REPORT B

Stockholm, Sweden

2015-09-07

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List of abbreviations

HM – horse manure

HWS – household waste skudge

MSW – municipal solid waste

PVC – polyvinyl chloride

RDF – refuse derived fuel

TGA – thermogravimetric analysis

1. OBJECTIVE

The objective of Action B8 was to evaluate different waste-based substrates for gasification, resources that are not suitable for neither wet nor dry fermentation. Cortus has performed small scale tests of municipal solid waste (MSW), horse manure (HM), and household waste sludge (HWS). Within the scope of the project, both dry fermentation and gasification will be performed for these substrates and the results will be evaluated and compared to determine the best biomethane production technology (Action B1). The waste-based substrate that prove to be the most suitable will be used in the methanation process and production of biomethane in Action B11.

1.1. Pre-Treatment of Waste-Based Substrates

In order to perform gasification tests, each potential biomass substrate neede to be evaluated for suitability in a WoodRoll® gasification process. Therefore, data about chemical and physical conditions needs to be collected for each biomass substrate. Small samples of each waste-based substrate was analyzed in a Cortus laboratory. It is important that each waste-based substrate is homogeneously mixed to get representative data. Additional elementary analysis will be conducted for each waste-based substrate in order to predict if any unexpected contaminants will be generated during a WoodRoll® gasification process.

1.2. Thermogravimetric Analysis (TGA) of Three Waste-Based Substrates

Next step after pre-treatment was to perform lab-scale gasification tests, thermogravimetric analysis (TGA). By using the TGA instrument great knowledge is gained about how each waste-based substrate behave during drying, pyrolysis and gasification. During this analysis, moisture and ash content is also determined. After testing more than a hundred different biomass and waste species Cortus has established a specific routine of a testing procedure via TGA, this to meet conditions and standards required for a Woodroll system [1]. The test period for TGA is three days per biomass substrate, and the generated results give an indication of the suitability of each certain fuel in a WoodRoll® process. Moreover, critical process parameters was also determined based on the TGA results.

1.3. Up-scaling of Experiments

Based on the results from above activities a proper waste-based biomass substrate will be chosen for further testing in Cortus pilot plant, a 500 kW gasification plant placed I Köping, Sweden. The main process steps for WoodRoll®, drying, pyrolysis and gasification, will be further evaluated in a larger scale. Moreover, grindability of the char formed during pyrolysis of biomass will also be studied. Analysis of product gas and condensate will be performed in order to design the gas and condensate (water) cleaning system. Samples of char and ash will be collected and sent for further analysis.

2. IMPLEMENTATION

Implementation of Action B8, Section 1.1 and 1.2, was carried out during the fall of 2014 (August - October). The pre-selected waste-based biomass substrates were municipal solid waste, horse manure and household waste sludge.

2.1. Pre-Treatment of Waste-Based Substrates

Activities for Section 1.1 was collecting data for chemical and physical conditions of each biomass sample, moreover, a proper mixing is substantial for this type of material due to a very heterogeneous raw material. In order to get a homogeneous mixture the raw material was treated by grinding, cropping and cutting. Lower heating value calculated for dry basis using Boie's formula for solids fuels. Ash content determined as the residue after burning all of the organic matter using the standard gravimetric method. All analysis performed in an external reference lab (DLAB and Belab) following standard methods.

