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# Intermediate Pyrolysis of Agricultural Waste: A Decentral Approach towards Circular Economy

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The sustainable utilization and recycling of secondary raw materials is the backbone of the Circular Economy (CE), which aims at the efficient conversion of resources and energy while minimising the impact on the environment. Intensive farming generates large amounts of waste streams such as litter and manure. At present, they are not recovered systematically in the sense of CE. Chicken manure is an interesting feedstock due to the content of nutrients, in particular of phosphorus, which makes chicken manure a suitable feedstock for fertilizer applications. However, such streams are often contaminated with antibiotics and other organic pollutants, which must be thermally destroyed before disposal or further utilisation. Certain technologies are arising with the aim of combining nutrients recycling and energy recovery. Among them, intermediate pyrolysis targets at decentral application for production of carbonized solids and organic vapours for fertilizer application and heat generation, respectively.
The aim of this work is to evaluate the combined nutrients recycling and energy recovery for the example of pyrolysis of chicken manure in a proprietary screw pyrolysis reactor with integrated hot gas filtration. After a brief description of the bench-scale pyrolysis unit the feedstock is characterized. The effect of reactor temperature on yields and properties of the pyrolysis products is investigated experimentally. The chemistry and the mineralogy of the pyrolysis chars are evaluated applying a number of analytical techniques. The bio-availability of the main nutrients (NPK) is assessed adopting standard methods. Subsequently, the pyrolysis process is scaled-up and it is integrated in a CHP (Cogeneration of Heat and Power) unit for self-sustained operation of the pyrolysis reactor. The integrated system is evaluated in terms of energy production and of emissions.
Finally, the “break-even price” of the pyrolysis char is provided as result of a techno-economic analysis.

## 1. Introduction

The concept known as Circular Economy aims at the minimisation of waste and emissions from human activities by the conversion of secondary raw materials (waste streams) into valuable products. Intensive farming constitutes one of the main source of greenhouse emissions. Moreover, thousands of tons of manure are generated as by-products of livestock husbandry. It contains a large amount of macro and micronutrients, which are reintroduced into the soil for fertilization purposes. However, the direct utilization of manure should be discouraged for several reasons, such as emissions of methane and ammonia into the atmosphere and leaching of organic pollutants and eventually heavy metals. Nutrients such as chemically bound nitrogen and phosphorus are leached into the soil and groundwater, thus being lost. The aforementioned reasons encourage the utilization of a thermal treatment of manure for a more efficient recovery of the energy content in combination with generation of a carbonized solid, which could be adopted for fertilization purposes (Kahiluoto et al., 2015).
Pyrolysis is the thermal decomposition of organic materials in absence of a gasification medium, used to generate volatile organics, i.e. the pyrolysis vapours, and a stabilized carbonaceous solid, the pyrolysis char. The char retains quantitatively minerals and main nutrients (P, K, Ca, Mg) with the exception of nitrogen, which is only partly recovered in the solid. Pyrolysis processes have been applied to a large number of

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feedstocks with different targets, such as fast pyrolysis of woody biomass for the generation of a liquid and slow pyrolysis, or carbonisation, for the production of biochar. Intermediate pyrolysis in auger reactors appears to be a competitive alternative for the decentralized and combined generation of a carbonized solid for soil applications and of heat and power from the combustion of the pyrolysis vapours. Scientific literature reports works related to yields distribution of the pyrolysis products for agricultural waste, analyses of pyrolysis char and techno-economic assessment for pyrolysis-based CHP. However, to our knowledge, there is no systematic work which evaluates all the mentioned aspects for one specific feedstock.

This work is structured as follows: first, pyrolysis of chicken manure pellets is carried out at the proprietary bench-scale screw pyrolysis reactor STYX at the Karlsruhe Institute of Technology (KIT) in Germany, where about 100 kg of feedstock have been processed at different reactor temperatures. The results of the mass, elemental and energy balances are reported. Following, the pyrolysis char produced at a selected reaction temperature is characterized in terms of its chemistry and mineralogy. Elution tests are carried out to evaluate the solubility of the main nutrients and to assess the bio-availability. In the last section, the pyrolysis reactor is scaled up and integrated into a process, which provides the required heat for its self-sustained operation and additional heat to run an Externally-Fired Micro Gas Turbine (EF-MGT) and/or to produce hot water. Based on the mass and energy balances, a techno-economic analysis of the process is reported.

