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TECHNICAL ADVANCE ON THE PYROLYSIS OF USED TIRES IN CHINA

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ABSTRACT

There are many researches on the pyrolysis of used tire all over the world in the last decade due to the raising public awareness of environmental concerns. More than 200 papers were published recently in China concerning the utilization of the waste tire rubber. About 30 inventions on the pyrolysis of waste rubber were patented in P.R.China. The objective of this review is to outline the research activities of the pyrolysis of tire rubber being undertaken in China, which mainly involves the pyrolysis mechanism and kinetics, design of pyrolysis reactor. The trend of R&D on pyrolysis technologies was characterized by small-scale, lower investment, and easy to transfer and disperse in China. It is realized that re-utilization of waste tire rubber is comprehensive processes, and the overall economics will be dependent on the cost of acquiring the tires, processing them into an injectable feedstock, and the cost of possible fuel displacement. Although many experiments have been done, tire pyrolysis processes have been far from satisfactory either economically or environmentally. A recent advancement in Zhejiang University was presented here on the technology of pyrolysis of waste tire rubber. Two kind of demonstrated pilot plants, Internally Heating Cascade Moving Bed (CMB) pyrolyser and Externally Heating Rotary Kiln pyrolyser have been recently set up and put into operation continuously in Zhejiang University to investigate the large scale process for the pyrolysis of tire rubber.

1. INTRODUCTION

According to the statistics[1], each year about 9 million tonnes waste tire rubber were disposed of all over the world, and approximately 40 thousand tonnes every year from China. The disposal of rubber waste, such as that from used tires has increasingly caused in a serious environmental problem in the developed area of China. Land-filling has been favored because of its simplicity, however, a large space is required and the reusable resources are wasted. A large amount of tires have accumulated in nationwide stockpiles or uncontrolled dumps which provide breeding sites of mosquitoes spreading serious diseases and the sites pose potential fire hazards. Appropriate disposal or reuse options should be introduced to replace the problematic methods. One way to materially recycle waste tires is by directly reusing the whole tires, such as in construction materials. The other way is to reuse them after shredding, such as in highway building. As shown in Table 1, the heat content of the rubber tires is even higher than that of coal, tire rubber could be a source of alternate fuel for power generation and other usage. For example, the used tires can burn directly in co-fired boilers to generate power. However, environmental concerns must be addressed that the combustion flue gas may contain acid compounds, such as NO_x, CH_x, and SO_x, and heavy metals such as Zn, etc[3]. It is now widely recognized that waste tires pyrolysis can be potentially involved with the recovery of both energy and material among various options[4].

Table 1. Elemental Analysis of a waste tire and coal[2]

Wt %	Tire	Coal
C	79.7	75.5
H	7.5	6.1
N	0.5	1.0
S	1.7	0.5
O(by diff.)	11.1	16.9

Several pyrolysis processes have been developed such as the vacuum pyrolysis technology[5], the atmospheric, inert gas pyrolysis approach[4], the molten salt pyrolysis technology[6], flash pyrolysis[7], and thermal plasma pyrolysis reactor which is expected to produce syn-gas as a substitute for ignition oil[3]. Auto-thermal pyrolysis technology operated in fluidized bed reactor has been proposed with a limited oxygen supply, so that the heat for pyrolysis of scrap tires was provided by combustion of some portion of the tires[8].

In general, the scrap tires can produce approximately 55% oil, 10% gas, and 35% char[4]. Gases have been used to heat the reactor. Calorific values between 34.6 and 40.0 MJ/m^3 have been reported[9]. The gases were identified as a mixture of H_2, CO, CO_2, C_4H_6, CH_4, and C_2H_6, with lower concentrations of other hydrocarbon gases. Analysis of the oils indicated the presence of alkanes, ketones or aldehydes, aromatic, polyaromatic, and substituted aromatic groups.

The situation of disposal of solid waste in China has shown a great prospect in the past years. Bilateral cooperation relationship between China and German governments has been officially established since 1997 aimed at the establishment of regulation system, law, management, and organization for the disposal of solid waste in China. As known, the regulation and law for the collection and disposal of waste solid have been issued and released by the local government of Hangzhou at the end of last year. A DA-DI industrial waste disposal Co., Ltd was founded with a site field of 1.29 square kilometer approved by local government in 1998 in Hangzhou. Several technologies will be planned to demonstrate in the field site, which include the recycling of waste tires, and incinerator of municipal solid waste and sludge, and disposal of used washing liquid of acid and soda, and disposal of used battery. Within an area of the diameter accepted economically for collection and transportation, a tire pyrolysis plant with a capacity of 5,000,ton/year will be designed in the near future. In parallel with this, an overall national network system such as waste tires collection, pretreatment and regulatory considerations will expect to be provided for successful recycling of waste materials in China.