2.2. Thermogravimetric Analysis (TGA) of Three Waste-Based Substrates

Activities for section 1.2 was to perform thermogravimetric analysis on three pre-selected waste-based substrates. Thermogravimetric analysis is a type of testing used to determine changes in weight relative variations in temperature. In this case it was used to evaluate the three pre-selected fuels from a WoodRoll® perspective. Cortus has created a database of about 40 different types of biomasses. The thermogravimetric instrument consist of a thermo-balance (main component), water vapor furnace and a steam generator. Additional components are a drying furnace, a burning furnace and a scale to weigh biomass and ash. The thermogravimetric analysis enables observations of humidity content, reactivity at different pyrolysis and gasification temperatures, as well as determination of the ash content in each biomass sample. This method was used as a biomass screening tool since it enables comparison of gasification reactivity and other properties between different biomass substrates within a relatively low cost and short time period. Each biomass sample was pre-weighed prior testing, and each sample was analyzed twice, first at a gasification temperature of 850 °C for 90 minutes. The first run with a gasification of 850 °C was conducted in order to deliver kinetic data which can be used for comparison between different biomass fuels, and the second run at a gasification temperature of 1100 °C was conducted to mimic the WoodRoll® process, which has a process temperature for gasification of 1100 °C. When running gasification at 1100 °C, the reactions in the TGA are limited by diffusion and energy transfer, not the kinetics of the biomass. Hence, the gasification experiment is performed at two different temperatures. For all runs, three different pyrolysis temperatures were used: 360, 380 and 400 °C. Three blank tests with the same conditions as the experiments described above. These blank tests were conducted to deliver information about outer disturbances such as, for instance, the buoyancy effect. Each experimental session was controlled by a specifically designed temperature program developed to mimic a WoodRoll® process. Moreover, for each experiment a sample of the waste-based biomass was sent to Belab for ash and elementary analysis.

3. RESULTS AND DISSCUSION

The results generated in Action B8, section 1.1, were used to further develop the project to find an optimal waste-based substrate for methane production using the WoodRoll® process. Report B only covers section 1.1 and 1.2 for Activity B8. The last section 1.3 will be treated in the next phase of the project and presented in Report 2.

3.1. Pre-Treatment of Waste-Based Substrates

Table 1 collects the results of chemical analysis of several biomass/waste substances (cases, pre-selected for this project, have been bolded.

Table 1: Chemical characterization of tested fuels including comparison with reference fuels

Fuel	Moisture content	C	H	O	N	S	P	CL	Ash[%]	LHV DB [MJ/Kg]
Salix	20	47,5	6,1	43,2	0,3	0,2	0,2	-	1,9	18,1
Fiber sludge-Forest residues	42	47,8	5,9	39,6	0,8	0,5	0,2	0,0	6,0	18,0
Spruce Bark	29	50,8	5,7	39,3	0,5	0,2	0,2	-	3,5	18,6
RDF/MSW*	27	46,8	6,3	23,6	1,4	0,4	0,2	0,9	20,7	19,7
Mixed MSW**	-	-	-	-	-	-	-	-	-	**18-21**
Horse Manure	**58**	**26,0**	**3,8**	**18,2**	**2,57**	**2,34**	**2,93**	**4,66**	**47,8**	**11,1**
Household waste sludge	**68**	**25,0**	**3,1**	**14,7**	**1,7**	**0,4**	**0,6**	**0,8**	**54,4**	**10,2**

*RDF (mixed and processed MSW, composed of plastics, paper, wood residues from other source)

** None sorted and none homogenized fraction makes it hard for analysis and further treatment

Two out of three samples succeed the pre-selection process for chemical analysis and TGA tests: horse manure and household waste sludge. In case of municipal solid waste (MSW) it was impossible to collect a representative material for testing as the received material comprise non-sorted household waste as can be seen in Fig.1, it was therefore not tested in the TGA.

Figure 1: Pictures of the biomass samples (as received): 1- mixed MSW, 2-horse manure, 3-household waste sludge.

Mixed MSW, received from VAFAB Miljö AB, could be considered as a proper fuel for the WoodRoll system but it would require some pretreatment in order to homogenize and reduce the size of the fraction. One example of such pretreatment is RDF (refuse derived fuel) of processed plastic (excluding PVC) and paper fraction. MSW from another source has been tested in TGA by Cortus earlier; the results from that test will therefore be discussed in this report. Chemical analysis of RDF (see table 1) classifies this fuel as potentially attractive for gasification due to high calorific value and low moisture content. Due to differences in density, size and shape between components, some negative phenomena that may occur during transportation requires additional investigation. Homogenizing of the feedstock into pellets would solve perhaps some technical limitation of MSW but at the same time generate additional costs for the pretreatment leading to an increased price of the fuel.

