Process of obtaining diesel substitute through plastic pyrolysis using hydrogen from coke oven gas - material and energy balance

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Plastics

According to a report by the Główny Urząd Statystyczny statistical Pole produces 342 kg of municipal waste per year, of which 212 kg are mixed waste, that would not be recycled. About 7,7% of this waste stream are plastics. This presents great potential. The structure of plastics in municipal mixed waste is shown in table 1. (with exception for chlorinated).

***Table 1.** Structure of plastics in municipal mixed waste.*

Component	Vol. [%]
PP	14,9
LDPE	24,5
HDPE	20,2
PS	9,6
PET	10,6
Other	20,2

Generally recycling is the best possible way to manage plastics, however it is just a temporary solution, because after a few cycles it can not be repeated, it is laborious and its costs are big as well as loss of material. Also recycling products are often more expensive and lose some of the original properties. Conversion of plastic waste to fuel, from a sustainable development point of view, leads to a lot more ecological development than storing it. Scheme of this process is shown on figure 1. The quality of fuel made that way is comparable to regular fuels.

Goal

Develop a material and energy balance for the process of obtaining diesel substitute through plastic pyrolysis using hydrogen from coke oven gas

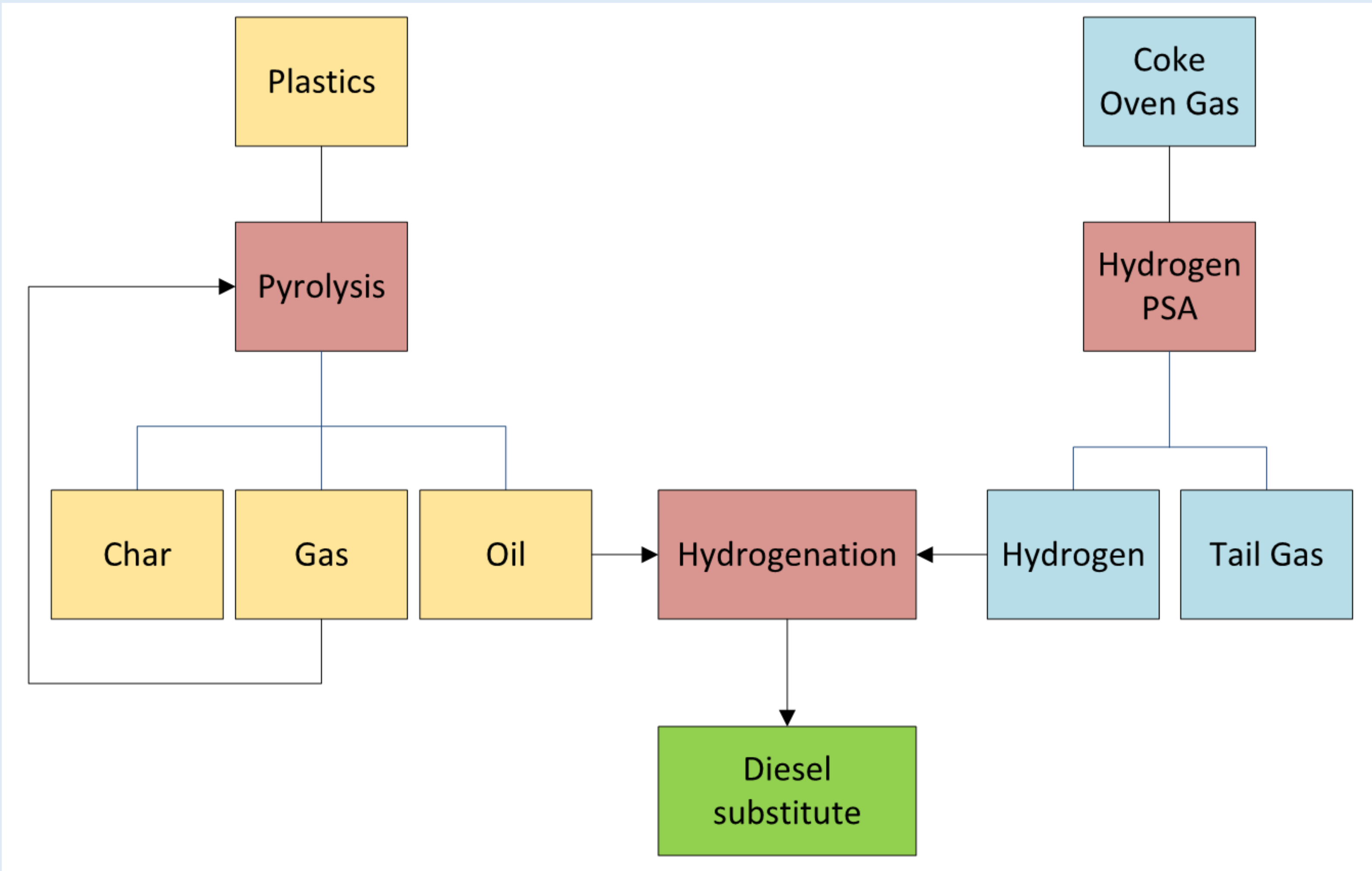

***Figure 1.** Diagram of the balanced system*

Coke oven gas

Coke oven gas is a by-product produced in the coking process. About half of this gas is returned for the coke plant to use in the combustion process in coking batteries. The rest of it could be used for energetic purposes, however often its excess is flared. Common composition of purified coke oven gas is shown in table 2.

