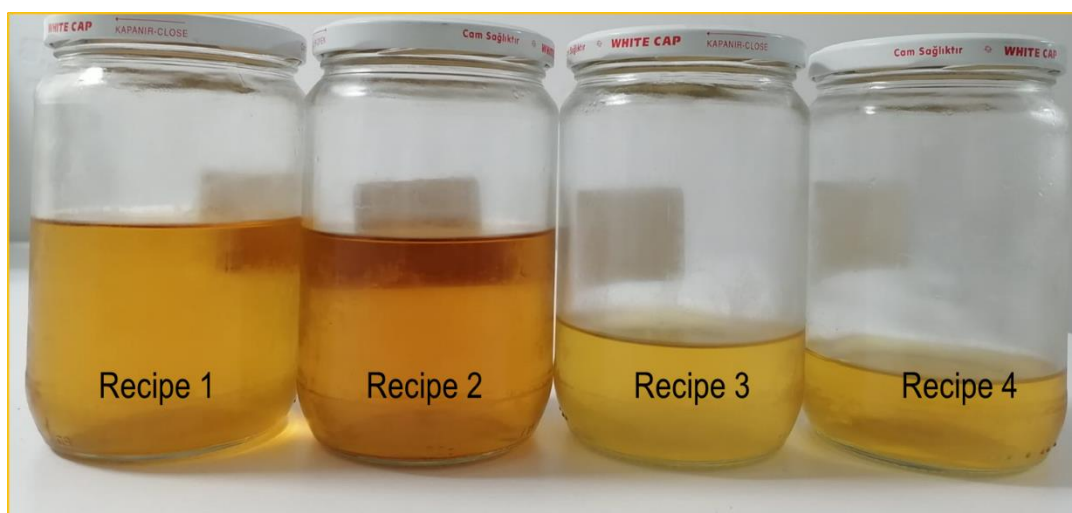


Figure 4.19: Pyrolytic oils obtained for four different recipes.

4.2.3.4 Composition and properties of syngas obtained in the continuous system

The syngas composition of the pyrolysis process in the continuous system was measured instantaneously throughout the experiment and the results were recorded. In this study, one of the most important parameters to be examined in terms of the gaseous product was the change in the percentage of H_2 and CH_4 in the syngas. During the pyrolysis process, graphs of the syngas composition in the steady state condition are shown in Figures 4.20, 4.21, 4.22 and, 4.23, for Recipe 1, Recipe 2, Recipe 3, and Recipe 4 respectively. In the graphs, syngas compositions during the one-hour period of the test are shown.

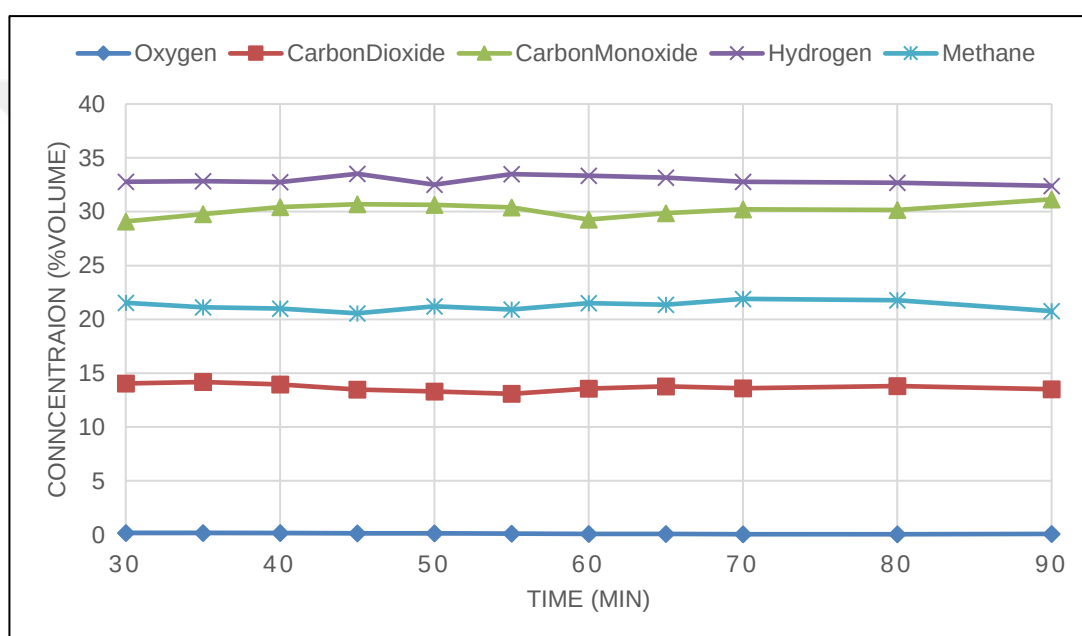


Figure 4.20: Syngas composition of Recipe 1 during the steady state condition.

