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Article:

PYROLYSIS OF LATEX GLOVES IN THE PRESENCE OF Y-ZEOLITE

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ABSTRACT

In this study we have investigated the possibility of processing waste rubber gloves using pyrolysis. Y-zeolite catalyst was employed to upgrade the pyrolysis products to give higher yields of valuable aromatic compounds such as toluene and xylenes. The composition of the pyrolysis products was determined using GC-MS, GC-FID, GC-TCD, and FT-IR. It was found that when rubber gloves were pyrolysed in the absence of a catalyst, the pyrolysis oil consisted mainly of limonene and oligomers of polyisoprene. When Y-zeolite was added to the reaction system, the yields of toluene, xylene, methylbenzenes, ethylbenzenes, and naphthalenes increased dramatically. The Y-zeolite also catalysed the decomposition of limonene, which was absent from the catalytic pyrolysis products. The presence of the Y-zeolite catalyst also increased the yield of hydrocarbon gases. The tests were carried out at both 380°C and 480°C and it was found that the higher reaction temperature led to increased yields of all the major compounds, both in the presence and absence of the Y-zeolite catalyst.

KEYWORDS: rubber glove, medical waste, pyrolysis, thermal treatment

1. INTRODUCTION

In recent decades, increased awareness about infectious diseases such as HIV and hepatitis and increased levels of personal protection required in scientific and technological industries, has meant an increased demand for latex gloves. As a consequence, the demand for natural rubber latex has risen from 159,000 tonnes in 1984 to 597,000 tonnes in 2003 (Rajan et al., 2006). In 2005, Malaysia, one of the worlds leading rubber glove manufacturers, consumed 226,218 tonnes of natural rubber for glove production and exported 1,311 million pairs of medical gloves (MARGMA, 2006). Rubber gloves (and medical waste in general) present several disposal problems, because they are a biological hazard and therefore must be disposed of in a manner which does not endanger public health. The World Health Organisation (WHO) is opposed to landfilling or incineration of medical waste (WHO, 2000) and alternative methods of processing waste natural rubber appear to be limited in comparison with synthetic rubbers (Rajan et al., 2006). In addition to waste post-consumer products, there is a large amount of waste natural rubber generated during the manufacturing process, as up to 15% of manufactured products do not meet the very strict specifications required (Rajan et al., 2006). Therefore, a new technology that is both environmentally

acceptable and biologically safe is required to process both post-consumer and feedstock natural rubber.

Pyrolysis is a process whereby organic compounds are heated to high temperatures in the absence of oxygen until they decompose into char, oil, and gas. The high temperatures used in pyrolysis mean that it would be an appropriate method for processing material that poses a biological hazard. Processing of waste rubber by pyrolysis has been intensively investigated in recent years, particularly with regard to scrap tyres (Berrueco et al., 2005; Conesa et al., 2004; Galvagno et al., 2007; Kyari et al., 2005; Li et al., 2005; Oledzka et al., 2006). The pyrolysis of natural rubber has also been investigated (Groves and Lehrle, 1992; Groves et al., 1991; Seidelt et al., 2006) as has the pyrolysis of natural rubbers main constituent, polyisoprene (Chen and Qian, 2002; Chiantore et al., 1995; Chien and Kiang, 1979). However, latex gloves present a special case because of the additives which are present, for example, calcium carbonate or cornstarch is used to powder the gloves. Additionally, the amount of sulphur used in the vulcanisation of rubber gloves differs from other rubber products. Therefore, the pyrolysis of rubber gloves is worthy of its own investigation to optimise the process conditions, which will ensure the maximum possible yield of valuable chemicals.

It is well known that natural rubber decomposes to form oligomers of isoprene, ranging from the monomer unit up to hexamers. The major compound is usually dipentene, also known as limonene, which represents the dimer, but isoprene can be the dominant pyrolysis product if the reaction temperature is sufficiently high. Although the liquid pyrolysis products of natural rubber might have some value as a fuel and limonene has many uses in the chemical industry, it would be more economical to convert the isoprene oligomers into more valuable chemical products. Several investigations have been carried out into catalytically upgrading pyrolysis products and one of the most promising types of catalysts are zeolites, which have been used to upgrade the pyrolysis products of a wide variety of materials (Bagri and Williams, 2002; Miskolczi et al., 2006; Olazar et al., 2000; Williams and Nugranad, 2000), including rubber tyres (Qu et al., 2006; Shen et al., 2007a; Shen et al., 2007b; Shen et al., 2006; Williams and Brindle, 2002a, 2002b, 2003).

In this work, we have investigated the pyrolysis of rubber gloves that were manufactured from natural rubber. The samples were pyrolysed in a fixed bed reactor at either 380 or 480°C and the pyrolysis products were analysed by gas chromatography and Fourier transform infra-red spectroscopy. In some of the tests, the pyrolysis products were passed over Y-zeolite catalysts before they exited the reactor, with the aim of upgrading the pyrolysis products to more valuable compounds.

2. EXPERIMENTAL

2.1 MATERIALS

Two different brands of commercial rubber gloves were used in this study. The first gloves were white in colour and were given the code Sample W and the second gloves were yellow in colour and were given the code Sample Y. The elemental composition of the gloves was determined using a CE Instruments CHNS-O analyser and the results are shown in table 1. The ash content of the samples was determined by ashing in a furnace at 550°C.