Anyway, environmental concerns result in a strict regulation. In response to both of the environmental pressures and economical driving force, many researchers and investors have launched a number of initiatives aimed at improving efficiency and reducing the cost of recycling process to explore an economically viable design for the pyrolysis process in China. More than 200 papers were published recently in China concerning the utilization of the waste tire rubber. About 30 inventions on the pyrolysis of waste rubber were patented in P. R. China (see Appendix A). In this respect, this review almost concentrates on Chinese R&D activities in the pyrolysis of waste tire rubber.

2. PYROLYSIS MECHANISM AND KINETICS

Research on pyrolysis mechanism and kinetics is very important for reactor design and desired product profiles. When tires particles heated in a pyrolysis reactor, pyrolysis occurs as a certain temperature is reached on the particle's surface. There are two stages in pyrolysis: primary pyrolysis and secondary cracking. The vapor or volatile produces firstly from the waste tires and is made up of wide variety of hydrocarbons that can then encounter secondary reactions. The pyrolysis kinetics involved the exothermic tire pyrolysis reactions and the endo-thermic evaporation of the pyrolysis products. As to the thermal decomposition of organic polymers, four general mechanisms can be identified: (1) random chain scission; (2) end chain scission; (3) chain stripping; and (4) cross-linking[8)].

Wey et al. [8)] showed that pyrolysis is governed by the following parameters: temperature, retention time of the volatile at the reaction zone, and pressure and type of gaseous atmosphere. Cracking occurs at higher temperatures and enables primary products to be converted into compounds which may have a higher market value. One method is the aromatization of products generated by primary pyrolysis. Pyrolysis produces maximum yields of aromatic components at temperatures between 700 °C and 800°C. Fuel oil is produced without much gas at low temperature (below 500°C) and the char fraction was found to decrease as temperature increases from 300 to 720°C.

Cui et al[10)] found that the pyrolysis kinetics of the scrap tire rubbers can be well represented by the first-order irreversible decomposition reactions of its components. Figure 1 gives some typical curves of derivative thermogravimetry (DTG) and thermogravimetric analysis (TGA) which were found to provide valuable information on pyrolysis kinetics and mechanisms of scrap tire rubbers. Heating at a rate of 10 °C/min in nitrogen, the peak at the lower temperature is caused by the decomposition of natural rubber, and that at the higher temperature is caused by the decomposition of butadiene rubber (for a trunk tires).

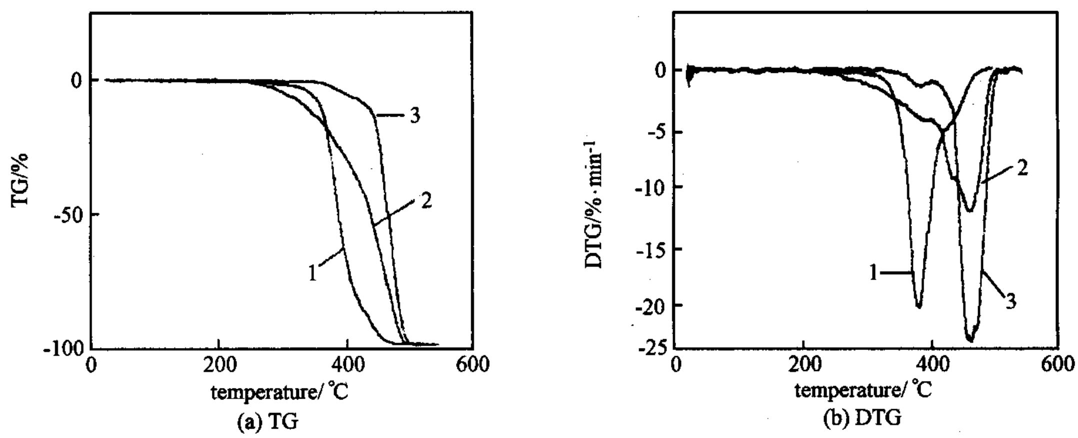


Figure 1. The pyrolysis TG and DTG plots of rubber materials

The decomposition patterns of each compositional compound can be formulated as follows [4,10,11] and the kinetic parameters of decomposition reaction are evaluated from the DTG and TGA curves.

