

Energimyndighetens titel på projektet – svenska Utvärdering av sampyrolys av plastavfall med lågvärdig biomassa	
Energimyndighetens titel på projektet – engelska Evaluation of co-pyrolysis of plastic waste and low value biomass	
Universitet/högskola/företag RISE Energy Technology Center AB	Avdelning/institution [Klicka här och skriv]
Adress Box 726	
Namn på projektledare Ann-Christine Johansson	
Namn på ev övriga projektdeltagare Lena Smuk, Henrik Jilvero, Klaas van der Vlist	
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Preface

The project has been financed to 45 % by RE:Source, a Swedish Strategic innovation program focusing on research and innovation within the resource and waste area. The rest has been financed by Smurfit Kappa (45 %) and Stena Metall AB (9 %) which also have acted as a reference group and contributed with valuable input to the project.

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Sammanfattning

Snabb pyrolys är en lovande termokemisk teknik för att konvertera organiskt material, till exempel biomassa och plast, till energi, kemikalier och/eller fordonsbränslen. Tidigare laborativa studier har visat att pyrolys av en blandning av plast och biomassa kan vara mer fördelaktigt jämfört med pyrolys av de separata materialen med avseende på kvalitet på produkter, effektivitet på pyrolyprocessen samt möjlighet att producera bio-baserade produkter i plaståtervinningen.

I detta arbete har tre relevanta plastavfall; pappersrejekt (plastfraktion från pappers- och kartongåtervinningen), plastfraktion från bilåtervinning (SLF) och kopparkabelplast; utvärderats tillsammans med biomassa med hjälp av analytisk pyrolys, Py-GC/MS, FID. Två verifieringsförsök har även utförts genom att två materialblandningar pyrolyserats i en industriell relevant pilotskala. Resultaten visade att tillsats av plastavfall till pyrolys av biomassa väsentligt påverkar sammansättningen och egenskaperna hos de framställda pyrolysoljeprodukterna. Den analytiska pyrolysen visade att positiva synergieffekter erhöles i sampyrolys av pappersrejekt och kabelplast tillsammans med biomassa. De reaktiva oxygenerade föreningarna, ketoner, aldehyder och syror, undertrycktes medan de mer stabila alkoholerna och estrarna främjades. Kolväten främjades också vid sampyrolys av pappersrejekt och biomassa. Biomasseblandningar med pappersrejekt och kabelplast valdes ut för verifiering i större pilotskala. Resultaten från experimenten i pilotskala visade på komplexiteten av att blanda in plastavfall i biomassepyrolysen. Kabelplasten orsakade en mycket högviskös olja som pluggade anläggningen och medförde att en massbalans inte kunde utföras. Den producerade pyrolysoljan från pappersrejektblandningen visade på både positiva och negativa egenskaper jämfört med biomasseolja. Exempel på positiva egenskaper var exempelvis lägre mängd reaktiva oxygenerade komponenter medan lägre pH, högre metallhalt och högre viskositet är exempel på mer negativa egenskaper. Oljeutbytet för pappersrejektblandningen var ungefär detsamma som för ren biomassa, men eftersom piloten inte optimerades för blandningen är det sannolikt att oljeutbytet skulle kunna öka något på grund av oreagerade flyktiga komponenter i den fasta återstoden.

Sammanfattningsvis kan det konstateras att sampyrolys av en blandning av plastavfall och biomassa kan ge både positiva och negativa effekter på såväl utbyte som kvalitet beroende på faktorer som exempelvis sammansättning av materialen och processförhållanden. Nya utmaningar erhålls emellertid när plastavfall adderas till biomassepyrolys, exempelvis hög klor- och metallhalt i råvaran och hög viskositet hos den producerade oljan som måste beaktas innan framtida implementering.