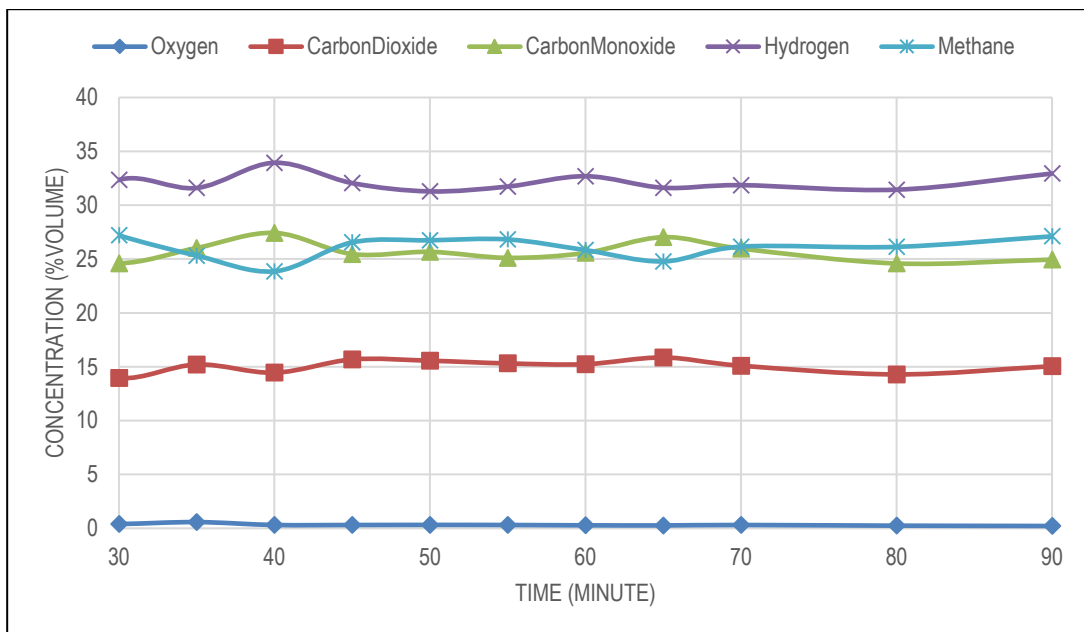


Figure 4.21: Syngas composition of Recipe 2 during the steady state condition.

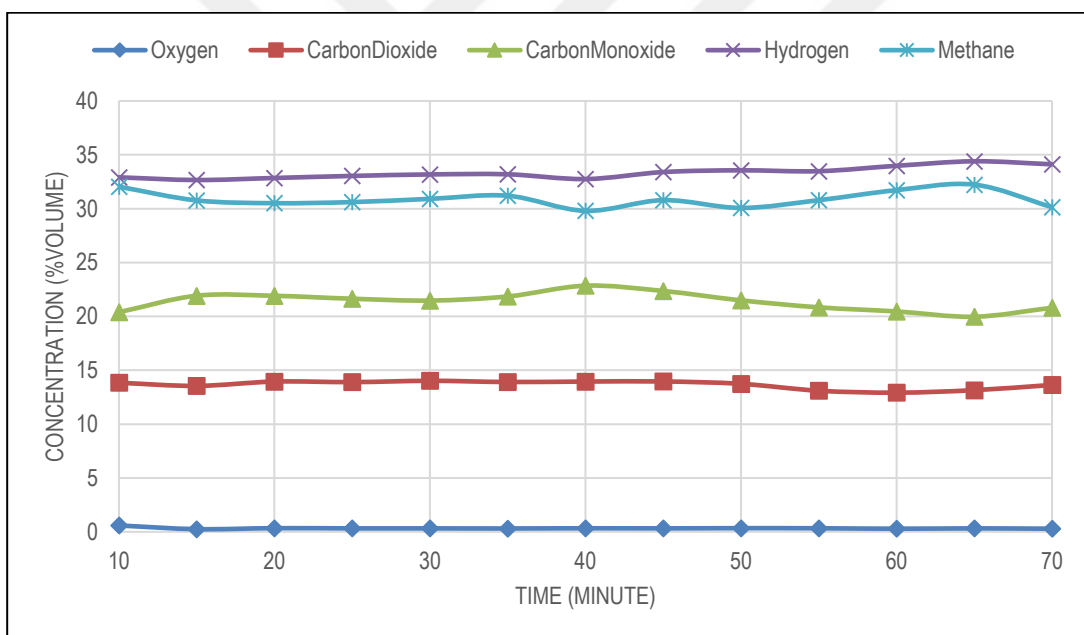


Figure 4.22: Syngas composition of Recipe 3 during the steady state condition.