Horse manure, received from VAFAB Miljö AB, was more homogenous than MSW but contains too low content of organic matter (20% as received). Biotechnological treatment methods seem to be more suitable for that type of waste. High moisture content and very high ash content disqualify this fuel for a direct use in WoodRoll process. In addition nearly 50% of the mass is ash that contains substantially high amounts of chlorine and alkali metals that reduce the melting point of the ash, making it unsuitable for a high thermal use in the Woodroll gasifier. Using this type of fuel for thermal treatment would require corrosion resistant material along the whole processing line and additional post-treatment gas -and -ash cleaning systems. Additional research is needed to see if fuels such as horse manure can be used as a small quantity additive to blend with a larger stream of accepted biomass for the WoodRoll process, such as, for instance, woodchips.

Although household sludge has the highest content of moisture and ash it is the most homogenous fuel from the three received biomass-waste samples. It was received from JTI (Agriculture Institute of Technology, Uppsala) from a bioresearch-plant. Household sludge is a byproduct (sediment) from the dry fermentation process and as such is under industrial control. In general, an advantage of industrial-type wastes is that the material is both chemically and physically more uniform. Due to very high moisture content and ash content (very low organic content), direct use of this fuel in a WoodRoll process would affect the overall efficiency drastically, and hence it is not recommended. Similar as with horse manure, blending the sludge with a larger amount of conventional biomass could be considered as potential option for utilizing this waste within a WoodRoll process.

3.2. Thermogravimetric Analysis (TGA) of Three Waste-Based Substrates

As before mentioned, the main role of TGA testing is to analyze the thermal behavior of samples subjected to the typical conditions existing in the WoodRoll system. It plays a vital role for the whole process to be able to estimate the distribution of mass during drying, pyrolysis and gasification and the chemical composition of each of the generated fractions, including by-products, as for instance, ashes. Those tests can reveal whether a sample (biomass, waste) can fit into the mass and energy balance of the system or not. In case of a negative result the sample can still be potentially attractive for the WoodRoll process but after applying more or less sophisticated pretreatment methods.

As mentioned in the previous part, the received MSW could not be used for TGA due to heterogeneity in size, fracture and type of the testing material leading to non-representative results. Such as unsorted fraction makes severe difficulties in predicting product distribution of the generated fractions and what seems to be more important in up-scaling the results from the lab to the pilot-scale.

The results of mass remaining after treatment of samples at 360, 380 and 400 °C (isothermal pyrolysis conditions) in N_2 atmosphere are present in Table 2 and Fig 2