Finally, the break-even price of the pyrolysis char is estimated.

## 2. Materials and Methods

### 2.1 Bench-scale experiments

A total of four experiments were carried out at the STYX pyrolysis reactor, which has been described elsewhere (Tomasi Morgano et al., 2015). Briefly, it is an auger reactor with integrated hot gas filtration for the generation of particle-free vapours and condensates, respectively. The estimated heating rate of about 200 K $min^{-1}$ at nominal conditions (intermediate pyrolysis). The temperature can be adjusted from 350 °C to 500 °C. The residence time of the solids can also be adjusted (2.5 - 40 minutes). In this work it was held constant at 10 minutes. The mass flow adopted in these experiments was also held constant at 4 kg $h^{-1}$. The pyrolysis products were collected at the end of each experiment following standardized procedures. The experiments were carried out successfully for a total operation time of about 24 hours. The online recleaning of the filtration unit was held in stand-by during operation, since the pressure drop never increased above the set value. However, the filters have been re-cleaned after each experiment to ensure comparable starting conditions.

### 2.2 Characterisation of feedstock and pyrolysis char

Chicken manure was provided in pelletized form from a German handling company. Concentrations of carbon, hydrogen, nitrogen, and sulphur were determined after combustion in oxygen by means of infrared spectroscopy (C, H, S) and thermal conductivity (N). The elements Na, Mg, Al, P, K and Ca were determined by ICP-OES (iCAP 7600, from Thermo Fisher Scientific): 50 mg of the samples (accuracy ± 0.01 mg) were dissolved in 9 ml nitric acid and 1 ml hydrofluoric acid at 523 K for 12 h in the pressure digestion vessel DAB-2 (Berghof). After complexation with boric acid analysis of the elements was accomplished with four different calibration solutions and an internal standard (Sc). The mineralogical composition of the samples was determined by X-Ray diffraction qualitatively and semi quantitatively using internal reference materials and measuring of calibration curves for each mineral phase. The availability of plant nutrients (NPK) was investigated by three European standard tests. Each test was developed for different purposes. A high portion of phosphate soluble in water (EN 15958) and / or neutral NH4-citrate (EN15957) provides a short and medium term bio-availability of the phosphorous. EN 15920 which was developed for Thomas phosphate only was used in this study to investigate the influence of an organic acid on the highly calcareous samples. P and K in eluates were measured by ICP-OES. N was determined as TNb (Total Nitrogen bound) in EN 15958 eluate using the EN 12260 procedure.

### 2.3 Process design and techno-economic analysis

Based on the experimental results, a pyrolysis-based decentral system was developed for the combined production of pyrolysis char and the recovery of heat for the self-sustained operation of the pyrolysis process through combustion of the pyrolysis vapours (see Figure 1). The scale-up of the reactor is limited to 0.5 $MW_{T,}$ i.e. 155 kg $h^{-1}$, with a moisture content of 10 wt.%. The yields of the pyrolysis products remain constant at increasing scale. The overall heat requirements of the pyrolysis process were assumed to be 10 % of the thermal capacity. The overall process shall be self-sufficient in terms of heat requirements. Therefore, the operability of the pyrolysis reactor using the heat generated by combustion of the pyrolysis vapours is the first priority in the development of the process flow-sheet. The aforementioned assumptions are based on our previous work related to sewage sludge (Tomasi Morgano et al., 2017). The hot pyrolysis vapours are fed to the adjacent combustion chamber. The flue gas from the combustion chamber passes through a high temperature gas-gas heat exchanger (HTHE) and it is cooled down to the required temperature for pyrolysis.