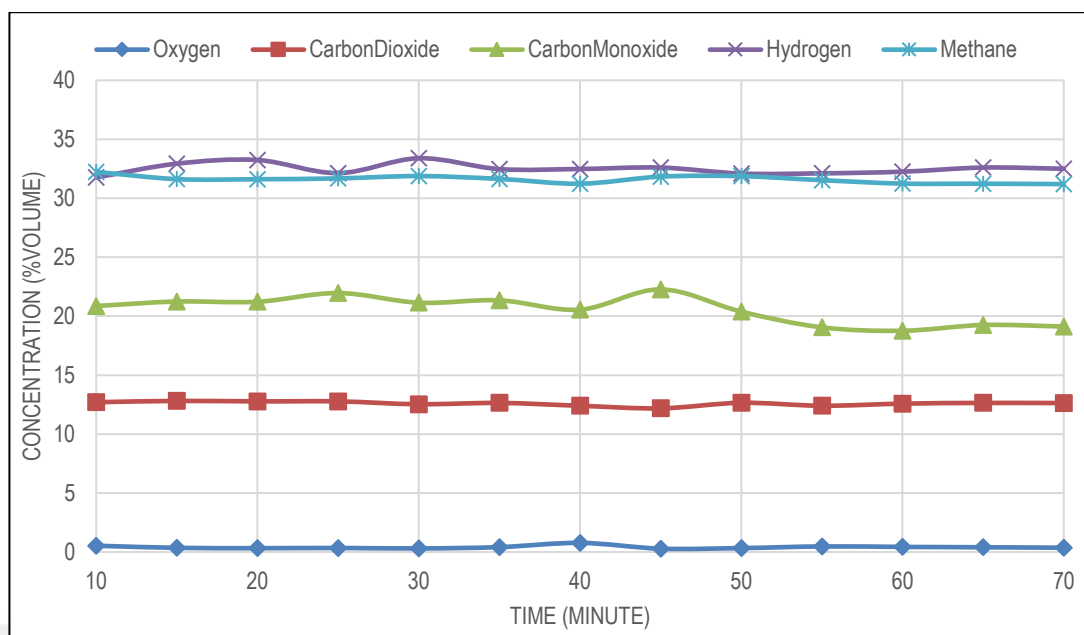


Figure 4.23: Syngas composition of Recipe 4 during the steady state condition.

In the pyrolysis experiments performed at 900°C with four different recipes, it was determined that H₂ was the most abundant gas in terms of volumetric concentration in the syngas compositions obtained. In all studies, it was measured that the H₂ was in the range of 30-35% in the syngas composition. In addition to H₂, CH₄ was observed as the second or third most abundant component depending on the amount of plastic-based label waste in the recipe.

In the pyrolysis study carried out with Recipe 1, which does not contain plastic-based waste in the feedstock, syngas with an average content of 32.66% H₂, 30.22% CO, 21.24% CH₄, and 13.82% CO₂ were obtained under steady-state conditions. Although the sum of the volumetric ratios of these gases is 97.94%, with the help of the appropriate insulation and sealing of the system, the oxygen content did not exceed 0.17% under steady-state conditions during the pyrolysis process.

In the study carried out with Recipe 2, the effect of plastic-based waste in feedstock was observed on syngas composition. The volumetric ratios of H₂, CH₄, CO, and CO₂ gases in the syngas under steady-state conditions were obtained as 31.60%, 26.90%, 25.35%, and 15.07%, respectively. Although the ratio of hydrogen is similar to Recipe 1, the change in CH₄ and CO ratios was one of the prominent findings in this study. With the addition of plastic-based waste in feedstock, the CO ratio decreased, and the CH₄ ratio increased. On the other hand, when Figure 4.21 is examined, it is seen that the ratios of CH₄ and CO in the steady-state conditions show proximity to each other,

and the curves are intertwined. Although the volumetric ratio of H_2 in the study conducted with Recipe 2 was about 1% lower than in Recipe 1, when the syngas yields were examined, it was found that the amount of H_2 produced was higher than in Recipe 1.

A pyrolysis study was carried out with Recipe 3 in order to examine the effect of plastic-based wastes on syngas composition more clearly. In the study, the average volumetric ratios of H_2 , CH_4 , CO , and CO_2 gases in syngas under steady-state conditions were determined as 33.67%, 30.79%, 21.25%, and 23.49%, respectively. In this study, it was seen more clearly that the concentration of H_2 and CH_4 in syngas increased with the increasing ratio of plastic-based wastes in the feedstock. As seen in Figure 4.22, the curve of CH_4 and the curve of CO diverged from each other, and the curve of CH_4 took place second after the H_2 curve. Also, it was obtained that the average concentration of H_2 increased compared to Recipe 1 and Recipe 2, while the CO_2 ratio decreased compared to Recipe 2.

Following the studies carried out with three different recipes consisting of composite label wastes, a pyrolysis test was performed with Recipe 4 (100% CWP content). The average volumetric concentrations of H_2 , CH_4 , CO , and CO_2 gases in the steady-state syngas composition were determined as 32.47%, 31.71%, 20.76%, and 12.60%, respectively. When the syngas compositions of Recipe 4 and Recipe 3 were examined, it was obtained that these two recipes have similar syngas compositions in steady-state conditions. It was concluded that the similar composition of these two recipes resulted in this finding. In addition to similar syngas compositions, when the syngas yields were examined it was obtained that the syngas yield of Recipe 4 (75.69%), where the highest efficiency was obtained, was also close to the syngas yield of Recipe 3 (74.27%). In summary, it was concluded that the behavior of the commercially available CWP in high-temperature pyrolysis is similar to Recipe 3, which only consists of domestic composite label wastes.