The catalyst used in this study was Y-zeolite, with a SiO_2/Al_2O_3 ratio of 80 and a surface area of $780m^2/g$ supplied by Zeolyst International (USA). The catalyst was used as received in its pellet form and was activated at 550^oC for 2 hours and then left to cool to room temperature in a desicator prior to use.

2.2 THERMOGRAVIMETRIC ANALYSIS

Both rubber glove samples were analysed using a Shimadzu TGA-50H thermogravimetric analyser (TGA). The sample size was 5mg and the reacting atmosphere was zero-grade nitrogen flowing at 50 mL min^{-1}. The TGA was programmed to ramp to 500°C at a heating rate of 10 °C min^{-1} and then held for 10 minutes to ensure that pyrolysis was complete.

2.3 FIXED BED PYROLYSIS REACTOR

The rubber gloves were pyrolysed in a fixed bed reactor (FBR) that measured 260mm in length by an internal diameter of 45 mm and was externally heated by a 1.5kW tube furnace (figure 1). Before each experiment, 10g of sample Y and sample W in a 1:1 ratio were cut into pieces measuring $1cm^2$ and the two samples were mixed before being loaded into the reactor crucible. If required, 10g of activated Y-zeolite was added to the reactor crucible giving a 1:1 catalyst to sample ratio. The zeolite was supported on wire gauze above the rubber glove sample so that when the rubber pyrolysed the volatile pyrolysis gases passed over the catalyst. The catalyst bed was at the same reaction temperature as the rubber sample.

After the sample and catalyst had been loaded, the reactor was sealed and purged with nitrogen before being heated to either 380°C or 480°C at a rate of 10°C min^{-1}. A 200mL min^{-1} flow of nitrogen was used throughout each pyrolysis experiment. Once the required temperature had been reached, the reactor was held in thermal equilibrium for 45 minutes to ensure that pyrolysis was complete. Upon pyrolysis of the rubber glove sample, the volatile pyrolysis products passed over the zeolite catalyst (if it was present) and then exited the reactor and were collected by a train of water-cooled and dry-ice cooled condensers. Any H_2S gas was collected by a bubbler system that was loaded with an alkaline solvent, the insoluble gases were collected in a Teflon gas bag and analysed off-line. The yield of pyrolysis oil was determined by measuring the mass of the condenser train before and after each experiment while the mass of pyrolysis gas was determined using gas chromatography, which is described in the following section. The reported results are an average of at least two repeatable tests.

2.4 ANALYSIS OF THE PYROLYSIS PRODUCTS

The gas was analyzed immediately after each run was completed. A Varian CP-3380 gas chromatograph equipped with a flame ionization detector (GC-FID) was used to determine the $C_1 - C_4$ hydrocarbons. The compounds were separated using a glass column (2.0m x 8mm) packed with n-octane Porasil C of 0-100 mesh size; the carrier gas was nitrogen. The oven was as held at 60^oC for 3 minutes and then ramped to 100°C at 10°C min^{-1} and held for 3 minutes before being ramped to 140°C at 20°C min^{-1} and held for 10 minutes. The injection temperature was 150^oC and the detector temperature was 200^oC. Standard alkane and alkene calibration gases were obtained from Scientific and Technical Gases Ltd (UK).

A second Varian CP-3380 gas chromatograph fitted with dual thermal conductivity detectors (TCD) was used to determine the permanent gases. The first TCD detector was equipped with a steel column (2m x 2 mm) packed with 60-80 mesh molecular sieve and was used for analysing H_2, O_2, N_2, and CO. The GC oven was held isothermally at 40^oC for 10 minutes. Carbon dioxide was analysed on the second TCD detector using a 2m x 2 mm diameter steel column packed with Haysep 80-100 mesh material, using a similar oven programme. Both injector temperatures were 120^oC and both detector ovens operated at 120^oC with a filament temperature of 160^oC. A standard calibration gas obtained from Scientific and Technical Gases Ltd was used for quantification of CO_2, O_2, CO, N_2, and H_2. O_2 was analysed in order to determine if any air dilution had occurred during sampling of the gases.

The pyrolysis oils were analyzed using gas-chromatography with linked mass-spectrometery (GC-MS), gas chromatography with flame ionization detection (GC-FID) and Fourier Transform Infra –Red Spectrometry (FT-IR). The GC-MS was used to identify the compounds present in each of the pyrolysis oils and the GC-FID was used to quantify the major compounds. The FT-IR was used to determine the functional groups present in each pyrolysis oil.

The GC-MS was a CE Instruments 2000 series GC fitted with a 30m RTX-5 column. The injector temperature was 300°C and the oven was held at 40°C for 15 minutes, then ramped to 280°C at 5° C/min, and then held for 15 minutes. The mass spectrometer electron energy was 70eV and the ion source and coupling temperatures were 220°C and 300°C respectively. The injector temperature was 285^oC and was operated in split mode to prevent overloading of the GC column and the mass spectrometer. The GC-FID was fitted with a 30m ZB-5 column and the oven programme was the same as for the GC-MS analysis. The injector and FID temperatures were 300°C and a split ratio of 1:30 was used. Standard solutions were used for calibration and quantification.