$$\beta \frac{dW_a}{dT} = \beta \sum_{i=1}^{n} \frac{dW_i}{dT} = -\sum_{i=1}^{n} A_i \exp\left(-\frac{E_i}{RT}\right) \cdot W_i$$

Since chemical compositions of tire vary widely according to manufacturing recipes, the conclusions derived might be limited to the specific scrap tire. For example, the side-wall and tread rubber exhibited different thermal degradation patterns although both rubbers were composed of three thermally degradable components below 850K. Processing oils, NR, and SBR were likely to be responsible for the tread rubber, whereas the components appeared to be processing oils, NR, BR for the side-wall rubber (Table 2).

Table 2. Calculation of pyrolysis kinetics parameters for tire samples[10]

Sample	ΔT_1 /℃	F_1 /%	A /s^{-1}	E_1 /$kJ \cdot mol^{-1}$	r_1	ΔT_2 /℃	F_2 /%	A /s^{-1}	E_2 /$kJ \cdot mol^{-1}$	r_2
NR	320 ~ 386	41.4	3.18×10^8	221.3	0.994	427 ~ 467	12.1	2.10×10^{15}	144.4	0.997
SBR	259 ~ 421	37.0	6.64×10^{11}	52.5	0.998	426 ~ 491	56.7	1.18×10	195.6	0.998
BR	341 ~ 376	1.62	1.62×10^6	290.4	0.998	417 ~ 516	92.2	1.67×10^{18}	202.3	0.993
NR/SBR/BR	346 ~ 381	10.3	7.28×10^{10}	172.6	0.997	431 ~ 497	57.2	1.21×10^{13}	183.8	0.998
Tire A	345 ~ 376	13.3	5.27×10^9	155.6	0.999	425 ~ 480	42.4	9.37×10^{10}	206.2	0.994
Tire B	351 ~ 386	17.4	3.33×10^8	141.4	0.993	441 ~ 496	39.2	3.33×10^{12}	163.5	0.997
Tire C	320 ~ 391	32.7	1.87×10^7	124.9	0.990	421 ~ 486	37.1	4.19×10^8	142.7	0.993
Tire D	335 ~ 380	21.2	1.24×10^7	122.2	0.997	421 ~ 476	32.8	1.21×10^8	215.7	0.995

Note: ΔT—temperature region of DTG peak for calculation; F_i—weight fractions of reaction content of the sample during each region of Arrhenius linearity; A—the frequency factor; E_i—the individual values of apparent activation energy obtaining over each corresponding period of Arrhenius linearity; r—correlation coefficient.

Isothermal pyrolysis results showed that the side-wall rubber would hardly be degraded at low temperature regions (<600K), whereas it would be more rapidly degrades than the tread rubber at higher temperatures (≥746K).

The pyrolysis residue of the scrap tire represented 34 wt % of the initial weight, of which carbon black constitutes 28 wt %, and other 6 wt % may be ascribed to charred residues of thermal decomposition. Most studies concentrated on the recovery of the solid phase for treatment of waste water when it had been activated.

Dong et al[12] studied the technologies of pyrolysis of waste tire rubber experimentally and found that the introduction of a carrier gas increases the oil yield and decreases the yields of gas and carbon black. But the pyrolysis yields are independent of the variety of carrier gas. However, use of H_2O steam as a carrier will produces the oil with lower sulfur content (0.12

wt %) and carbon black with higher sulfur content (2.5 wt %). And pyrolysis at N_2 or H_2 atmosphere has give an opposite results.

3. PYROLYSIS REACTOR CONFIGURATION

Thermal treatment devices should be properly designed and operated in order to be more economical in terms of cost-effective and energy-efficient operation. The pyrolysis time, one of the design criteria for a pyrolysis reactor, was calculated for tire rubber as a function of isothermal pyrolysis temperature[11)].

$$\tau_i = 9.2103/[A_i \cdot \exp(-E_i / RT)]$$

The optimum temperature may vary depending on different design objectives and valuable by-products. Table 3 gives characteristic times for the physical and chemical processes during the pyrolysis of a tire particle. It is found that the primary driving force during this process is intra-particle heat condition. However, the thermal conduction rate depends on the size and the property of the tire particle.