In order to make a more detailed comparison between syngas compositions, the average densities, the volumetric amounts of H_2 , CH_4 , and CO produced per kg of waste, and the HHV values of syngas were calculated. The methods used for calculating the average densities and calorific values are given in Equations 4.3 and 4.4. For the calculations, the density values of H_2 , CH_4 , CO , and CO_2 gases were taken as 0.08375, 0.657, 1.14, and 1.87 kg/m³ respectively, and the calorific values were

assumed as 141.80, 55.50, 10.112 MJ/kg respectively. The total concentrations of H₂, CH₄, CO, and CO₂ components in the syngas contents in four different studies were calculated as 97.95%, 98.92%, 98.90%, and 97.55% for Recipe 1, Recipe 2, Recipe 3, and Recipe 4 respectively. Since all of these ratios are over 97%, it was assumed that syngas consists of only these components in the calculations related to syngas.

In Equation 4.3, the average density of the syngas under the steady-state conditions was calculated by using the average volumetric ratios of the components in the syngas and the density values at a temperature of 25°C. C_{avg} represents the average concentration value of each component in the steady-state, d_i represents the density of each gas (m³/kg) and $d_{syngas,avg}$ represents the average density value of the syngas.

$$\sum(C_{avg,i} * d_i) = d_{syngas,avg} \quad (4.3)$$

As a result of the calculations, the average density values of the syngas produced in pyrolysis tests performed with four different recipes are given in Table 4.11. The obtained density values were also used to calculate the volumetric amount of the syngas produced. Total syngas volumes (V_{syngas}) were calculated with Equation 4.4 using the average density values (d_{avg}) calculated by Equation 4.3 and the syngas quantities (m_{syngas}) calculated from the mass balance equation (Equation 4.1). The calculated syngas volumes are given in Table 4.11.

$$m_{syngas} * d_{avg} = V_{syngas} \quad (4.4)$$

The volumetric quantities (m³) of each gas component were calculated with the help of Equation 4.5 using the average concentration value ($C_{avg,i}$) and the total volumetric quantity of the syngas, V_{syngas} (m³). Using the calculated volumetric quantities (V_i) and the density value of each component, the mass quantities m_i (kg) of the gases were obtained (Equation 4.6). For four different recipes, the yields of H₂, CH₄ and CO gases (m³_{component}/kg_{waste}) in the pyrolysis process of composite label wastes were calculated via Equation 4.7. The resulting yield values are shown in Figure 4.24 for four different recipes.

$$C_{avg,i} * V_{syngas} = V_i \quad (4.5)$$

$$V_i * d_i = m_i \quad (4.6)$$

$$Yield_i = V_i / m_{total} \quad (4.7)$$

When the calculated gas yields are examined, it was seen that the yields of H_2 , CH_4 , and CO vary depending on the ratio of plastic-based composite wastes in the feedstock. With Recipe 1, which consists of only cellulose-based composite label waste, 0.280, 0.180, and 0.260 m^3 gas are obtained for H_2 , CH_4 , and CO per kg of waste, respectively. These ratios were calculated as 0.290, 0.240, and 0.230 m^3 for Recipe 2, where the proportion of plastic-based waste in the feedstock is 15%. In Recipe 3, where the ratio of plastic-based waste in the mixture increased to 30%, H_2 and CH_4 yields increased compared to Recipe 2, reaching 0.340 and 0.315 m^3_{gas}/kg_{waste} respectively. In terms of CO , 0.260, 0.240 and 0.220 m^3_{gas}/kg_{waste} yield values were obtained for recipes where the plastic content was 0%, 15% and 30%, respectively. These results show that with the increasing ratio of plastic-based waste in the feedstock, H_2 and CH_4 yields increase, while CO yields decreases. In addition, it was concluded that the results obtained with Recipe 4 has similarity with Recipe 3. It was concluded that this situation was due to the similarity of the cellulose-based and plastic-based waste ratio in the CWP content with Recipe 3.