Summary

Fast pyrolysis is a promising thermochemical technology for converting organic material, such as biomass and plastics, into energy, chemicals and/or fuels. Previous laboratory studies have shown that pyrolysis of a mixture of plastics and biomass may be more advantageous compared to pyrolysis of the separate materials with regard to product quality, pyrolysis efficiency, and the ability to produce bio-based products in the plastic recycling. In this work three relevant plastic wastes; paper reject, shredded light fraction and cable plastics; have been evaluated together with biomass using analytical pyrolysis, Py-GC/MS, FID. Two verification experiments have also been performed by pyrolyzing two material mixtures in an industrially relevant pilot scale. The results showed that addition of plastic waste to biomass pyrolysis significantly affects the composition and properties of the produced pyrolysis products. The analytical pyrolysis showed that synergetic effects were obtained in the co-pyrolysis of paper rejects and cable plastics together with biomass. The reactive oxygenated compounds, ketones, aldehydes and acids, were suppressed while more stable alcohols and esters were promoted. The hydrocarbons were also promoted in the co-pyrolysis of paper rejects and biomass. Biomass blends with paper reject and cable plastics were selected for verification in a larger pilot scale. The results of the pilot scale experiments showed the complexity of addition of plastic waste into biomass pyrolysis. The cable plastics produced a highly viscous oil that plugged the plant that resulted in that a mass balance could not be performed. The produced pyrolysis oil from the paper reject blend showed both positive and negative properties compared with biomass oil. Examples of positive properties were, for example, lower amount of reactive oxygenated components, while lower pH, higher metal content and higher viscosity are examples of more negative properties. The oil yield for the paper reject blend was about the same as for pure biomass, but since the pilot was not optimized for the blend, it is likely that the oil yield could increase slightly due to unreacted volatile components in the solid residue.

In summary, it can be noted that co-pyrolysis of a mixture of plastic waste and biomass can give both positive and negative effects on both product yield and quality due to factors such as composition of materials and process conditions. However, new challenges are obtained when plastic waste is added to biomass pyrolysis, for example high chlorine and metal content in the raw material and high viscosity of the oil produced, which must be considered before future implementation.

Introduction/Background

Cellulosic biomass is a non-food based renewable feedstock that have the potential to be further converted to energy, high value chemicals and biofuels via pyrolysis. However, the pyrolysis oil produced from biomass has undesired properties in a biofuel perspective, mainly related to the high proportion of reactive oxygenated compounds. Extensive research has been done on improving

the oil quality by reducing the oxygen content for example by using methods as catalytic cracking and catalytic hydrotreatment. However the main challenges with these methods are short catalyst lifetimes, low carbon efficiencies and high coke formation (Dickerson and Soria, 2013). These factors of course affects the total economy of the process and is probably one of the reason the company KiOR, that built a commercial plant in Columbus, Mississippi, USA, suffered from financial problems and went bankrupt in 2014 (Mufson, 2014). An alternative route to improve the quality of the liquid product, reduce the coke formation and improve the efficiency can be to co-pyrolyse the biomass with plastic materials rich in carbon and hydrogen (Abnisa and Wan Daud, 2014; Zhang, 2016). A feedstock with high hydrogen content can act as a hydrogen donor to the hydrogen deficient biomass in the biomass conversion (Dorado et al., 2015). In addition, studies have shown that co-pyrolysis of biomass and plastic can induce synergetic effects compared to pyrolysis of the separate components in terms of increased pyrolysis oil quantity and quality (Dorado et al., 2014; Zhang et al., 2014; Brebu et al, 2010, Ojha and Vinu, 2015; Rutkowski and Kubacki, 2006; Chattopadhyay et al., 2016). For example Dorado et al. 2014, 2015 showed that a positive synergy exists between plastics and biomass in terms of increased aromatic hydrocarbon yield at catalytic pyrolysis using ZSM-5. However, the reaction mechanisms between different biomasses and plastics are very complex and the synergetic effects depend upon a number of factors including type and contact of components, pyrolysis duration, temperature and heating rate, removal or equilibrium of volatiles formed, and addition of solvents, catalysts and hydrogen donors (Johannes et al, 2013).