Table 3. Characteristic time for kinetic and transport process[13)]

Phenomenon	Characteristic times(s)
Conduction heat transfer	10^4
Tire pyrolysis	10^2
Viscous flow	10
Tar transportation	10^5

The principles of tire pyrolysis design should take heat transfer and contact mode into account. Gas fluidized bed reactor can be chosen as a more efficient approach to tire pyrolysis. Tire rubber suspending around heating medium suffers from the pyrolysis by means of immersed heating tubes and gas-solid convective heat transfer. But it costs much to construction and is difficult to scale up at present. The fluidized bed reactors have been designed to pyrolysis waste tire rubber chunk in Taiwan[8)] and in Hangzhou[14)]. A schematic apparatus of fluidized bed pyrolyser is shown in Figure 2. It consisted of blower, tire rubber feeder, cyclone and scrubber. The reactor was constructed with cylindrical column and a expanded freeboard. The distributor was a perforated plate. An inert matrix composed primarily of crystal sand was used as the bed materials. Heating is needed to surround the outer wall of the bed. The blower supplied the inert gas for fluidization or the amount of air for the partial combustion requirement. Tire particles were fed by means of a specially designed feeder. The cyclone was used to collect fine particles. Scrubbers served to quench the off gas and remove condensibles that were withdrawn from reactor.

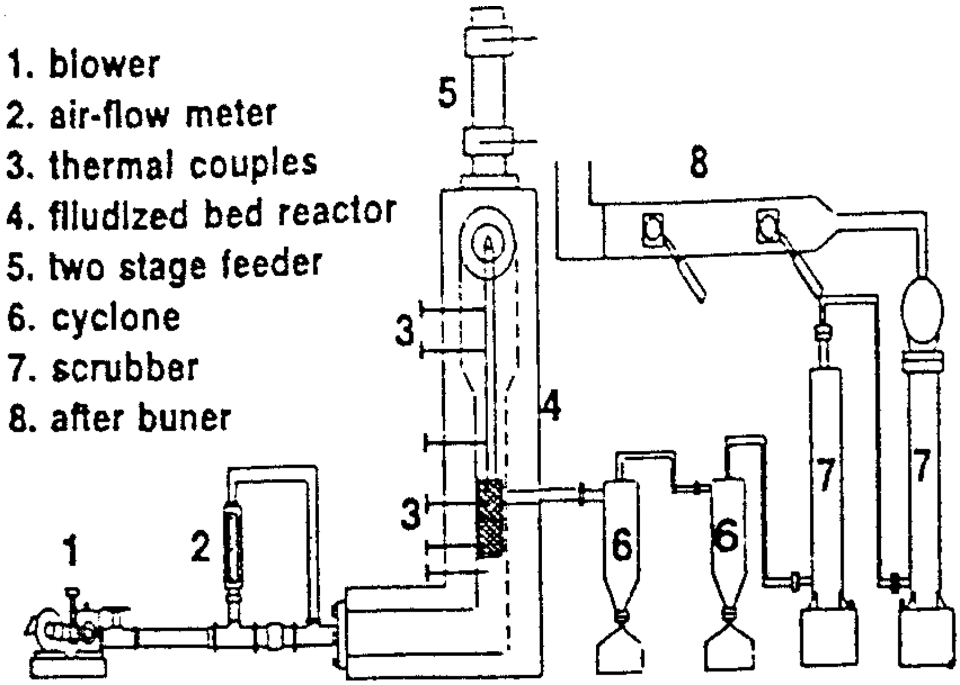
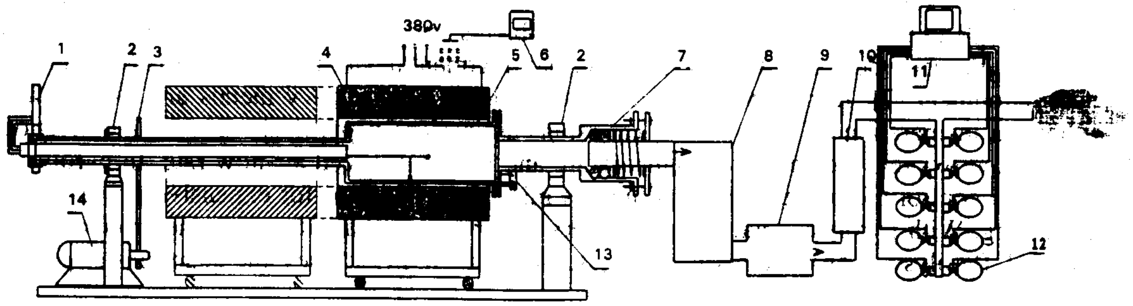


Figure 2. Apparatus of auto-thermal fluidized bed pyrolyser.