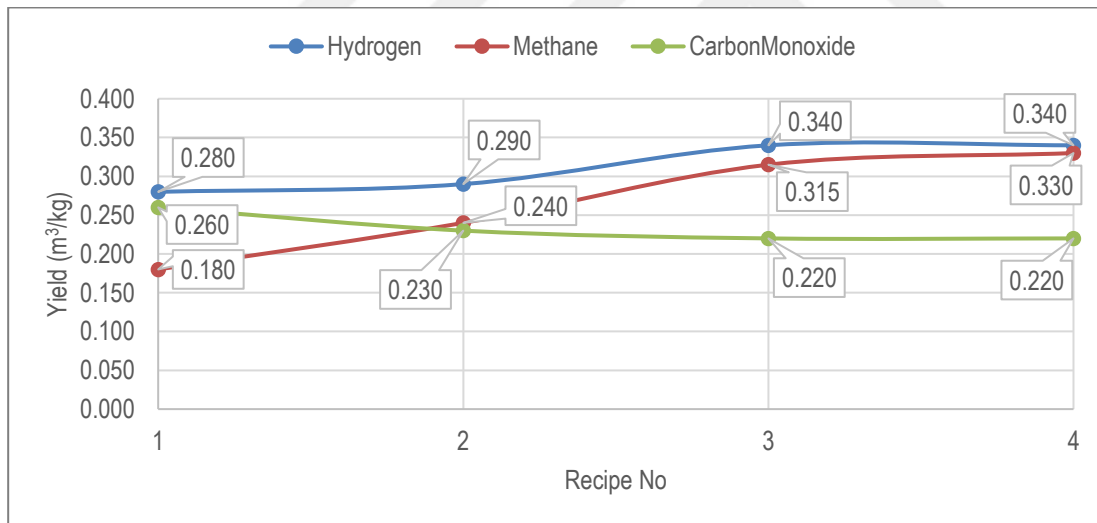


Figure 4.24: Gas yields obtained with four different recipes.

In addition to the average density values, the average calorific values (HHV_{syngas}) of the syngas (MJ/kg) were also calculated. The corresponding calculation was done by the high heating values (HHV_i) of each gas component, the average concentration values of the gases in the steady-state ($C_{avg,i}$), the total mass of syngas, and the total volumetric amount of syngas as shown in Equation 4.8. When this calculation was made, it was assumed that CO_2 gas has no effect on high heating value of syngas.

$$\frac{\sum (HHV_i * C_{avg,i}) * V_{syngas}}{m_{syngas}} = HHV_{syngas} \quad (4.8)$$

The obtained calorific values were used to calculate the cold gas efficiencies. Cold gas efficiency (CG_{eff}) was determined depending on the average calorific value of the recipe and the calorific value of the syngas for four different recipes. The method used for the CG_{eff} calculation is shown in Equation 4.9.

$$\frac{HHV_{syngas} * Syngas\ Yield}{HHV_{waste}} * 100 = CG_{eff} \quad (4.9)$$

The results obtained in the calculations of the properties of syngas obtained in pyrolysis studies performed with four different recipes and cold gas efficiencies are given in Table 4.11.

Table 4.11: Average densities, high heating values of syngases, and cold gas efficiencies for different recipes.

Recipe No	$d_{syngas,avg}$	HHV_{syngas}	CG_{eff}
	kg/m ³	MJ/kg	%
1	0.770	21.34	84.78
2	0.774	23.16	81.92
3	0.725	26.51	83.11
4	0.708	27.37	76.48

The results given in Table 4.11 show that the syngas densities are close to each other for four different recipes. On the other hand, when the calorific values are examined, it is determined that the calorific value of the syngas increases with the rise in the plastic ratio in the feedstock. Considering the high calorific value of plastic-based composite label wastes compared to cellulose-based composite wastes, it is a result that can be expected for syngas to have a higher calorific value with the increasing plastic ratio. In the aspect of cold gas efficiency, efficiencies of the syngas produced in the pyrolysis tests performed with domestic composite label wastes vary between 83.11% and 84.78%. The cold gas efficiency of the syngas produced in the pyrolysis study with CWP was calculated as 76.48%. It was concluded that the main reason for this difference between domestic label wastes and CWP was the high fixed carbon content and calorific value of char obtained in the pyrolysis of Recipe 4. According to characterization results of the char samples, the char of the Recipe 4 has the fixed

carbon content of 56.49% and the calorific value of 22.42 MJ/kg. On the other hand, the chars of domestic composite label waste samples have fixed carbon contents in the range of 39.33-49.59% and calorific values in the range of 17.50-20.10 MJ/kg. In summary, it was concluded that the high calorific value of the char causes a decrease in the cold gas efficiency of the syngas obtained in the pyrolysis of CWP.



5. CONCLUSIONS AND RECOMMENDATIONS

The high volatile matter and low ash contents of the composite wastes provide a great advantage in terms of their suitability for utilization with pyrolysis technology. Another advantage was the similar composition of the mixtures prepared from composite label wastes in Turkey with the commercial waste pellets used in boilers international both of which show close thermal behaviors and characteristics. TGA results showed that the CWP was mainly composed of cellulose and plastic wastes. The similar DTG peaks of CWP supports this fact.