The main component of this gas is hydrogen. It can be separated by the pressure swing absorption (PSA) process, which efficiency is 85%. This way purified hydrogen stream could be used for example in the hydrogenation process.

***Table 2.** Composition of purified coke oven gas.*

Component	Vol.[%]
H_2	55
CH_4	25
CO	9
N_2	4,6
C_xH_y	2,8
CO_2	2,8
O_2	0,5
H_2S	0,3
Calorific value [MJ/m³]	17,9

Results and discussion

Characteristic of pyrolyzed oil/ Characteristic of diesel substitute

As a result of the pyrolysis process 3 products had been obtained with the following mass share: char (12%), pyrolytic oil (53%), pyrolytic gas (35%). Oil had been subject to hydrogenation to obtain diesel substitute. Comparison of the oil and its substitute parameters is shown in table 3.

***Table 3.** Comparison of the oil and its substitute parameters.*

Wt. %	Pyrolytic oil	Diesel substitute
C	88,16	85,60
H	9,60	14,10
S	0,17	0
N	1,08	0,30
O	0,99	0
Calorific value [MJ/kg]	39,9	43,6

By-product characteristics

After the PSA process coke oven gas is divided into two streams – pure hydrogen and tail gas. Entire hydrogen is directed to the hydrogenation process. Tail gas is a by-product that could be used for energetic purposes. Composition and calorific value of this gas are shown in table 7.

***Table 7.** Composition and calorific value of tail gas.*

Component	Vol. [%]
H	15,5
CH_4	47,0
CO	16,9
N_2	8,6
C_xH_y	5,3
CO_2	5,3
O_2	0,9
H_2S	0,6
Calorific value [MJ/m³]	24,8

Overall process material and energy balance

Table 4 shows amount of substantions, that would be produced as a result of the following processes as well as the amount of those needed for said processes in relation to single mass unit of plastic waste.

Table 5 shows heat values that are needed to be delivered or would be produced according to given operation or proces.

***Table 4.** Material balance.*

For 1 Mg of plastics	
Pyrolytic oil	0,53 Mg
Pyrolytic gas	225 m³
Char	0,12 Mg
Coke oven gas	722 m³
Hydrogen	398 m³
Tail gas	384 m³
Diesel substitute	0,55 Mg

***Table 5.** Energy balance.*

For 1 Mg of plastics	MJ
Heating plastics	898
Pyrolysis	5030
Hydrogenation	2140
Heating coke oven gas	20,3
Heating hydrogen	258
Heating pyrolytic oil	254
Cooling diesel substitute	-645
Cooling char	-85,8
Cooling pyrolytic gas	-280
Tail gas combustion	-9,29
Pyrolytic gas combustion	**-14800**
Overall needed	**8600**

Characteristic of pyrolyzed gas

To confirm that the whole process can be autothermal, energetic potential of pyrolytic gas should be evaluated. As a result of its combustion energy is obtained, which could be used to sustain the whole process. Its parameters are shown in table 6.

***Table 6.** Parametrs of pyrolysed gas.*

Component	Vol.[%]
H	12,6
Metane	22,1
Etane	9,0
etene	25,5
propane	4,0
propene	13,6
butane	0,6
butene	3,5
CO2	4,8
CO	4,4
Caloric value [MJ/kg]	42,2

Pyrolysis conditions

Pyrolysis is conducted at a temperature of 500 °C using a zeolite catalyst with a heating rate of 10 °C/min. These conditions direct the pyrolysis process for the greatest yield of oil.

Hydrogenation conditions

Hydrogenation of pyrolytic oil occurres at temperatures above 700 °C, pressures around 70 bar, and in the presence of a catalyst (such as ZSM-5) can alter unsaturated compounds into saturated ones and makes the oil more stable.

Conclusions

The process could be autothermal. To accomplish that 58,25% of pyrolytic gas should be used. Assuming that the coking battery produces 30 000 m3 of coke oven gas, where about only half of it is being used for combusting processes of the coke plant, the rest of it in a matter of one day could allow a development of 500 Mg of plastic waste, hence the production of 272,7 Mg of diesel substitute (about 0,55 kg of diesel per 1 kg of plastic). Additional energy from the process could be acquired through cooling of the products and also tail gas and excessive pyrolytic gas combustion. Most energy-consuming operations would be pyrolysis (58,5% of overall needed) and hydrogenation (24,9% of overall needed) and the liest-consuming would be heating coke oven gas. Additionally char could have a trade value.