The rotary-kiln pyrolyser was built in Zhejiang University as shown in Figure 3. The furnace has an adjustable rotation rate from 0.5-10 rpm. The kiln is heated externally. Sealing of rotary kilns is a difficulty technology, especially for a pyrolyser. The internal pressure of the kiln was higher than atmospheric. A special friction-type seal was designed and successfully applied to the pyrolysis system with high temperature. But the use of rotary kilns is advantageous for other pyrolysis technologies. Solid wastes with different shapes, sizes, and heating values can be fed into rotary kilns in batches or continually.

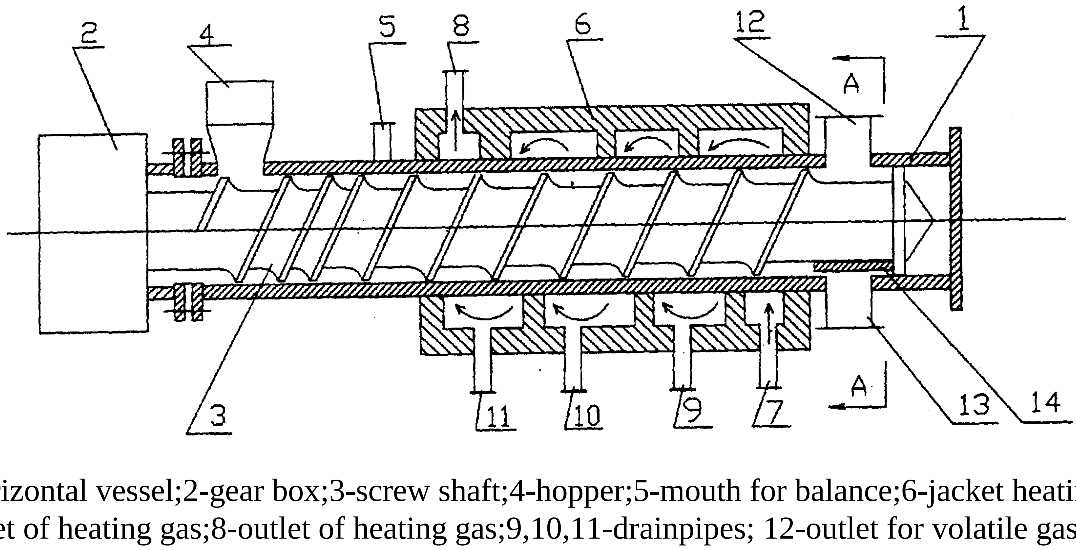


1 = thermometer, 2 = bearing, 3 = gear transmission, 4 = electric furnace, 5 = rotary kiln, 6 = temperature controller, 7 = seal, 8 = two-step condenser, 9 = filter, 10 = total flowmeter, 11 = computer, 12 = gas sampler, 13 = feed and discharge opening, 14 = adjustable-speed motor.

Figure 3. Schematic of the apparatus of rotary-kiln pyrolysis

Another kind of pyrolysis, a so-called cascade moving bed (CMB) with an internal heating mode, have also been built in Zhejiang University and put into operation recently. The shredded tire rubber continuously fed into CMB moves outward and inward with plate by plate. The plates consisted of heat transfer tubes and have internally heating capacity due to the induction of high temperature medium or electrical power. An agitator with scraper blade was installed to clean the coke attached on each plate. There are plenty of passageway left for tire particles and volatile gases along bed wall and central shaft. Char product was conveyed by screw machine from bottom of the reactor continuously. Volatile gas from the top flows into a series of scrubbers as usual. CMB pyrolyser has a higher efficiency of heat transfer and large throughput and lower cost for construction.

Other pyrolysers patented in P.R.China have listed in Appendix A. It is interesting that some of invention involve the catalytic pyrolysis for valuable by-products. Among these inventions, Screw Pyrolysers[1)] with internally and externally heating mode may show some prospect as result of lower cost for construction and operation, as shown in Figure 4. It is shown that the coke of pyrolysis reactor is generally a threat to heat transfer and continuous operation, therefore, the reactors like Screw, CBM, and Rotary-Kiln have a special configuration. More attention should be paid to the possible presentation of steel wire contained in waste tire chunk which may enhance the heat conduction within a rubber, but the abrasion of internals and twine of steel wires may possibly destroy the reactor and give rise to a increase of energy consumption.