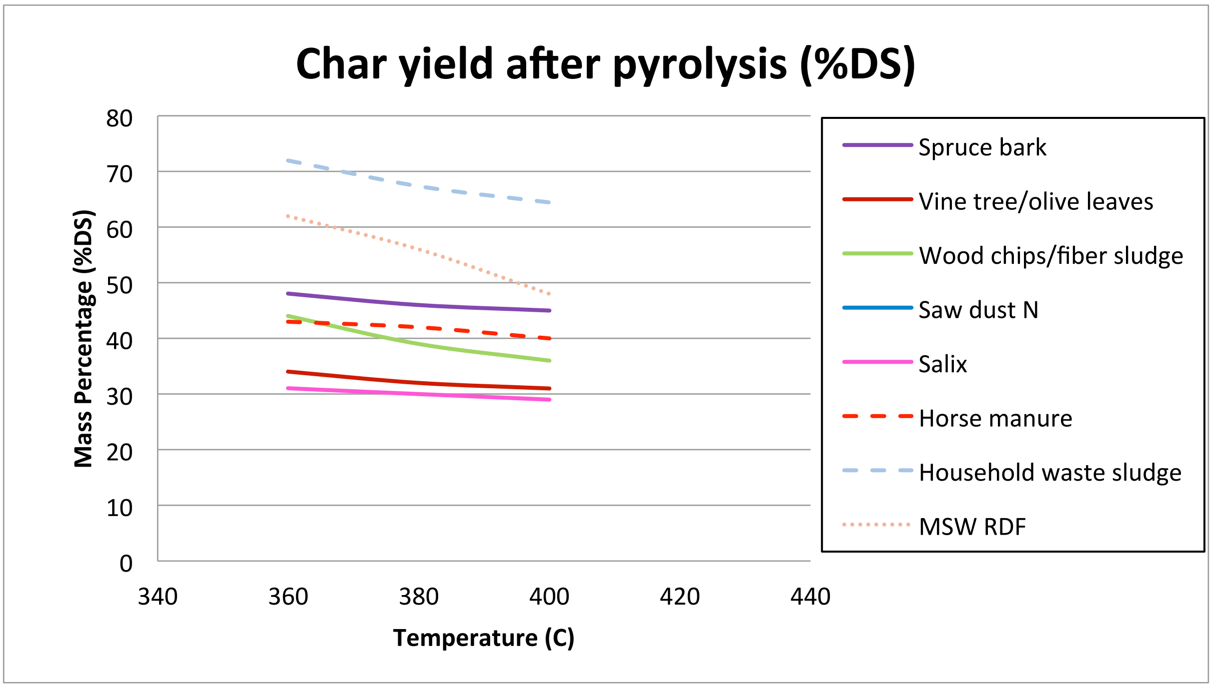

Figure 2: Char yield after pyrolysis at 360, 380, 400 °C in N2

Table 2: Char yield and ash content in the residues after pyrolysis at 400C

Biomass	After pyrolysis [%DS] 360	380	400	ash [%]
Vine tree/olive leaves	34	32	31	2
Salix	31	30	29	7
Wood chips + fiber sludge	44	39	36	3
Spruce bark	48	46	45	1
Horse manure	43	42	40	10
Household waste sludge	72	67	64	37
MSW RDF	62	56	48	2

As can be seen both from Table 2 and Fig 2, a typical yield of char including ash from woody type biomass around 400 °C is between 30-40%. The higher pyrolysis temperature the higher yield of volatiles and therefore less solid product is remaining. This trend is the same for all organic materials but the specific distribution between the solids and volatiles can be varied dependently upon the pyrolysis conditions and the type of fuel. The yields of solid fractions obtained from woody type biomass are much lower compared to house hold waste sludge, and slightly lower compared to horse manure. This occur mainly due to high content of ash and low content of organic matter in the waste fuel. In the WoodRoll process all volatiles from the pyrolysis process (pyrolysis gas) are consumed for the process heat generation (mainly for indirect heating of the gasifier while rest of the heat is recovered for the drying and pyrolysis). Although the drying process is conducted at low temperature ca 150 °C it costs a lot of heat to evaporate all water from the biomass (approximately 2MW per 1000kg of water evaporated). The higher humidity of the fuel the more heat is required and more of pyrolysis gas is needed for heat. Char, on the other hand, is consumed in the gasification process with steam to produce the syngas. The lower amount of ash and the higher amount of carbon the larger amount of syngas is obtained from a unit of fuel. Finding optimal conditions is therefore extremely important not only for the overall efficiency of the WoodRoll process, but also to be able to close the mass and energy balances.

Fig 3 shows the result of gasification with steam at 850 °C of various biomass species including waste-samples.