A preferable hydrogen containing material with both low bulk cost and call for an urge of reduction in environmental stress is so called plastic end-of-life products. A large environmental achievement could be reached if these products were utilized in the co-pyrolysis process since the disposal of waste polymers would be reduced and new bio-based products could be produced. This brings needs of further research to determine relevant and suitable biomass-polymer mixtures that improve the performance, quality and yield of desired products. The overall objective with this work is to evaluate how co-pyrolysis of relevant industrial plastic waste and biomass can be improved with regards to quality of pyrolysis products and pyrolysis oil yield. In this project three industrial plastic waste streams are evaluated; paper reject, shredded light fraction (SLF) and Cu cable plastics, and biomass, stem wood from pine and spruce. The evaluation is carried out using both analytical pyrolysis complemented by experiment in an industrially relevant cyclone pilot reactor system.

The project is led by RISE ETC, who also carried out most of the work within the project, complemented by RISE Built Environment/Energy and circular economy supported by the reference group that consists of representatives from Smurfit Kappa and Stena Metall AB. The project was carried out from the 9th of September 2016 to the 30th of January 2018.

Implementation

The project was divided into three work packages; Analytical evaluation of feedstocks and mixtures (WP 1), Pilot experiments (WP 2) and Analysis of other methods suitable for feedstock recycling of paper reject (WP 3).

In the first work package (WP1) the pyrolysis properties of three different plastic wastes, one biomass and mixture of these were evaluated. The studied plastic wastes were plastic from paper and board recycling (paper reject), Shredded Light Fraction (SLF) and Cu cable plastic. They were evaluated by chemical analysis and analytical pyrolysis (Py-GC/MS, FID). The analytical pyrolysis was carried out both with and without catalysts. This work was used as a screening to be able to select suitable mixtures for further pilot experiments. This work package was performed by Ann-Christine Johansson, RISE ETC.

In work package 2 (WP2) the pyrolysis properties of two selected mixtures (Cu cable plastic:stemwood and paper reject: stemwood) were evaluated in industrial relevant pilot scale. This work was started by pretreatment of the feedstocks to produce a homogenous fine powder that could be fed into the pyrolysis process. This work included mainly milling, mixing and feeding. The two mixtures were then pyrolysed in the pyrolysis oil cyclone (POC) and compared to pyrolysis of pure stemwood. This work included preparations, feeding, pyrolysis, cleaning, mass balance calculations and characterization of the produced products. This work package was performed by the pyrolysis group (including technicians, operators, chemists and project leader) at RISE ETC.

The analysis conducted in the framework of WP3 was based on literature studies and a number of interviews with leading Swedish experts in feedstock recycling. The interviews have been conducted in connection with the ongoing project on the construction of the Swedish Feedstock Recycling Platform (funded by Re: Source as an individual project/"enskilt projekt"). Lena Smuk (RISE, building environment / energy and circular economy) has been responsible for this work package.

Results

In a first approach to study the feedstocks and select suitable plastic biomass mixtures the feedstocks were evaluated by chemical characterization and by analytical pyrolysis. The chemical analysis was used to determine the composition of the sample and to predict the pyrolysis properties. The analytical pyrolysis was used to understand the thermal behavior and determine the produced relative amount of volatile compounds and to identify the typical pyrolysis products (chemical compounds) and chemical groups. The result from the first evaluation was used to select suitable feedstocks and mixtures for further verification in pyrolysis pilot experiments.

For more in-depth information about the experimental part, including more information about the materials, pretreatment of the materials, analytical instruments, the pilot plant, product analysis, experimental plan etc the reader is referred to the manuscript “Co-pyrolysis of woody biomass and plastic waste in both analytical and pilot scale”, appendix 2.