Functional group compositional analysis of the oils was determined using a Nicolet Magna 560IR FT-IR spectrometer equipped with a spectral library search facility. An aliquot of each pyrolysis oil was spread thinly over a potassium bromide disk and the spectrometer scanned the sample from 4000 to 400 cm^{-1}. The spectral peak heights were normalized to the largest spectral band and the FT-IR software was used to determine the functional groups present, although manual identification of the spectral bands was also required due to the complex nature of the spectra.

Analysis of the pyrolysis chars and the spent catalysts was carried out using a Camscan 4 scanning electron microscope (SEM) fitted with an energy dispersive X-ray (EDX) analyser. The solid samples were coated with a 5nm mixture of platinum and palladium prior to analysis.

3. RESULTS AND DISCUSSION

3.1 THERMOGRAVIMETRIC ANALYSIS

TGA analysis of the two rubber glove samples was carried out to determine their decomposition profile. As shown in figure 2, under a nitrogen atmosphere both sample Y and sample W undergo one period of mass loss, this indicates that pyrolysis of both samples occurs in a single stage. The mass loss due to pyrolysis of sample Y was found to be 98% while sample W only lost 84% of its mass during pyrolysis. The peak decomposition

temperature for both samples was 376°C and the pyrolysis was completed at 472°C and 450°C for Y and W gloves respectively. Previous authors have investigated the thermal decomposition of natural rubber (Bhowmick et al., 1987; Williams and Besler, 1995) and have reported similar decomposition temperatures to those reported here.

3.2 FIXED BED REACTOR

The two rubber glove samples were mixed together and pyrolysed in a fixed bed reactor. The pyrolysis temperature was either 380°C or 480°C; these temperatures were chosen because they represent the temperature at which peak decomposition occurred and the temperature at which pyrolysis of both samples was completed according to the TGA results (figure 2). The mixed rubber glove sample was tested at both temperatures with and without the Y-zeolite catalyst being present, to establish both the effects of temperature on the pyrolysis of rubber gloves and the effect of the catalyst.

3.2.1 Mass Balance and Product Yield. – The mass balance was calculated by measuring the mass of the reactor, crucible, and condensers and analysing the pyrolysis gases by GC. Each reaction condition was tested at least twice and the average results are presented. In the absence of a catalyst, it was found that temperature had a significant impact on the yield of liquid products increasing them from 57.9 to 79.8 wt% as the reaction temperature increased from 380°C to 480°C. However, when the Y-zeolite catalyst was present, the mass of liquid products decreased to 35.5 wt% at 380°C and 46.1 wt% at 480°C. The decreased yields of liquid products was balanced by increased gas yields of 7.4 wt% at 380°C and 11.7 wt% at 480°C. When no catalyst was present, the gas yields were around 1 wt%. There was also a significant amount of coke formed on the surface of the catalyst, 19 wt% and 16 wt% at 380 and 480°C respectively. Other researchers have found that the yield of liquid products decreases when a zeolite catalyst is present during the pyrolysis of rubber (Shen et al., 2007a; Williams and Brindle, 2003) and it is assumed that this is due to coke formation on the surface of the catalyst.

It is significant that the yield of volatile pyrolysis products increases with increasing temperature as this indicates that at the lower pyrolysis temperature (380°C) pyrolysis of the sample was not complete despite the sample being held at high temperature for 45 minutes. In fact, when the reactor crucible was examined after the low temperature tests, the residue consisted of dark grey material that melted when it was heated up. The pyrolysis residue produced at 480°C was a black crumbly material, indicating that pyrolysis was complete at this temperature. It would therefore appear that the higher temperature is required to complete the pyrolysis process and maximise the yield of valuable pyrolysis products.

3.2.2 Characterization of the volatile pyrolysis products. – Pyrolysis of the rubber glove samples resulted in the production of oil, gas, and residue/ char. The oils produced by the non-catalytic pyrolysis of rubber gloves were dark brown or black in colour and had a medium viscosity. Once the Y-zeolite catalyst was introduced into the reactor, the pyrolysis oils transformed to a pale-yellow/brown colour and their viscosity decreased. All of the oils were collected from the fixed bed reactor's first condenser, which was water cooled.

Figure 3 shows the infrared spectra of the pyrolysis oil resulting from the four different reaction conditions studied. It is obvious from figure 3, that the reaction temperature had little effect on the functional groups present in the liquid pyrolysis products, but the presence of the Y-zeolite catalyst had a significant effect.

When no catalyst was used, the most dominant liquid pyrolysis products were aliphatic, as indicated by the large methyl and methylene bands at 2956, 2923, and 2868 cm^{-1}. The bands at 1606 and 1495 cm^{-1} relate to stretching vibrations in aromatic rings, but these bands are very small, indicating that only low concentrations of aromatics were present. The band at 1644 cm^{-1} can be attributed to non-conjugated C=C stretching vibrations indicating the presence of alkenes in the pyrolysis oil. The large bands around 1460 cm^{-1} can be attributed to methylene and asymmetrical methyl C-H deformation and the band at 1376 cm^{-1} can be attributed to symmetrical methyl deformation. Seen as the band at 1376 cm^{-1} is significantly smaller than the band at 1460 cm^{-1}, it can be assumed that a large proportion of methylene groups are present in the pyrolysis oil. The absence of a doublet at 1376 cm^{-1} indicates that there were probably no branched alkanes present in the oil. However, there is evidence of branched alkenes being present, the band at 887 cm^{-1} can be attributed to out-of-plane deformation in $R_1R_2C=CH_2$ groups while the band at 800 cm^{-1} can be attributed to $R_1R_2C=CHR_3$ groups. There is also some evidence of *trans* -CH=CH- bonds with the band at 965 cm^{-1}. The =CH stretching vibrations are also present, although only the band at 3079 cm^{-1} can be clearly distinguished with the 3019 cm^{-1} band being somewhat masked by the CH_3 band at 2956 cm^{-1}.