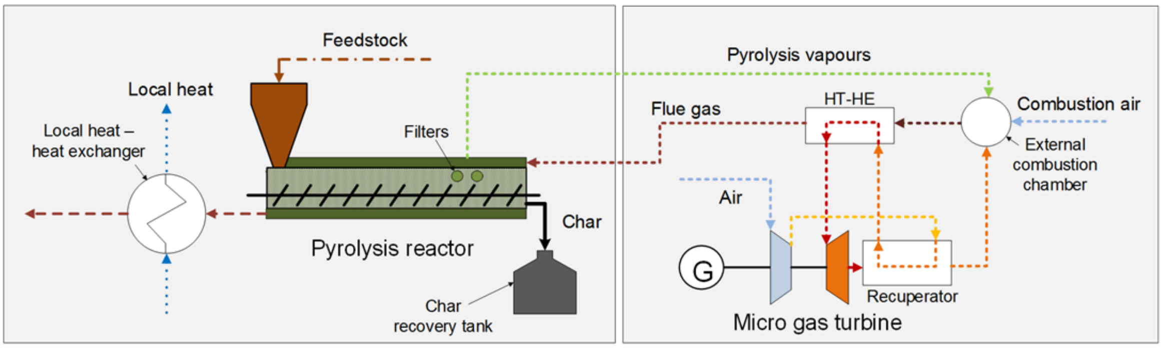


*Figure 1: Flow sheet of the pyrolysis-based decentral system for the combined production of pyrolysis char as well as heat and power using an externally-fired micro gas turbine*

The waste heat is recovered for local heating (hot water at 85 °C). The main configuration adopts an Externally-Fired Micro Gas Turbine *(EF-MGT)* to generate electricity. The micro gas turbine Turbec T100 is used as reference for the analysis. An alternative configuration (*Only Heat*) was also implemented, in which the flue gas is used to sustain the pyrolysis process and to produce hot water without power generation. The process is simulated using Ebsilon Professional®. The results of the process simulations are used for the selection of the main items of the process and consequently for the evaluation of the investments. The assumptions used for the economic analysis are reported in Table 1.The procedure for price estimation of the process items is described in Chauvel et al. (2003). The investment costs for the pyrolysis reactor are estimated on experience considerations of the authors. The feedstock costs include pre-treatment and preparation costs. The price of hot water is given by the heating value equivalent half year price of natural gas for home consumers in Germany in 2015. Since the pyrolysis waste heat is not standardised, a reduction of 20 % of the price was considered. The electricity price is assessed adopting the cogeneration index (KWK-Index) of the European Energy Exchange (EEX). Finally, the pyrolysis char is considered to be the main product of the process. Since there is no standard or reference price for a pyrolysis char, its “break-even” price is determined.

*Table 1: Assumptions adopted in the economic analysis*

| Costs | | Revenues | |
|---|---|---|---|
| Plant factor | 3 | Electricity | 36.4 € $MWh^{-1}$ |
| Service life | 10 years | Hot water | 64.0 € $MWh^{-1}$ |
| Availability | 7000 h $y^{-1}$ | | |
| Maintenance costs | 5 % of annual investment | | |
| Feedstock costs | 40 € $t^{-1}$ | | |

## 3. Results and Discussion

### 3.1 Mass, species and energy balance

The increase of the reactor temperature leads to a decrease of the yield of the pyrolysis char and to an increase of the pyrolysis vapours, which are further divided into three phases. The permanent gas is made of light hydrocarbons and carbon oxides; the water phase contains the water soluble organics as well as most of the moisture and reaction water; the oil phase or pyrolysis oil is constituted by the liquid organics and some water. The yields distribution is reported in Table 2. Due to the high mineral content, the yield of the pyrolysis char is much higher if compared to those obtained from lignocellulosic biomass (Tomasi Morgano et al., 2015). On the other hand, the yields of the pyrolysis oil increases constantly with increased temperature. The yield of the pyrolysis oil (16.5 wt.%) is higher than that obtained from the pyrolysis of beech wood at comparable conditions (Tomasi Morgano et al., 2015). Chicken manure generates lower yields of permanent gas. Interestingly, there is almost no difference between the overall yield of the vapours for pyrolysis at 450 °C and 500 °C. The only relevant difference is given by the ratio oil to water phase, which increases with increasing temperature. The total yield of the liquid organics increased by 1 wt.%, indicating that the main reason for the changing ratio is the changed phases equilibrium. The elemental distributions are reported in Table 3.The carbon distribution among the two condensates phases confirms a shift to the oil-phase from 22 wt.% to 24.5 wt.%. The elemental yields of the pyrolysis char decrease with increasing temperature. On the other hand, the carbon yield of the permanent gas constantly increases with increasing temperature mainly yielding $CO_2$, which is produced from pyrolysis reactions as well as from the decomposition of dolomite, which is present in the feedstock as drying medium (see also Figure 2). The distribution of hydrogen follows a similar trend. Most of the hydrogen (not reported) is found in the aqueous condensate.