Chemical characterization

The chemical characterization of the feedstocks was used to determine the composition of the sample and to predict the pyrolysis properties. In Table 1 the chemical and physical composition of the feedstocks can be found.

Table 1. Feedstock properties

	Unit	Paper reject	SLF	Cable plastic	Stem wood	Pelletized paper reject: Stem wood (20:80)
Moisture	% w/w, dried	1.0	1.7	0.3	4.3	4.2
Volatiles	% w/w, dry	76.5	53.3	95.9	83.8	83.4
Ash	% w/w, dry	21.0	46.1	5.9	0.3	1.6
C	% w/w, dry	52.9	33.5	76.2	51.3	50.4
H	% w/w, dry	7.5	4.3	12.4	6.2	6.5
N	% w/w, dry	0.49	1.47	0.10	0.1	0.1
O	% w/w, dry	16.6	13.9	5.0	42	41.2
S	% w/w, dry	0.138	0.313	0.020	0.021	0.034
Cl	% w/w, dry	1.34	0.479	0.365	<0.02	0.23
H/C_{eff}		1.193	0.787	1.460	0.206	0.310
LHV	MJ/kg, ds	24.294	14.148	39.163	19.305	20.336
HHV	MJ/kg, ds	25.898	15.109	41.806	19.364	20.831
HHV	MJ/kg, ds, ash free	30.752	26.322	41.618	19.422	20.666
Si	mg/kg, ds	20 661	59 831	4 609	67	845
Al	mg/kg, ds	8 997	19 264	6 404	17	1847
Ca	mg/kg, ds	36 664	25 372	7 718	587	3273
Cu	mg/kg, ds	1 890	1 940	6 910	3	85
Fe	mg/kg, ds	13 300	67 603	716	6.6	407
K	mg/kg, ds	971	4 524	269	303	290
Mg	mg/kg, ds	1 966	5 994	1 652	106	232
Mn	mg/kg, ds	264	1 673	29	65	73
Na	mg/kg, ds	3 643	7 492	470	23	168
P	mg/kg, ds	349	969	53	26	33
Ti	mg/kg, ds	1817	3 825	629	0.6	362
Zn	mg/kg, ds	1900	18 400	1 910	8.73	34

For pyrolysis, important parameters are mainly the volatility, ash content (mainly the alkali content), the elemental content and the heating value. To improve the oil yield the volatile matter should be high and the ash content (alkali content) low. Last but not least it is favorable to have a high heating value in the feedstock to get a high heating value in the liquid product. From the analyses of the cable plastic it can be seen that in relation to the other plastics the volatile matter, the H/C_{eff} and the heating value are relatively high and the alkali metals are relatively low. Contrary, the SLF has the lowest volatile matter, H/C_{eff} and heating value and the highest ash content (highest alkali content). The properties of the paper reject are in between the other plastics. It can also be noted that the paper reject contain rather high chlorine content which can cause corrosion problem in the equipment and formation of chlorinated organics. In Table 1 also the properties of the mixture between pelletized paper reject and stem wood can be found. In the

pellets some metals have been removed and therefore the concentration of the metals Si, Ca, Fe, Na and Zn are lower than in the un-pelletized reject .

Analytical pyrolysis

In the analytical pyrolysis both thermal, without catalyst, and catalytic pyrolysis, with HZSM-5 catalyst, were conducted using both the separate feedstocks and the plastic and biomass mixtures. For more in-depth information about the analytical pyrolysis the reader is referred to the manuscript “Co-pyrolysis of woody biomass and plastic waste in both analytical and pilot scale”, appendix 2.

The results from the analytical pyrolysis show indications of synergetic effects when pyrolyzing blends of biomass (stem wood) with paper rejects and copper cable plastics. It seems that pyrolysis of these mixtures promotes the formation of hydrocarbons and suppresses the formation of reactive oxygenated compounds such as aldehydes and ketones, compared with pyrolysis of the individual materials, an example of this can be seen in Figure 1. The blends of biomass with paper reject and with cable plastics were therefore selected to be studied further in larger scale. Addition of HZSM-5 zeolite to the pyrolysis suppressed the formation of oxygenated compounds and promoted aromatic hydrocarbons but no synergetic effects were obtained.