The presence of the Y-zeolite catalyst had a significant impact on the infra-red spectra of the pyrolysis oils (figure 3), most importantly, the bands at 1606 and 1495 cm^{-1} indicate the presence of aromatic compounds, as they can be assigned to ring stretching vibrations. The bands at 2956, 2922, and 2868 cm^{-1} can be attributed to methyl and methylene C-H stretching and the bands at 1456 and 1378 cm^{-1} can be attributed to the matching C-H deformation, although aromatic compounds also show a band at 1456 cm^{-1}. The complexity of the spectra between 1000 – 650 cm^{-1} meant it was not possible to accurately determine the type of substitution present on the aromatic rings, but it did give an indication that a wide variety of different benzene-substitution patterns were present. It was also notable that when the catalyst was present in the reaction system, the band at 887 cm^{-1}, which relates to out-of-plane deformation in $R_1R_2C=CH_2$ groups was absent, as was the C=C stretching vibration at 1644 cm^{-1}, although this might be due to masking by the large band at 1606 cm^{-1}.

A more detailed characterization of the pyrolysis products was carried out using GC analysis. The pyrolysis gases were characterised by using GC-FID and GC-TCD, while the pyrolysis oils were characterised using GC-MS and GC-FID. The yield of products is shown in table 2, where the results are presented in the form of mg/g$_{sample}$, because this is the most accurate way of representing the changes in the pyrolysis products when the catalyst is used. If the results were presented as the percentage composition of the pyrolysis oil they could be misleading, because the amount of pyrolysis oil produced altered depending on whether the catalyst was present or not. For example, the mass of toluene produced during pyrolysis could remain the same no matter whether the catalyst is present or not, but its concentration in the pyrolysis oil might increase or decrease because the total mass of pyrolysis oil produced increases or decreases.

An example of the GC analysis of the pyrolysis oils is shown in figure 4; the identification of the numbered peaks is given in table 2. In non-catalytic pyrolysis, the oil consists of a number of compounds grouped into dimers, trimers, tetramers, pentramers and hexamers. Limonene (dimer) was the most abundant compound, with a yield of 108.8 and 120.5 mg/g$_{sample}$ at 380 and 480°C respectively. A similar oil composition has been noted by other authors during their investigations into the pyrolysis of natural rubber and polyisoprene

(Chen and Qian, 2002; Chien and Kiang, 1979). The presence of oligomers confirms the FT-IR analysis, which suggested that the non-catalytic pyrolysis oil mainly consisted of aliphatic material. The FT-IR analysis also suggested the presence of $R_1R_2C=CH_2$ and $R_1R_2C=CHR_3$ groups, which would tie in with the presence of oligomers and their variants that contain double bonds at various positions along the molecule chain. Additionally, the $R_1R_2C=CH_2$ and $R_1R_2C=CHR_3$ groups are both found in limonene.

Other components of the pyrolysis oil included toluene, xylenes, and alpha-methylstyrene, all of which increased in yield as the reaction temperature increased from 380 to 480°C (table 2). P-cymene was also a significant product of rubber glove pyrolysis and was presumably formed from limonene by dehydrogenation of the hexene ring and saturation of the methylene group. Interestingly, the yield of p-cymene decreased as the pyrolysis temperature increased, suggesting the either p-cymene does not form or that it decomposes at the higher reaction temperature.

Thermal degradation of cis-1,4-polyisoprene (or natural rubber) has been suggested to occur through a radical mechanism involving beta-scission of the original polymer to generate the monomer (isoprene) and the dimer (limonene). The formation of aromatic species is explained by secondary reactions involving cyclisation, dehydrogenation, and aromatization of short chain olefins through the Diels-Alder mechanism (Chen and Qian, 2002; Chien and Kiang, 1979; Groves et al., 1991).

When the Y-zeolite catalyst was added to the reaction system, the composition of the pyrolysis oil changed considerably, with limonene being almost eliminated and a large increase in the yield of single and multiple ring aromatics (table 2). When the reaction temperature was 380°C, the yield of limonene fell from 108.8 to 0.9 mg/g$_{sample}$ and when the reaction temperature was 480°C, the yield of limonene fell from 120.5 to 2.2 mg/g$_{sample}$, an almost 100% decrease in both cases. While the introduction of the catalyst caused a large decrease in the yield of limonene, the yield of toluene, m/p-xylene, and styrene/o-xylene all increased. For example, at a reaction temperature of 480°C, the yield of toluene increased from 11.8 to 74.3 mg/g$_{sample}$ and the yield of m/p-xylene increased from 5.8 to 80.5 mg/g$_{sample}$, an increase of 530 and 1300 % respectively.