*Table 2: Yields (wt.%) of the pyrolysis products at the selected temperatures of the reactor*

| | Pyrolysis Char | Pyrolysis Oil | Aqueous Condensate | Permanent Gas |
|---|---|---|---|---|
| 350 °C | 55.7 | 7.5 | 27.0 | 8.7 |
| 400 °C | 47.3 | 12.5 | 25.3 | 11.5 |
| 450 °C | 40.0 | 12.9 | 27.8 | 13.9 |
| 500 °C | 39.1 | 16.5 | 25.0 | 19.8 |

The distributions of nitrogen and sulphur follow similar trends, decreasing constantly with increasing temperature; on the other hand, the yield of chlorine reaches a minimum at 450 °C. Further increasing temperature leads to the re-adsorption of chlorine gas into the char matrix, probably as alkali metal chlorides. The yield of nitrogen shifts from the solid to the condensates, whereas that of sulphur is equally distributed among the pyrolysis products. Chlorine remains to a large extent in the solid matrix. Chlorine in the permanent gas was not directly measured but it is expected to be found mainly as hydrogen chloride (HCl). The energy distribution among the pyrolysis products closely reproduces the elemental distribution of carbon, showing a shift from the solids to the oil phase. The energy content of the permanent gas is not sufficient to generate the heat required by the pyrolysis process, which correspond to about 15 % of the energy content of the feedstock.

*Table 3: Elemental selectivities (wt.%) to the pyrolysis products at the selected temperatures of the reactor*

| | Pyrolysis Char | | | | Pyrolysis Oil | | | | Aqueous Condensate | | | | Permanent Gas (diff) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | N | S | Cl | C | N | S | Cl | C | N | S | Cl | C |
| 350 °C | 61.9 | 79.3 | 59.6 | 87.8 | 13.7 | 6.6 | 9.5 | 0.7 | 6.7 | 11.5 | 8.6 | 1.5 | 7.1 |
| 400 °C | 50.7 | 54.6 | 50.6 | 69.6 | 18.2 | 14.9 | 13.1 | 1.6 | 7.5 | 20.0 | 10.9 | 1.8 | 9.6 |
| 450 °C | 43.4 | 34.4 | 44.9 | 66.9 | 21.9 | 17.9 | 13.4 | 1.0 | 8.5 | 31.3 | 11.6 | 2.1 | 12.6 |
| 500 °C | 40.9 | 30.3 | 40.9 | 84.7 | 24.6 | 27.8 | 22.8 | 2.1 | 7.1 | 30.4 | 10.3 | 3.5 | 19.6 |

### 3.2 Characterization of the pyrolysis char

The pyrolysis char is the solid carbonaceous residue from the pyrolysis process, in which the minerals and the metals are embedded. The elemental compositions of the char obtained at 450 °C and of the original feedstock are reported in Table 4. The pyrolysis char is enriched in carbon and in the nutrients, whereas nitrogen is rather volatile and its concentration in the pyrolysis char is reduced. The content of sulphur remains almost unaltered.

*Table 4: Elemental compositions (wt%) of the feedstock (chicken manure) and of the pyrolysis char*

| | C | H | N | S | Al | Ca | K | Mg | Na | P |
|---|---|---|---|---|---|---|---|---|---|---|
| Chicken Manure | 35.4 | 4.78 | 5.96 | 0.78 | 0.16 | 5.84 | 2.24 | 0.70 | 0.26 | 1.38 |
| Pyrolysis Char | 42.1 | 2.30 | 4.71 | 0.83 | 0.35 | 12.40 | 4.75 | 1.52 | 0.56 | 3.01 |