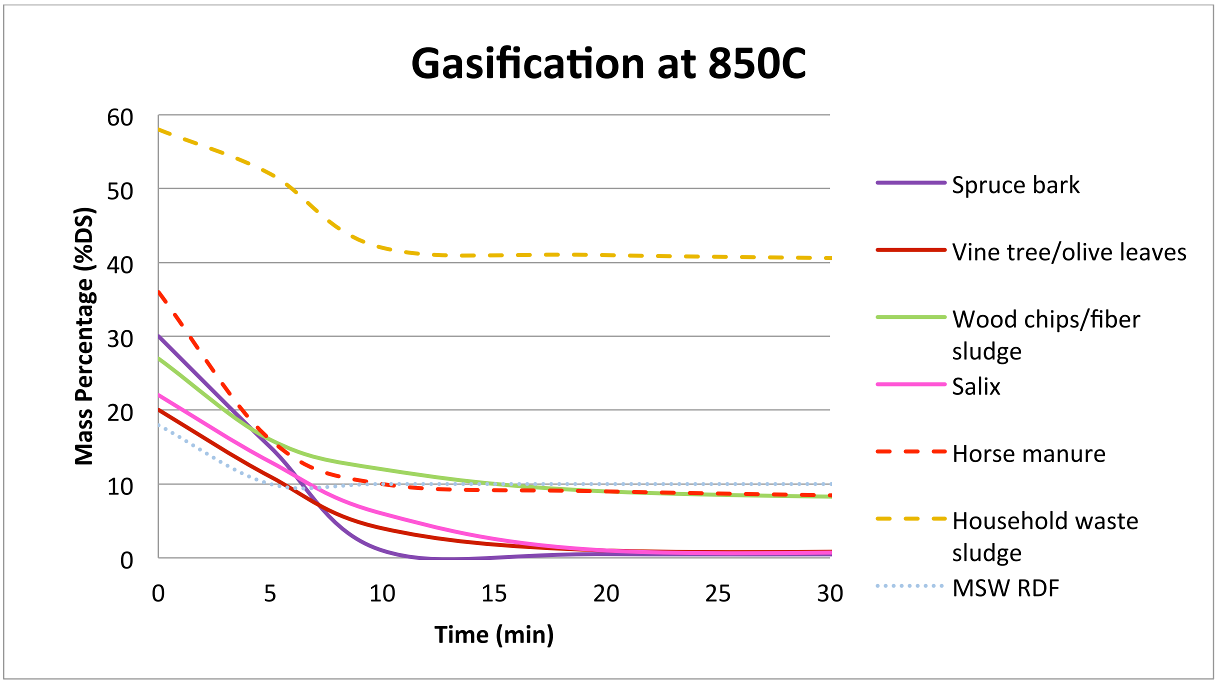

Figure 3: Mass decomposition (TGA) of the solid pyrolysis products during steam gasification at 850C

Gasification by means of TGA is not an exact reflection of the process that occurs in a large reactor. For instance it does not include effects of mass and thermal diffusion during intensive mixing at high temperatures. It can however give some hints regarding char reactivity (the faster mass decrement the more reactive char is) and enable the comparison between the char yielded from different materials. It also gives an indication of the reactive part of solid matter that remains from pyrolysis.

Most of the low-ash-content chars (where the ash content is below 5%wt.) indicate a massive loss on mass around five minutes and during the following five minutes nearly all of the carbonic matter is converted to gas, Fig. 3. The mass continues to decoy until ash or non-reactive product is left. The char obtained from horse manure shows medium reactivity compared to a reference fuels, whereas the one obtained from household waste sludge shows lower reactivity. It is however not clear whether the lower gasification rate for sludge is due to poorer char reactivity (kinetically slower) or higher amount of inert material (ash) that reduce transfer of steam to the carbon (diffusion hinder). One could also see that the decomposition of RDF is quicker even than i.e. salix. This could be explained by higher content of plastics in MSW which does not create a typical char (based on lingo-cellulosic structure). In contrary to this, plastics melt and release volatiles during thermal treatment. Pyrolysis at 400 °C does not complete decomposition of thermoplastics [2] and some of the volatiles can be released at the transition between the pyrolysis and gasification temperature.

Fig.4 illustrates the mass decomposition of the solid pyrolysis products during steam gasification at 1100 °C.