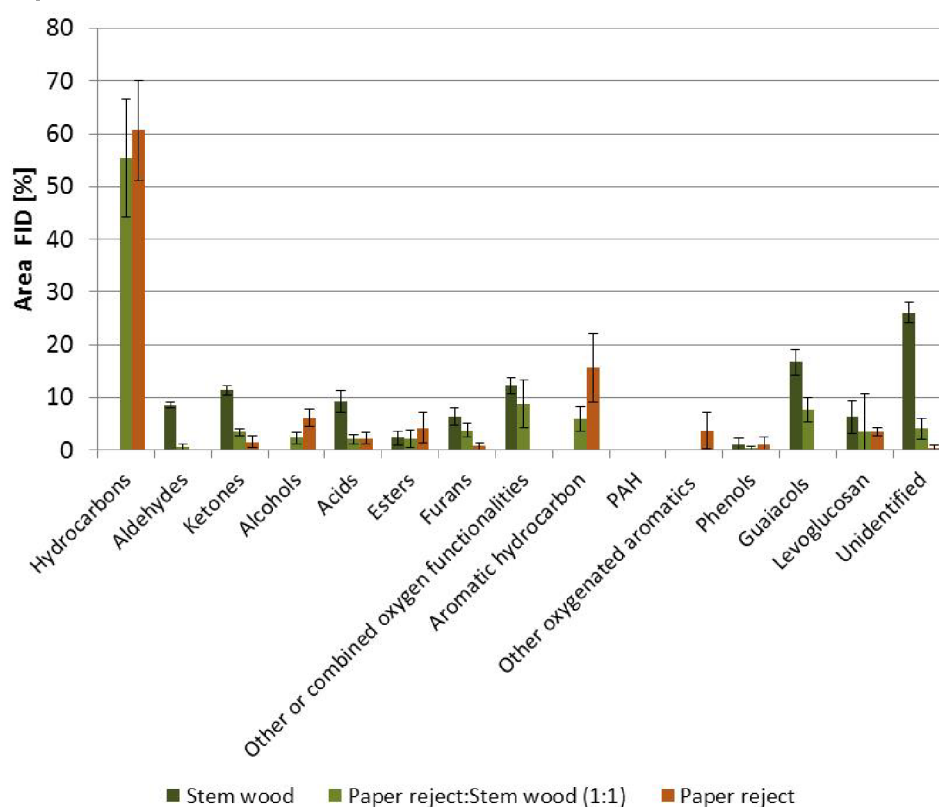


Figure 1. Pyrolysis products, grouped into compounds groups, produced during analytical pyrolysis of stem wood (dark green), paper rejects (orange) and a mixture of paper reject:Stemwood (1:1) (light green).

Pilot scale pyrolysis

The analytical pyrolysis is an adequate quantitative screening method for determination of the produced volatile compounds but it has some limitations, for example that no actual product yields or pyrolysis oil are obtained. Therefore analytical pyrolysis should be complemented with larger scale pyrolysis to provide more insights of the process. Therefore verifications of the results from the analytical scale were made for selected mixtures in pilot scale.

Before the pyrolysis the material has to be pretreated to efficiently be converted in the process. Sufficient pretreatment includes milling and mixing of the materials. It is also important that the material can be feed into the process is smooth and stable. In order to assure that these parameters were fulfilled milling, mixing and feeding experiments were performed on the selected mixtures. The main result from this part was that it was possible to produce a fine homogenous transportable powder from both of the mixtures. It was possible to mill the plastics to a fine powder (below 2 mm), mix it with biomass and smoothly feed it to the pyrolysis process. (Smaller particles were however not possible to produce using the existing equipment since the plastics then formed a “fluff” that was difficult to transport.)