Pyrolysis chars from lignocellulosic biomass find extensive utilization as soil conditioner. The content of nutrients in pyrolysis char from chicken manure may be additionally used as a mineral fertilizer. XRD analysis (see Figure 2) shows that in chicken manure P as well as N-compounds cannot be identified, which indicates that both the elements are mainly bound in organic (amorphous) phases. Organic phosphorus and nitrogen are readily available to the plants and quickly released to the soils and eventually to groundwater, leading to a net loss in the nutrients cycles. Various P-phases, mainly Hydrophosphate (Apatite) and Diphosphates, can be distinguished in the char. K-feldspar can be found in chicken manure and the pyrolysis char. Moreover, other K phases like Diphosphates and Sylvine were identified in the char. The main phase, calcite, in chicken manure and pyro char derives from the substrate used in gathering the chicken manure. Figure 3 shows the results of the elution tests for the plant nutrient P, K, and N highlighting very different solubility. In general, water solubility is higher for chicken manure than for pyrolysis char. In fact P is nearly insoluble with water from pyrolysis char.

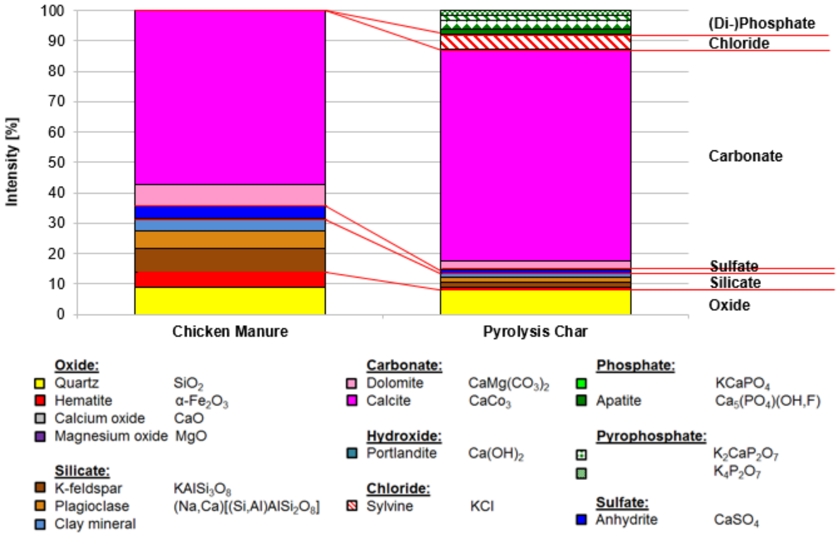


*Figure 2: Minerals in chicken manure and pyrolysis char*

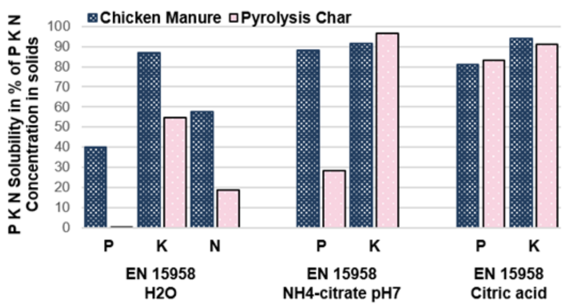


*Figure 3: Solubility of P, K, and N from chicken manure and pyrolysis char in different solutions*

Leaching with neutral Ammonium citrate reveals high solubility for P (about 88% of total P concentration) and K (about 92% of total K concentration). Both materials show similar behaviour. This is also true for the solubility with citric acid, which is also higher than 80 and 90 % of total concentration of P and K, respectively. According to these results it can be expected that P and K from pyrolysis char are plant available.

### 3.3 Process design and techno-economic analysis

A main CHP plant configuration, which implements an EF-MGT for power generation and produces hot water at 85 °C, was balanced and compared to an alternative configuration without power generation. The *EF-MGT* plant generates 44 $kW_E$ of electricity and 4.14 t $h^{-1}$ of hot water. The *Only Heat* alternative configuration focuses on the production of hot water. About 5.82 t $h^{-1}$ of hot water are generated in this configuration, which corresponds to an increase of about 30 %. The overall first law efficiency based on the LHV of the feedstock is about 28 % and 27 % for *EF-MGT* and *Only Heat*, respectively. The overall efficiencies and the electric efficiency in *EF-MGT* are poor compared to other thermochemical process for energy generation. However, it should be kept in mind that more than 40 % of the chemical energy content of the feedstock is stored in the pyrolysis char. Based on the enthalpy content of the vapours, the electric efficiency would be about 20 % and the overall efficiencies would be 63 % and 65 %, for the sub-configurations *Only Heat* and *EF-MGT*, respectively. The techno-economic analysis is carried out setting costs against the revenues, using the break-even price of the char to reach the parity. The results of the analysis are depicted graphically in Figure 4. The pyrolysis reactor is the most important investment, while the contribution of the power unit to the overall CAPEX of the *EF-MGT* is of about 30 %. The configuration *Only* Heat saves about 25 % of the investment. The revenues from the sales of heat and electricity are able to cover less than 25 % of the annual costs. It is