The effect of the pyrolysis temperature on product yields and syngas composition were determined with the tests carried out both at batch and continuous reactor systems. Higher syngas yields with high concentrations of H_2 and CH_4 at $850^\circ C$ were indicative of secondary cracking reaction which decreases the relative content of condensable hydrocarbon vapors. Addition of plastics had an effect on the formation of wax products which makes the process complicated. Wax formation brings difficulties in sampling and hence lead the inaccurate mass balance calculations. Wax formation was more at lower temperatures. That was reasonable since wax undergoes secondary cracking at increasing temperatures. Besides, quenching of the reaction products was another concern in two of the pyrolysis units. In batch system, slow quenching and the absence of hot trapping led the plugging problems due to the uncontrolled formation of was products in the presence of plastics. As a conclusion, it was found that the wax formation caused by the plastic-based wastes may have deceptive effect on syngas yield and syngas composition. The necessity of an effective secondary thermal cracking for obtaining higher syngas yield was proved by the results obtained in the batch reactor system. Therefore, the second sets of experiments were conducted at continuous pyrolysis reactor unit at pilot scale. This pilot scale continuous unit looks like more the industrial systems and the unit was integrated with char collection traps together with hot cyclone unit. Thanks to its industrial design based on Auger type pyrolysis, pyrolyzed samples and condensable hot vapors take more time exposing to high temperatures. In this way, the syngas yield in the range between 66-76% was obtained in the tests performed in continuous reactor system. The increase in the

syngas yield might be attributed to the secondary thermal cracking unit in the system. Besides, charring may occur as well that might contribute to decrease the pyrolytic oil yield in the ranges of between 6-9%. Also, it was determined that pyrolytic oil samples were quite aqueous and its water content was in the range of 95-97%. The high-water content of the pyrolytic was interpreted as improved pyrolysis of cellulosic fractions of the samples through dehydration reactions.

The synergetic effect of plastic-based wastes in the pyrolysis was observed in both syngas yield and composition. The average H_2 concentration in steady-state condition was measured as 30% for the feedstock contains only cellulose-based composite wastes. When the plastic-based waste ratio increased to 15% and 30%, the H_2 concentration rose to 31.60% and 33.67% respectively. Moreover, it was observed that the concentrations of the CH_4 and CO depends on the plastic ratio in the feedstock. The results showed that, the increasing ratio of plastic-based waste in the feedstock resulted in higher CH_4 concentration. In the tests, CH_4 concentration increased from 21.14% to 26.90% and 30.79% with the addition of plastic-based wastes in the ratios of 15% and 30% respectively.

Lastly, it was found that the high temperature pyrolysis behavior of commercial waste pellet has similarities with behavior of the recipe 3 that includes 70% of cellulose-based and 30% plastic-based composite wastes. In the test of commercial waste pellet, the yields of H_2 and CH_4 (m^3 gas/kg waste) were calculated as 0.340 and 0.330 respectively. As similar, 0.340 m^3 H_2 and 0.315 m^3 CH_4 per kg waste were obtained during the tests of composite waste mixtures as prepared from internally procured waste labels with 70% cellulose and 30% plastic content. Thus, it was concluded that this cellulose-plastic mixing ratio may be appropriate for the utilization of sustainably supplied composite label wastes for syngas production via high temperature pyrolysis technology.

REFERENCES

- Alvarez, J., Kumagai, S., Wu, C., Yoshioka, T., Bilbao, J., Olazar, M., & Williams, P. T.** (2014). Hydrogen production from biomass and plastic mixtures by pyrolysis-gasification. *International Journal of Hydrogen Energy*, 39(21), 10883–10891. <https://doi.org/10.1016/J.IJHYDENE.2014.04.189>
- Anca-Couce, A., Dieguez-Alonso, A., Zobel, N., Berger, A., Kienzl, N., & Behrendt, F.** (2017). Influence of Heterogeneous Secondary Reactions during Slow Pyrolysis on Char Oxidation Reactivity of Woody Biomass. *Energy and Fuels*, 31(3), 2335–2344. <https://doi.org/10.1021/ACS.ENERGYFUELS.6B02350>
- Arenales Rivera, J., Pérez López, V., Ramos Casado, R., & Sánchez Hervás, J. M.** (2016). Thermal degradation of paper industry wastes from a recovered paper mill using TGA. Characterization and gasification test. *Waste Management*, 47, 225–235. <https://doi.org/10.1016/J.WASMAN.2015.04.031>
- Basu, P.** (2018). *Biomass Gasification, Pyrolysis and Torrefaction: Practical Design and Theory*.
- Bober, P., Oriňák, A., Oriňáková, R., Zamostný, P., Ladomerský, J., & Fedorková, A.** (2011). Hydrogen production by catalysed pyrolysis of polymer blends. *Fuel*, 90(6), 2334–2339. <https://doi.org/10.1016/J.FUEL.2011.02.001>
- Bolt, A., Dincer, I., & Agelin-Chaab, M.** (2020). A critical review of synthetic natural gas production techniques and technologies. *Journal of Natural Gas Science and Engineering*, 84. <https://doi.org/10.1016/J.JNGSE.2020.103670>
- Bosmans, A., Vanderreydt, I., Geysen, D., & Helsen, L.** (2013). The crucial role of Waste-to-Energy technologies in enhanced landfill mining: A technology review. *Journal of Cleaner Production*, 55, 10–23. <https://doi.org/10.1016/J.JCLEPRO.2012.05.032>
- BP.** (2022). *Statistical Review of World Energy 2022*. <https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2022-full-report.pdf>
- Bridgwater, T.** (2006). Biomass for energy. *Journal of the Science of Food and Agriculture*, 86(12), 1755–1768. <https://doi.org/10.1002/JSFA.2605>