1-horizontal vessel;2-gear box;3-screw shaft;4-hopper;5-mouth for balance;6-jacket heating; 7-inlet of heating gas;8-outlet of heating gas;9,10,11-drainpipes; 12-outlet for volatile gas;13-char discharge;14-baffle.

Figure 4. Schematic of the apparatus of screw pyrolysis

4. CONCLUSION

There are great potential for development of pyrolysis technologies of waste tire rubber in China due to environmental pressure and economical driving force. Techniques developed in China were recently characterized by small-sized device, lower cost to construction and operation, easy to transfer and disperse where it is needed.

The pyrolysis has been essentially governed by the heat transfer of tire particles. The objective of pyrolyser design is cost-effective and energy-efficient operation by using an appropriate operation condition and contact mode between tire particles and heating medium. Cascade Moving Bed (CMB) pyrolyser and Screw pyrolyser may be of prospect in China in near year in view of technological and economical considerations.

One of the major trend in the future is the co-processing of co-mingling waste tire rubber, and other polymers with some motor oils through a recycling technique which can achieve the purpose of waste recycling into commercially viable chemicals or fuel oils. Because waste oil is primarily paraffinic and can provide good solvency and heat transfer medium for waste rubber and plastics, simultaneous processing of mixed waste plastics and rubber with waste oil can yield synergistic effects and thus can increase the production of fuel oils or chemical feedstock of environmentally acceptable grade. At the present time, it is thought that efficient co-processing processes feasible in technical and economical aspects should be developed.

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APPENDIX A

A list of tire pyrolysis patented in P. R. CHINA

Inventor	Patent Number	Title of Invention	Type of pyrolysis reactor used
Hong zhenwen		Recovery of waste tire to make reclaimed rubber	
Li chuanqi te al	CN1117517A	A Method of catalytic cracking of waste tire	Screw convey reactor
Jin zhaoyu	CN2214873Y	Apparatus for recovery of tire rubber by thermal pyrolysis	Cylindrical reactor
Wang xuanyu	CN112953A	Manufacture of carbon black, liquid oil, gases by waste tire rubber	
Song junlu	CN1123822A	Apparatus of making oil products from the mixture of waste rubber and plastics by catalytic cracking	
Peng zhenhong		Making cropland by using waste tire.	
Zhou dingli	CN2223297A	Production of gasoline diesel and carbon black by pyrolysis of waste tire rubber.	Scew reactor
Song junru	CN2228081Y	Catalytic pyrolysis furnace for making gasoline diesel from waste tire	Agitator reactor with impeller as scraper blade
Chen lijun	CN2242891Y	A thermal pyrolysis reactor of rotary tank	Rotary tank
Zhou dingli et al	CN1145395A	Method and apparatus for production of gasoline diesel and carbon black by pyrolysis of waste tire rubber.	
Zhou dingli et al	CN1155571A	Method of production of gasoline diesel and carbon black by pyrolysis of waste tire rubber.	
Li yong	CN1147008A	Method for manufacture of industrial solvent and carbon black from waste rubber, and fiber, and foam plastics	
He shunsheng	CN1184825A	Comprehensive utilization of waste rubber, and fiber, and foam plastics	
Li wanchun	CN1201816A	A method of production of fuel oil of gasoline and diesel by waste rubber	With catalyst
Feng jinru	CN1201349A	A mechanical approach for scraping waste tire.	
Dong genjin et al	CN1208742A	A method and apparatus of production of gasoline diesel and carbon black by waste tire rubber.	Screw reactor
Dong genjin et al	CN2296886A	An apparatus for pyrolysis of waste tire	Screw reactor
Deng jianlang et al	CN1212949A	A method and apparatus of production of activated carbon from waste tire by batch and continuous process	
Huang lin et al	CN2313927Y	Apparatus for production of gasoline diesel by waste plastic and rubber.	Agitator reactor with impeller as scraper blade
Chen huangchuan	CN1094434	Apparatus for scrap and pyrolysis of waste tire	Mechanical scraper and thermal pyrolysis
Chen huangchuan et al	CN1097794	Pyrolysis process for waste tire rubber	Pyrolysis with catalysis