Mixtures of cable plastics and biomass (50:50) and paper reject and biomass (20:80) by weight were pyrolyzed in the pilot plant, under similar process conditions as normally used for pure biomass. Both the pyrolysis experiments were stable by means of gas production and process temperature. However, the pyrolysis oil produced from the cable plastics was very viscous resulting in clogging of the condensing equipment of the pilot plant that resulted in that a mass balance could not be performed. The cable plastics contain polyethylene which can produce wax-like compounds during thermal pyrolysis, which probably was the case. The produced pyrolysis oil from the paper reject blend showed both positive and negative properties compared with biomass oil. Examples of positive properties were, for example, lower amount of reactive oxygenated components, while lower pH, higher metal content and higher viscosity are examples of more negative properties. The oil yield for the paper reject blend was about the same as for pure biomass, but since the pilot was not optimized for the blend, it is likely that the oil yield could increase slightly due to unreacted volatile components in the solid residue.

Methods suitable for feedstock recycling of paper reject

Work package 3 would originally contain a system analysis, environmental mapping and climate impact analysis of the co-pyrolysis process based on paper reject. However, due to obtained result from the work package 2 it was decided to change the aim with work package 3 and instead do a literature study of other suitable methods for recycling paper reject. Below follows a short summary of the results from the study.

An essential parameter to be taken into account when selecting feasible methods for processing paper reject is the high moisture content (up to 40%). To avoid drying steps in treatment is highly desirable to achieve a good economy in the process.

Steam gasification can be recommended as the most promising option if the desired product is syngas. While different types of reactors can be used for steam gasification, fluidized beds are generally considered to be more advantageous than other types of reactors. This is due to both rapid heat transfer and thus shorter processing times, but also because they permit the application of chemically active bed material (e.g., olivine) that can act as catalysts for in-situ reforming of tars, for shifting the equilibrium in the water-gas reaction, and for char conversion (Monchida et al., 2008).

Direct liquefaction can be suggested as an alternative to steam gasification if the obtaining of liquid products from the recycling of plastic residues is preferred. Hydrothermal liquefaction (HTL) process converts carbon-containing materials into liquid hydrocarbons - liquid fuels and petrochemicals by breaking down their organic structure in the presence of solvents and /or catalysts and at elevated temperature /pressure. HTL is carried at temperatures in the range 250–450 °C, and pressures in the range 5–20 MPa. Under these conditions, water is in a liquid state, and thus high moisture content in the material to be processed is acceptable (Elliott et al., 2015).

Discussion

Co-pyrolysis of a mixture of plastic waste and biomass can give both positive and negative effects on both product yield and quality due to factors such as composition of materials and process conditions. It appears as if the reactive oxygenated compounds can be reduced but introduction of plastic waste can also incorporate new challenges into the biomass pyrolysis. Challenges that need to be addressed before further implementation is for example issues related to chlorine content in the plastic waste, increased viscosity of the produced oil and need of different process conditions caused by different properties of the materials. The results from this work also indicates that co-pyrolysis can be an alternative for mixed wastes that already contain both biomass and plastics such as paper reject, but it is probably better to pyrolyse cleaner plastic waste and biomass streams separately due to the diverse properties of the components.

Depending on the type of product that is desired, there are also other processes that can fit for conversion of plastic waste. Based on the results of the analysis performed in WP3 steam gasification and direct liquefaction can be recommended as alternative methods.

Publication list

Johansson A-C, Sandström L., Öhrman O.G.W., Co-pyrolysis of woody biomass and plastic waste in both analytical and pilot scale, manuscript in progress (A confidential draft manuscript can be found in appendix 2)

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Appendix

1. Administrative attachment
2. "EJ SPRIDNING" Manuscript in progress Co-pyrolysis of woody biomass and plastic waste in both analytical and pilot scale