worth noting that the price of heat is higher than that of electricity. Consequently, a plant configured for only hot water production performs better than the *EF-MGT* configuration. However, more convenient tariffs may be applied to the sales of electricity depending on national legislations. Nevertheless, the sales of the pyrolysis char is required to allow the profitability of the process in any credible scenario. The break-even price of the char was 359 € $t^{-1}$ (*Only Heat*) and 484 € $t^{-1}$ (*EF-MGT*).
The results of the analysis are slightly higher than those reported by Kuppens et al. (2014) in their review and related to the production of biochar from fast and slow pyrolysis of corn stover. The cost of the feedstock, plays a major role. Overall, the break-even price of the pyrolysis char is not competitive against conventional fertilizers under the described basis scenario and therefore valorisation policies, which go beyond the scope of this work, are required in order to improve the feasibility of the process.

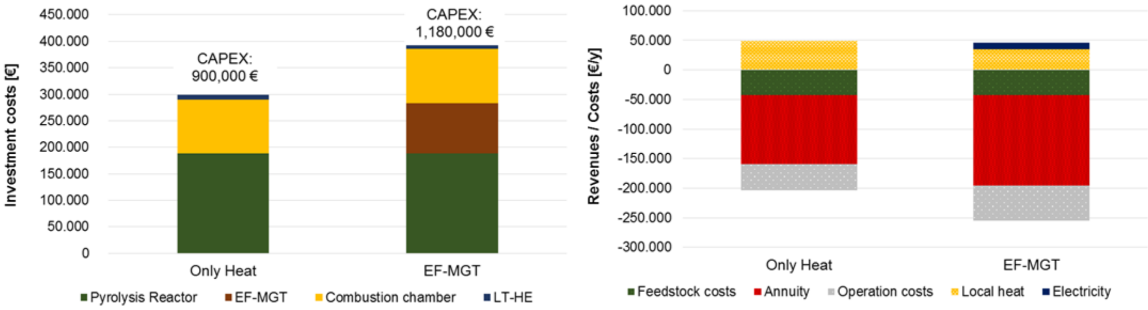


*Figure 4: Investment costs (left) and annual cash flows (right) for the selected plant configurations*

## 4. Conclusions

The valorisation of the nutrients contents of agricultural wastes is an important target of the circular economy, which may lead to a better utilization of natural resources. This study focused on the conversion of chicken manure into pyrolysis char for soil applications by means of a proprietary intermediate pyrolysis technology. On the basis of experiments carried out at bench scale, the paper investigated the relevant aspects of the novel process chain. The pyrolysis char obtained at 450 °C was further characterized to evaluate the relationships chemistry/mineralogy/bio-availability of the nutrients. It was found that phosphorus is retained in the pyrolysis char and it is converted from organic to mineral potassium and calcium phosphates, which are bio-available in the mid to long term (solubility in citric acid and neutral ammonium citrate above 90 %) but not in the short term (non-soluble in water). Therefore, it may be suggested that its action mirrors that of a soil enhancer being not a straight forward fertilizer. The mass, species and energy balances were examined and used to develop the flow sheet of a decentralized pyrolysis plant for the combined production of pyrolysis char and heat and power. Two configurations of the plant were evaluated under the common constrain of generating the heat for the pyrolysis process in a self-sustainable manner. The overall efficiencies of the two configurations were similar (27 % and 28 %) and generally low compared to waste-to-energy combustion facilities. On the basis of the flow sheet, the techno-economic analysis was carried out. It was found that heat production performs better (break-even price of the char of 359 € t-1 vs. 484 € t-1), under the considered legislative scenario, i.e. no incentives for renewable energy generation nor CO2 saving incentives, etc. The feasibility of the process is strongly dependent on the sales price of the pyrolysis char.

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