- Bridgwater, A. v., Meier, D., & Radlein, D.** (1999). An overview of fast pyrolysis of biomass. *Organic Geochemistry*, 30(12), 1479–1493. [https://doi.org/10.1016/S0146-6380\(99\)00120-5](https://doi.org/10.1016/S0146-6380(99)00120-5)
- Campuzano, F., Brown, R. C., & Martínez, J. D.** (2019). Auger reactors for pyrolysis of biomass and wastes. *Renewable and Sustainable Energy Reviews*, 102, 372–409. <https://doi.org/10.1016/J.RSER.2018.12.014>
- Ding, Y., Huang, B., Li, K., Du, W., Lu, K., & Zhang, Y.** (2020). Thermal interaction analysis of isolated hemicellulose and cellulose by kinetic parameters during biomass pyrolysis. *Energy*, 195. <https://doi.org/10.1016/J.ENERGY.2020.117010>
- Fagbemi, L., Khezami, L., & Capart, R.** (2001). Pyrolysis products from different biomasses: Application to the thermal cracking of tar. *Applied Energy*, 69(4), 293–306. [https://doi.org/10.1016/S0306-2619\(01\)00013-7](https://doi.org/10.1016/S0306-2619(01)00013-7)
- Felix, C. B., Ubando, A. T., Chen, W. H., Goodarzi, V., & Ashokkumar, V.** (2022). COVID-19 and industrial waste mitigation via thermochemical technologies towards a circular economy: A state-of-the-art review. *Journal of Hazardous Materials*, 423. <https://doi.org/10.1016/J.JHAZMAT.2021.127215>
- Foss, M.** (2022). *The impact of renewables on energy security*. <https://doi.org/10.1080/11926422.2022.2118138>
- Gil, A.** (2022). Challenges on waste-to-energy for the valorization of industrial wastes: Electricity, heat and cold, bioliquids and biofuels. *Environmental Nanotechnology, Monitoring and Management*, 17. <https://doi.org/10.1016/J.ENMM.2021.100615>
- Hillier, J., Bezzant, T., & Fletcher, T. H.** (2010). Improved method for the determination of kinetic parameters from non-isothermal thermogravimetric analysis (TGA) data. *Energy and Fuels*, 24(5), 2841–2847. https://doi.org/10.1021/EF1001265/ASSET/IMAGES/EF-2010-001265_M008.GIF
- International Energy Agency.** (2022). *World Energy Outlook 2022*. www.iea.org/t&c/
- Jaffar, M. M., Nahil, M. A., & Williams, P. T.** (2019). Methane Production from the Pyrolysis-Catalytic Hydrogenation of Waste Biomass: Influence of Process Conditions and Catalyst Type. *Energy and Fuels*, 33(8), 7443–7457. https://doi.org/10.1021/ACS.ENERGYFUELS.9B01524/ASSET/IMAGES/LARGE/EF-2019-015248_0014.JPEG
- Kwon, E. E., Kim, S., & Lee, J.** (2019). Pyrolysis of waste feedstocks in CO₂ for effective energy recovery and waste treatment. *Journal of CO₂ Utilization*, 31, 173–180. <https://doi.org/10.1016/J.JCOU.2019.03.015>
- Lee, J., Lin, K. Y. A., Jung, S., & Kwon, E. E.** (2023). Hybrid renewable energy systems involving thermochemical conversion process for waste-to-energy strategy. *Chemical Engineering Journal*, 452. <https://doi.org/10.1016/J.CEJ.2022.139218>