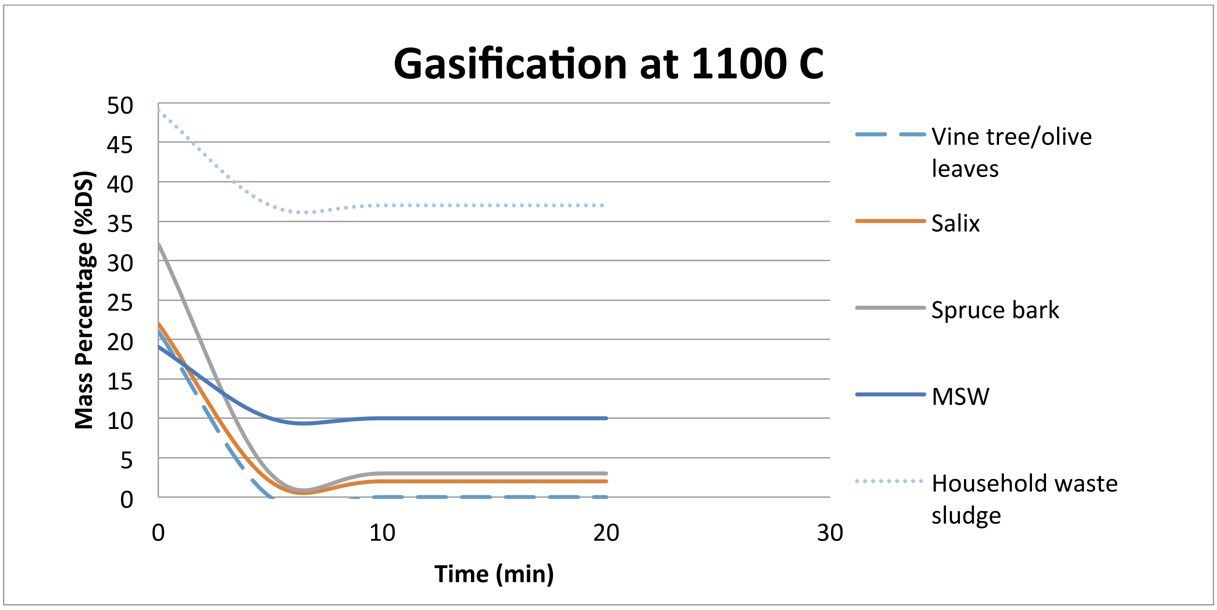

Figure 4: Mass decomposition (TGA) of the solid pyrolysis products during steam gasification at 1100 °C

It can be seen that almost all of the samples are gasified during the first five minutes from the start of the process. This is due to the fact that at so high temperature as 1100 °C the gasification rate (reaction of steam and carbon) is very fast. The only obstacles reducing the rate are limitations in diffusive transports of heat and mass into the sample. The major parameters affecting the rate are: size of the particles, flow (velocity) and turbulence of mixing of the reactants and availability of the active carbon sites. What is worth to stress here is that approximately 7% lower remaining mass of residues after gasification of household waste sludge at 1100 °C than at 850 °C suggesting melting/evaporating of some ash components. This hypothesis corresponds to observation occurred during TGA investigation where part of the ash was melted and sintered to the crucible. On the other hand it could indicate error in sampling and/or uneven distribution of components comprising virgin sample. Due to ash melting it was not possible to carry on the investigation with gasification at 1100°C of horse manure.

4. CONCLUSION

Three pre-selected waste-based substrates (mixed MSW, horse manure, household waste sludge) were tested via TGA in order to evaluate their sustainability for further testing in pilot scale with the Cortus' WoodRoll gasification system. This with the aim of finding the most suitable fuel for a methanation process and production of biomethane (Action B11). The investigation comprises chemical analysis, mass loss at isothermal pyrolysis temperature (360, 380 and 400 °C), mass loss during gasification with steam at 850 and 1100 °C.

Testing of mixed MSW was not successful due to lack of homogeneity of the received material. Analysis was however made on the RDF (fraction of plastics, paper and wood) showing promising results. Two other samples were characterized by having high moisture and ash content and therefore low organic content. High moisture content not only reduces the potential process efficiency but makes the fuel unstable requiring additional logistic issues (storing, grinding, pre-drying, unpleasant odor trap).

The results from pyrolysis and gasification reveal relatively similar thermal behavior as the reference material: woody type biomass. However, much higher amount of inert material was released. In case of horse manure pyrolysis and gasification, rates were satisfying but the low ash melting temperature disqualifies this fuel for large scale testing. Melting of ash cannot preferably start at 1000-1100°C as it makes it unsuitable for direct use in the gasifier where the operating temperature is 1100°C. Household waste sludge was the most homogenous fuel, but the 20-30% of the organic matter is too low to maintain stable operating conditions for gasification.

Neither of the waste-based substrates can be directly used in the WoodRoll gasification system without additional treatment. The treatment may include homogenation, size reduction and sieving, pre-drying, mixing with "accepted" fuel at low ratio so that negative impact of a low value fuel cannot significantly reduce the process performance. Additional treatment might be considered at the intermediate steps (leaching of inert from char to reduce ash content and lower the risk of fouling the char grinder). If the current fuels are considered for further testing, the investigation should include effect of mixing at different ratios on ash melting temperature and overall performance during pyrolysis and gasification. It is also important to check how the reactants can be mixed in order to reduce the problems that may occur in the fuel transportation system (segregation, clogging, accumulation).

5. REFERENCES

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[2] Donaj P., Kaminsky W., Buzeto F., Yang W. Pyrolysis of polyolefins for increasing the yield of monomers' recovery. 2012 May; 32(5):840-6.