

## COKE DEPOSITION ON THE REACTOR SURFACE IN WASTE TIRE PYROLYSIS

Jeong-Geol Na, Ho Se Lee, Chang Hyun Ko Soo Hyun Chung\*

*Climate Change Technology Research Division, Korea Institute of Energy Research,  
Daejeon 305-343, Korea.*

Waste tire is mainly composed of natural and synthetic rubber and regarded as renewable energy resource since it has 9,000 kcal/kg of calorific value. Approximately 270,000 tonnes of scrap tires are generated in Korea each year and most of them are recycled with energy by incineration. For national energy security, it is necessary to diversify use of waste tires. The contents of volatile matters are high in waste tires and therefore oil production by pyrolysis could be one of the attractive options of energy recovery from waste tires.

The formation of coke deposits is a major problem in waste tire pyrolysis. The mechanism of coke formation is as follows: Reactor tube is heated indirectly and the metals such as iron and nickel in the reactor surface catalyze dehydrogenation reaction. Then, pyrolysis vapors recovered from waste tires lose their hydrogen atoms and carbons are deposited on the reactor surface. Carbon blacks in tires for giving wear resistance and wet traction could worsen the situation. Coke formation reduces products yields, increases energy consumption and shortens life time of reactor. Fig. 1 shows a reactor tube after waste tire pyrolysis. This obstacle has delayed commercialization of the process and it is necessary to develop a technology for suppression of coke deposition on reactor surface.

In this study, the behavior of coke formation in pyrolysis reactor was investigated. Waste tire pyrolysis experiments have been carried out at various reaction temperatures and coke formation was observed using a coking sampler. Also, ceramic coatings on metal surface were attempted for suppression of coke deposition.

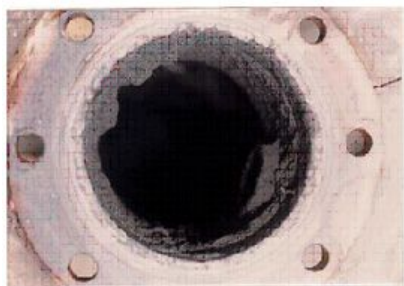


Fig. 1 Reactor tube after  
waste tire pyrolysis

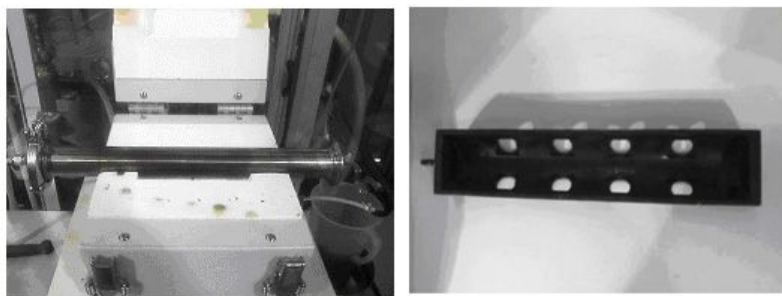


Fig. 2 Coking sampler

## PART I PYROLYSIS

A coking sampler was specially designed in order to simulate the environment near heating surface where coke formation is severe. Coking sampler is composed of a reactor tube, a tray for uploading metal plates and a heating furnace (Fig. 2). Eight SUS304 plates (1 by 1 cm) were loaded with the position in tray and they were covered with 30 grams of waste tires. The tray was inserted into the reactor tube and heated to 400, 500 and 600 °C in N<sub>2</sub> atmosphere, after which the temperature was kept at the set point for 1 hour. Then, the reaction tube was cooled to 200 °C by flowing N<sub>2</sub> gas and the tray was pulled out of the tube. Coke formation was determined from the weight difference before and after the reaction of the metal plates. To investigate the effect of unvolatilized oils on coke formation, two samples were wiped with acetone and the weights were measured. The experiments were repeated ten times to get accumulated amounts of coke formation.

The amounts of coke formation at various temperatures are summarized in Tab. 1. The coke formation at 400 °C seemed insignificant. On the other hands, the accumulated coke amounts at 500 °C (87.1 g/m<sup>2</sup>) and 600 °C (85.5 g/m<sup>2</sup>) were comparable. The difference in color change can be seen in the metal surface after pyrolysis as shown in Fig. 3. Some deposits on the surface seem to be unvolatilized oils rather than coke particles for which the weight difference of the plates wiped by acetone (position 1 and 2) was lower than that of other samples. The tendency of coke formation increased near the outlet due to active contact with pyrolysis vapors.