- Mastral, F. J., Esperanza, E., García, P., & Juste, M.** (2002). Pyrolysis of high-density polyethylene in a fluidised bed reactor. Influence of the temperature and residence time. *Journal of Analytical and Applied Pyrolysis*, 63(1), 1–15. [https://doi.org/10.1016/S0165-2370\(01\)00137-1](https://doi.org/10.1016/S0165-2370(01)00137-1)
- Mortezaeikia, V., Tavakoli, O., & Khodaparasti, M. S.** (2021). A review on kinetic study approach for pyrolysis of plastic wastes using thermogravimetric analysis. *Journal of Analytical and Applied Pyrolysis*, 160. <https://doi.org/10.1016/J.JAAP.2021.105340>
- Obobisa, E. S.** (2022). Achieving 1.5 °C and net-zero emissions target: The role of renewable energy and financial development. *Renewable Energy*, 188, 967–985. <https://doi.org/10.1016/J.RENENE.2022.02.056>
- Oreggioni, G. D., Monforti Ferraio, F., Crippa, M., Muntean, M., Schaaf, E., Guizzardi, D., Solazzo, E., Duerr, M., Perry, M., & Vignati, E.** (2021). Climate change in a changing world: Socio-economic and technological transitions, regulatory frameworks and trends on global greenhouse gas emissions from EDGAR v.5.0. *Global Environmental Change*, 70. <https://doi.org/10.1016/J.GLOENVCHA.2021.102350>
- Pan, S. Y., Du, M. A., Huang, I. te, Liu, I. H., Chang, E. E., & Chiang, P. C.** (2015). Strategies on implementation of waste-to-energy (WTE) supply chain for circular economy system: a review. *Journal of Cleaner Production*, 108, 409–421. <https://doi.org/10.1016/J.JCLEPRO.2015.06.124>
- Qureshi, M. S., Oasmaa, A., Pihkola, H., Deviatkin, I., Tenhunen, A., Mannila, J., Minkinen, H., Pohjakallio, M., & Laine-Ylijoki, J.** (2020). Pyrolysis of plastic waste: Opportunities and challenges. *Journal of Analytical and Applied Pyrolysis*, 152. <https://doi.org/10.1016/J.JAAP.2020.104804>
- Rada, E. C., Ragazzi, M., Torretta, V., Castagna, G., Adami, L., & Cioca, L. I.** (2018). Circular economy and waste to energy. *AIP Conference Proceedings*, 1968. <https://doi.org/10.1063/1.5039237>
- Serio, M. A., Cosgrove, J. E., Wójtowicz, M. A., Wignarajah, K., & Fisher, J.** (2012). Methane production from pyrolysis of mixed solid wastes. *42nd International Conference on Environmental Systems 2012, ICES 2012*. <https://doi.org/10.2514/6.2012-3567>
- Sophonrat, N., Sandström, L., Johansson, A. C., & Yang, W.** (2017). Co-pyrolysis of Mixed Plastics and Cellulose: An Interaction Study by Py-GC×GC/MS. *Energy and Fuels*, 31(10), 11078–11090. https://doi.org/10.1021/ACS.ENERGYFUELS.7B01887/ASSET/IMAGES/LARGE/EF-2017-01887Q_0014.JPEG
- Su, C., & Urban, F.** (2021). Circular economy for clean energy transitions: A new opportunity under the COVID-19 pandemic. *Applied Energy*, 289. <https://doi.org/10.1016/J.APENERGY.2021.116666>
- Tsai, W.-T., Musmarra, D., Kozinski, J., Garcia, B., Alves, O., Rijo, B., Lourinho, G., & Nobre, C.** (2022). *Biochar: Production, Applications, and Market Prospects in Portugal*. <https://doi.org/10.3390/environments9080095>

- Uday, V., Harikrishnan, P. S., Deoli, K., Zitouni, F., Mahlknecht, J., & Kumar, M.** (2022). Current trends in production, morphology, and real-world environmental applications of biochar for the promotion of sustainability. *Bioresource Technology*, 359. <https://doi.org/10.1016/J.BIORTECH.2022.127467>
- Uzoejinwa, B. B., He, X., Wang, S., El-Fatah Abomohra, A., Hu, Y., & Wang, Q.** (2018). Co-pyrolysis of biomass and waste plastics as a thermochemical conversion technology for high-grade biofuel production: Recent progress and future directions elsewhere worldwide. *Energy Conversion and Management*, 163, 468–492. <https://doi.org/10.1016/J.ENCONMAN.2018.02.004>
- Wang, Z., Burra, K. G., Lei, T., & Gupta, A. K.** (2021). Co-pyrolysis of waste plastic and solid biomass for synergistic production of biofuels and chemicals- A review. *Progress in Energy and Combustion Science*, 84. <https://doi.org/10.1016/J.PECS.2020.100899>
- Wijayasekera, S. C., Hewage, K., Hettiaratchi, P., Siddiqui, O., Razi, F., Pokhrel, D., & Sadiq, R.** (2022). Sustainability of waste-to-hydrogen conversion pathways: A life cycle thinking-based assessment. *Energy Conversion and Management*, 270. <https://doi.org/10.1016/J.ENCONMAN.2022.116218>
- Wijayasekera, S. C., Hewage, K., Siddiqui, O., Hettiaratchi, P., & Sadiq, R.** (2022). Waste-to-hydrogen technologies: A critical review of techno-economic and socio-environmental sustainability. *International Journal of Hydrogen Energy*, 47(9), 5842–5870. <https://doi.org/10.1016/J.IJHYDENE.2021.11.226>
- World Bank.** (n.d.). *The Impact of the War in Ukraine on Commodity Markets Commodity Markets Outlook*.
- Yang, K., Huang, J., Dong, B., Liu, P., Chen, L., Wang, Z., & Jia, L.** (2021). Secondary Reactions of Primary Tar from Biomass Pyrolysis: Characterization of Heavy Products by FT-ICR MS. <https://doi.org/10.1021/acs.energyfuels.1c01723>
- Zhai, M., Wang, X., Zhang, Y., Dong, P., Qi, G., & Huang, Y.** (2015). Characteristics of rice husk tar secondary thermal cracking. *Energy*, 93, 1321–1327. <https://doi.org/10.1016/J.ENERGY.2015.10.029>

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