In addition to the compounds mentioned above, the Y-zeolite catalyst also aided the formation of ethylbenzene, ethyltoluenes, trimethylbenzenes, and diethylbenzenes. 3-ethyltoluene was the most abundant ethyltoluene, with yields of 18.5 and 18.9 mg/g$_{sample}$ when the reaction temperature was 380°C and 480°C respectively. 1,2-Diethylbenzene, the most abundant diethylbenzene, was not detected when no catalyst was present in the reaction system, but in the presence of Y-zeolite, 6.1 and 6.4 mg/g$_{sample}$ was detected when the reaction temperature was 380 and 480°C respectively (table 2). Although ethylbenzene, ethyltoluenes, and trimethylbenzenes were present when no catalyst was employed, their yields all increased dramatically once Y-zeolite was present in the reaction system. For example, at a reaction temperature of 480°C, the yield of 3-ethyltoluene increased from 0.1 to 18.9 mg/g$_{sample}$ when the catalyst was used. The presence of Y-zeolite also catalysed the formation 1,2,4,5-tetramethylbenzene, which had a yield of 3.0 and 3.3 mg/g$_{sample}$ at a reaction temperature of 380 and 480°C respectively.

In addition to increasing the formation of single ring aromatics, the presence of Y-zeolite also increased the formation of polyaromatic hydrocarbons (PAH). The yield of naphthalene during catalytic pyrolysis was 1.5 and 3.6 mg/g$_{sample}$ at 380 and 480°C respectively. The

most predominant PAH was 1,7-dimethylnaphthalene which had a yield of 9.9 and 15.0 mg/g_{sample} at the lower and higher reaction temperature respectively. Other significant PAH's present in the pyrolysis oil were methylnaphthalenes, ethylnaphthalenes, and dimethylnaphthalenes.

Work by previous authors into the pyrolysis of rubber tires has shown that the presence of zeolite catalysts reduces the yield of limonene and increases the concentration of aromatics (Shen et al., 2007a). Williams and Brindle (Williams and Brindle, 2002a, 2003) have reported that Y-zeolite increases the yield of benzene, toluene, xylenes, ethyltoluenes, trimethylbenzenes, and tetramethylbenzenes when scrap tires are pyrolysed, they also reported increased yields of naphthalene and substituted naphthalenes. Some work has been published where zeolite catalysts were found to have little effect on the pyrolysis of tires (Qu et al., 2006).

In the absence of a catalyst, the pyrolysis gases consisted of alkanes and alkenes in addition to a small amount of hydrogen. No CO_2 or CO was present and no hydrogen sulphide was detected in the pyrolysis gas down to a detection limit of 0.01mg / $g_{plastic}$. The most abundant gas was butene / butadiene, which had a yield of 4.0 mg/g_{sample} when the reaction temperature was 380°C (table 2). The high yields of butene / butadiene might be due to the decomposition of isoprene to butadiene via the loss of the methyl group, or, butene could be formed by the decomposition of limonene. Methane was the second most predominant gas during non-catalytic pyrolysis of rubber gloves followed by C_2 and C_3, which were evenly distributed between the alkanes and the alkenes.

Once the Y-zeolite catalyst was introduced into the reactor, the composition of the gas changed significantly (table 2). Again butene / butadiene was the most abundant gas, with yields of 33.5 and 40.3 mg/g_{sample} at a reaction temperature of 380 and 480°C respectively. However, the yield of propane increased dramatically to give yields of 23.1 and 30.5 mg/g_{sample} at a reaction temperature of 380 and 480°C respectively. We have noted the high yields of propane when pyrolysing polymers in the presence of Y-zeolite in our previous work (Hall and Williams, 2007). At the higher reaction temperature, the yields of methane and ethane were also dramatically increased when the Y-zeolite catalyst was present in the reaction system (table 2).

3.3 ANALYSIS OF THE SPENT CATALYSTS

The spent catalyst was removed from the reactor crucible and examined by SEM-EDX. No other analysis techniques were attempted because of the very heterogeneous nature of the sample. The top half of the spent-catalyst bed was black in colour, presumably due to the formation of coke on the surface of the particles. The bottom half of the spent-catalyst bed was white in colour, which was probably caused by deposition of filler material released during the pyrolysis of the rubber gloves.

SEM-EDX analysis of the black particles (figure 5) showed that the only elements present were aluminium, silicon, sodium, and oxygen from the zeolite catalyst and carbon from the coke on the surface of the catalyst. However, the white particles (figure 6), in addition to the above mentioned elements, also contained sulphur, chlorine, calcium, titanium, and zinc. The sulphur obviously came from the vulcanised rubber, but it is likely that the other elements were all present in the glove samples in the form of fillers and additives.

When the catalyst was absent from the reaction system, there was a large amount of white powder coating the walls of the reactor crucible, which was identified as being calcium based. Therefore, it can be concluded that calcium additives in the rubber glove sample were reaching the upper regions of the reactor during pyrolysis and that the additives found on the surface of the catalyst were due to material deposition rather than the catalytic action of the zeolites. However, it is still possible that some of the sulphur and chlorine identified on the surface of the catalyst was organic in origin and that it had been removed from the pyrolysis oil by the catalytic action of the zeolites.

4. CONCLUSIONS

Two different rubber glove samples were mixed together and then pyrolysed in a fixed bed reactor at either 380 or 480°C. Some of the tests were carried out in the presence of Y-zeolite to upgrade the pyrolysis products to more valuable compounds. When the rubber gloves were pyrolysed in the absence of a catalyst, the pyrolysis oil consisted of dimers, trimers, tetramers, pentamers, and hexamers, with limonene (dimer) being the most abundant compound. Some aromatic compounds such as toluene, xylenes, and ethyltoluenes were also present in the pyrolysis oil. At the higher reaction temperature, the yields of limonene and the aromatic compounds was increased.