Tab. 2 Accumulated amounts of coke formation on SUS304 metal plates

Position	Temperature/°C		
	400	500	600
1	2.0	27.0	7.0
2	2.0	36.0	94.0
3	0.0	131.0	57.0
4	0.0	73.0	42.0
5	0.0	59.0	77.0
6	0.0	32.0	137.0
7	0.0	97.0	79.0
8	9.0	131.0	121.0
Average	1.6	87.1	85.5

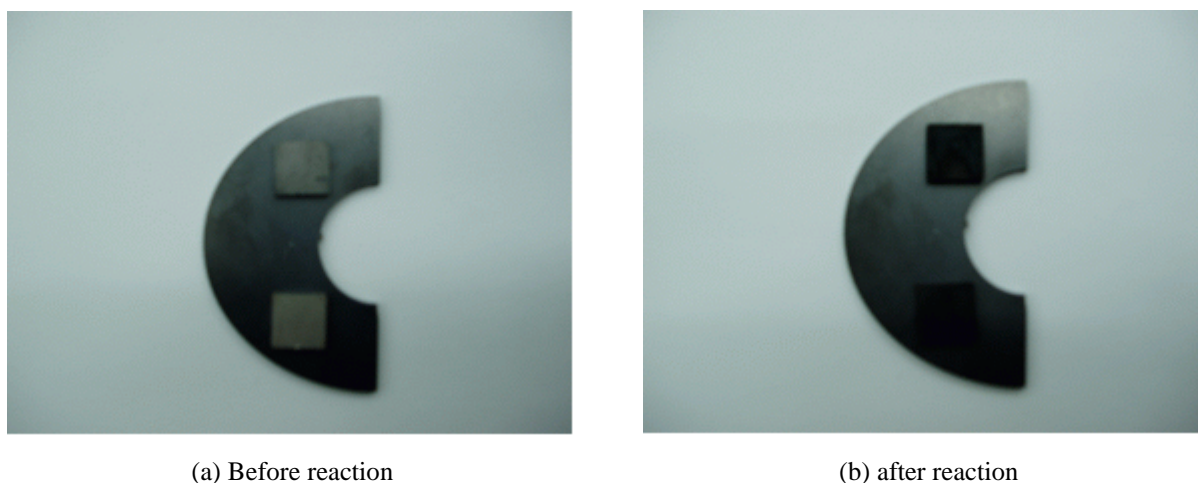


Fig. 3 Metal plates before and after pyrolysis

The ceramic coating on metal surface was conducted for suppression of dehydrogenation reaction. For efficient coating, SUS304 metal plates were pretreated in three steps. [1] sonication with acetone, [2] 0.1 M nitric acid treatment and [3] calcination at 300 °C in air. The pretreated plates were coated by dip-coating method in silica or alumina solution and their coking tendencies were determined using the coking sampler at 500 °C. The coated plates were loaded at the position of outlet part of the tray.

Tab. 2 shows that coke deposition could be repressed by ceramic coating. The accumulated coke amounts at 500 °C with coated plates were lower than 25 g/m<sup>2</sup> whereas the amounts of the plates without coating were 87.1 g/m<sup>2</sup>. Particularly, the coking amounts of the sample with all of pretreatments including washing, oxidation and calcination were 2 g/m<sup>2</sup>. It is noteworthy that the coated plates were on the outlet part where coking formation was vigorous.

Tab. 2 Accumulated amounts of coke formation on SUS304 metal plates

	Coke amounts	Coating material	Pre-treatment condition
	87.1	No coating	Coke amounts at 500 °C
1	14	SiO <sub>2</sub>	Acetone washing
2	8	Al <sub>2</sub> O <sub>3</sub>	Acetone washing
3	23	SiO <sub>2</sub>	Acetone washing followed by 0.1 N nitric acid treatment
4	8	Al <sub>2</sub> O <sub>3</sub>	Acetone washing followed by 0.1 N nitric acid treatment
5	4	SiO <sub>2</sub>	Acetone washing, 0.1 N nitric acid treatment followed by calcination at 300 °C
6	2	Al <sub>2</sub> O <sub>3</sub>	Acetone washing, 0.1 N nitric acid treatment followed by calcination at 300 °C

In conclusion, the metal plates coated with ceramic material was proof against coke deposition probably owing to inhibition of dehydrogenation and this method would offer a way for stable operation of waste tire pyrolysis.

### References

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