When the Y-zeolite catalyst was added to the reaction system, the composition of the pyrolysis products changed considerably. More organic gases were produced during catalytic pyrolysis and the yields increased at the higher reaction temperature. The Y-zeolite catalysed the formation of aromatic compounds such as toluene, xylenes, ethyltoluenes, and naphthalenes, including naphthalene itself. The Y-zeolite also eliminated limonene and the polyisoprene oligomers that were present in the non-catalytic oil. At the higher reaction temperature, the yields of aromatic compounds were increased.

Although the presence of Y-zeolite significantly upgraded the pyrolysis oil, it also reduced the yield of oil. Therefore, an evaluation of the benefits of upgrading the pyrolysis oil needs to be carried out, taking into account the increased value of the upgraded oils and the reduced yield. Currently, it is unclear if the upgrading of rubber glove pyrolysis oils is economically viable.

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REFERENCES

Bagri, R. and Williams, P.T., 2002. Fluidised-bed catalytic pyrolysis of polystyrene. Journal of the Institute of Energy 75, 117-123.

Berrueco, C., Esperanza, E., Mastral, F.J., Ceamanos, J. and Garcia-Bacaicoa, P., 2005. Pyrolysis of waste tyres in an atmospheric static-bed batch reactor: Analysis of the gases obtained. Journal of Analytical and Applied Pyrolysis 74, 245-253.

Bhowmick, A.K., Rampalli, S., Gallagher, K., Seeger, R. and McIntyre, D., 1987. The Degradation of Guayule Rubber and the Effect of Resin Components on Degradation at High-Temperature. Journal of Applied Polymer Science 33, 1125-1139.

Chen, F.Z. and Qian, J.L., 2002. Studies on the thermal degradation of cis-1,4-polyisoprene. Fuel 81, 2071-2077.

Chiantore, O., Guaita, M., Lazzari, M., Hadjichristidis, N. and Pitsikalis, M., 1995. Thermal-Degradation of Model Linear and Star-Shaped Polyisoprene Molecules. Polymer Degradation and Stability 49, 385-392.

Chien, J.C.W. and Kiang, J.K.Y., 1979. Polymer Reactions 10. Thermal Pyrolysis of Poly(Isoprene). European Polymer Journal 15, 1059-1065.

Conesa, J.A., Martin-Gullon, I., Font, R. and Jauhiainen, J., 2004. Complete study of the pyrolysis and gasification of scrap tires in a pilot plant reactor. Environmental Science & Technology 38, 3189-3194.

Galvagno, S., Casu, S., Martino, M., Di Palma, E. and Portofino, S., 2007. Thermal and kinetic study of tyre waste pyrolysis via TG-FTIR-MS analysis. Journal of Thermal Analysis and Calorimetry 88, 507-514.

Groves, S. and Lehrle, R., 1992. Pyrolysis Mechanisms of Natural-Rubber Deduced from the Dependence of Product Yields on Sample-Size. European Polymer Journal 28, 373-378.

Groves, S.A., Lehrle, R.S., Blazso, M. and Szekely, T., 1991. Natural-Rubber Pyrolysis - Study of Temperature-Dependence and Thickness-Dependence Indicates Dimer Formation Mechanism. Journal of Analytical and Applied Pyrolysis 19, 301-309.

Hall, W.J. and Williams, P.T., 2008. Removal of organobromine compounds from the pyrolysis oils of flame retarded plastics using zeolite catalysts. Journal of Analytical and Applied Pyrolysis 81, 139-147.

Kyari, M., Cunliffe, A. and Williams, P.T., 2005. Characterization of oils, gases, and char in relation to the pyrolysis of different brands of scrap automotive tires. Energy & Fuels 19, 1165-1173.

Li, S.Q., Yao, Q., Wen, S.E., Chi, Y. and Yan, J.H., 2005. Properties of pyrolytic chars and activated carbons derived from pilot-scale pyrolysis of used tires. Journal of the Air & Waste Management Association 55, 1315-1326.

MARGMA (Malaysian Rubber Glove Manufacturers Association), 2006. Domestic consumption of natural rubber by the rubber products industry (January - June 2006).

Miskolczi, N., Bartha, L. and Deak, G., 2006. Thermal degradation of polyethylene and polystyrene from the packaging industry over different catalysts into fuel-like feed stocks. Polymer Degradation and Stability 91, 517-526.

Olazar, M., Aguado, R., Bilbao, J. and Barona, A., 2000. Pyrolysis of sawdust in a conical spouted-bed reactor with a HZSM-5 catalyst. AICHE Journal 46, 1025-1033.

Oledzka, E., Pysklo, L., Sobczak, M. and Luksa, A., 2006. Technological and economical aspects of the pyrolysis of end-of-life tyres and the refining of the products obtained. Polimery 51, 407-414.

Qu, W., Zhou, Q.A., Wang, Y.Z., Zhang, J., Lan, W.W., Wu, Y.H., Yang, J.W. and Wang, D.Z., 2006. Pyrolysis of waste tire on ZSM-5 zeolite with enhanced catalytic activities. Polymer Degradation and Stability 91, 2389-2395.

Rajan, V.V., Dierkes, W.K., Joseph, R. and Noordermeer, J.W.M., 2006. Science and technology of rubber reclamation with special attention to NR-based waste latex products. Progress in Polymer Science 31, 811-834.

Seidelt, S., Muller-Hagedorn, A. and Bockhorn, H., 2006. Description of tire pyrolysis by thermal degradation behaviour of main components. Journal of Analytical and Applied Pyrolysis 75, 11-18.

Shen, B.C., Wu, C.F., Guo, B.B., Wang, R. and Liangcai, 2007a. Pyrolysis of waste tyres with zeolite USY and ZSM-5 catalysts. Applied Catalysis B-Environmental 73, 150-157.

Shen, B.X., Wu, C.F., Liang, C., Guo, B.B. and Wang, R., 2007b. Pyrolysis of waste tyres: The influence of USY catalyst/tyre ratio on products. Journal of Analytical and Applied Pyrolysis 78, 243-249.

Shen, B.X., Wu, C.F., Wang, R., Guo, B.B. and Liang, C., 2006. Pyrolysis of scrap tyres with zeolite USY. Journal of Hazardous Materials 137, 1065-1073.

WHO (World Health Organisation), 2000. Wastes from health-care activities.

Williams, P.T. and Besler, S., 1995. Pyrolysis-Thermogravimetric Analysis of Tires and Tyre Components. Fuel 74, 1277-1283.

Williams, P.T. and Brindle, A.J., 2002a. Catalytic pyrolysis of tyres: influence of catalyst temperature. Fuel 81, 2425-2434.

Williams, P.T. and Brindle, A.J., 2002b. Fluidised bed catalytic pyrolysis of scrap tyres: Influence of catalyst: tyre ratio and catalyst temperature. Waste Management & Research 20, 546-555.

Williams, P.T. and Brindle, A.J., 2003. Aromatic chemicals from the catalytic pyrolysis of scrap tyres. Journal of Analytical and Applied Pyrolysis 67, 143-164.

Williams, P.T. and Nugranad, N., 2000. Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks. Energy 25, 493-513.

Table 1
Ultimate analysis of the rubber glove samples (wt%)

Element	Sample W	Sample Y
N	0.4	0.5
C	71.3	83.5
H	10.1	12.0
S	0.8	0.8
O	0.0	0.0
Ash	17.5	3.2

Table 2
Quantification of the major compounds when rubber gloves were pyrolysed in a fixed bed reactor (mg / g_{sample})

|	no catalyst		Y-zeolite		RT (mins)	Peak #
	380°C	480°C	380°C	480°C		
H_2	0.4		0.1	0.8		
Methane	1.9		3.1	17.0		
Ethene	0.6		3.5	6.7		
Ethane	0.6		3.0	10.1		
Propene	1.1		3.6	6.0		
Propane	1.3		23.1	30.5		
Butene / butadiene	4.0		33.5	40.3		
Butane	1.1		4.1	5.7		
toluene	8.7	11.8	68.0	74.3	2.3	1
ethylbenzene	0.6	1.0	7.3	8.4	4.4	
m / p-xylene	4.2	5.8	72.0	80.5	4.6	2
Styrene / o-xylene	0.7	1.4	22.1	25.0	5.4	3
allylbenzene	0.5	1.8	0.1	n/d	8.3	
propylbenzene	1.6	1.4	0.9	0.9	8.8	
3-ethyltoluene	n/d	0.1	18.5	18.9	9.5	4
4-ethyltoluene	1.7	2.5	n/d	n/d	9.7	
2-ethyltoluene	n/d	n/d	3.2	3.5	10.9	
alpha-methylstyrene	6.2	8.6	0.1	n/d	11.4	
1,2,4-Trimethylbenzene	n/d	1.7	28.7	31.5	12.3	5
p-methylstyrene	n/d	n/d	n/d	n/d	12.7	
1,2,3-Trimethylbenzene	1.1	0.7	4.8	5.5	15.3	6
p-cymene	6.6	1.7	0.7	1.4	15.9	
limonene	108.8	120.5	0.9	2.2	16.4	
1,3-diethylbenzene	n/d	n/d	0.7	0.7	18.1	
1,4-diethylbenzene	n/d	n/d	1.3	1.6	18.5	
1,2-diethylbenzene	n/d	n/d	6.1	6.4	18.9	7
1,2,4,5-tetramethylbenzene	n/d	n/d	3.0	3.3	21.9	
naphthalene	n/d	n/d	1.5	3.6	24.5	8
2-methylnaphthalene	n/d	n/d	4.4	8.1	28.5	9
1-methylnaphthalene	n/d	n/d	1.8	3.2	29.0	
2-ethylnaphthalene	n/d	n/d	0.7	0.9	31.6	
1-ethylnaphthalene	n/d	n/d	n/d	0.1	31.6	
2,6-dimethylnaphthalene	n/d	n/d	3.1	4.7	31.9	
1,7-dimethylnaphthalene	n/d	n/d	9.9	15.0	32.2	10
1,4-dimethylnaphthalene	n/d	n/d	1.1	1.5	32.8	
1,2-dimethylnaphthalene	n/d	n/d	0.5	0.7	33.2	
1-phenylnaphthalene	n/d	n/d	0.1	0.1	42.8	
1,3,5-triphenylbenzene	n/d	n/d	0.2	0.1	61.0	
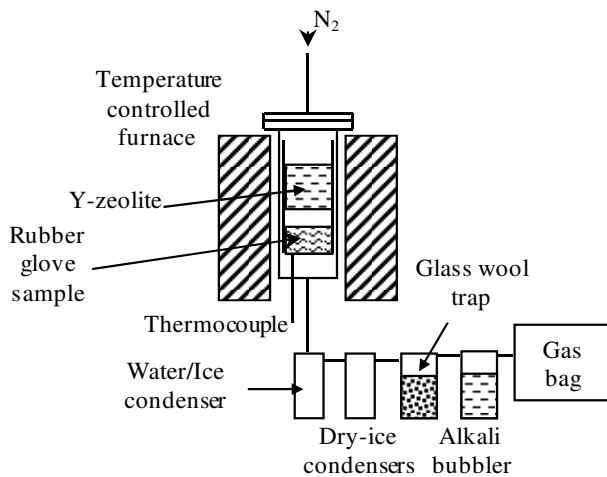
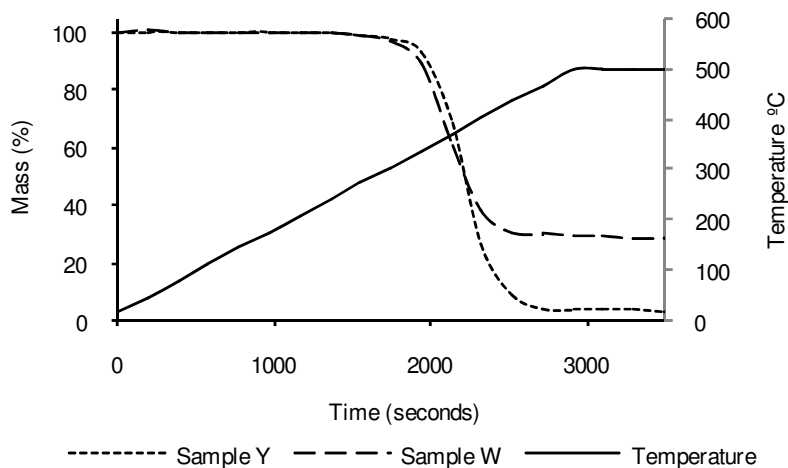**Figure 1 Fixed bed reactor schematic**

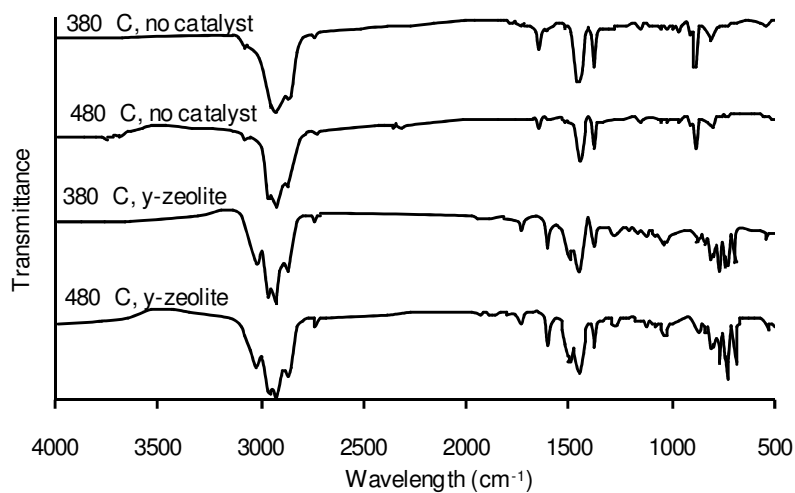**Figure 2 TGA analysis of the two rubber glove samples**

Figure 3 FT-IR spectra of the oils produced by the pyrolysis of rubber gloves in the fixed bed reactor
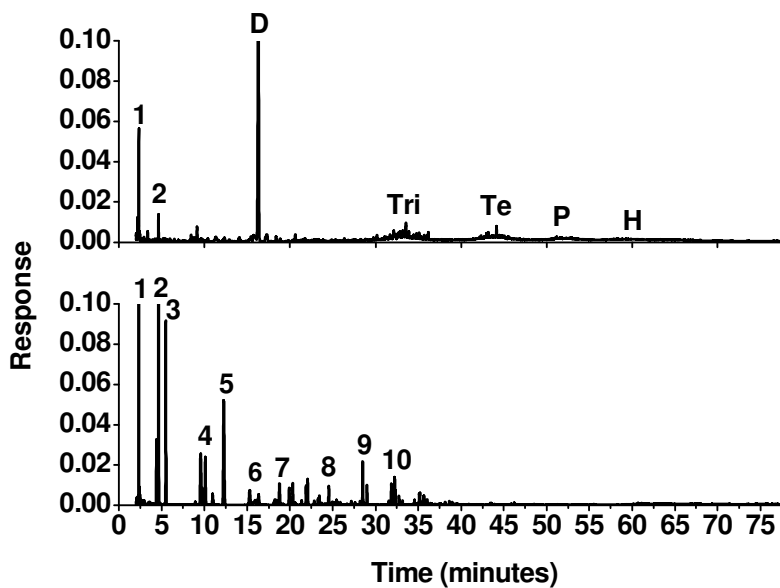
Figure 4 Gas chromatography analysis of the rubber glove pyrolysis oil produced without a catalyst (top) and with Y-zeolite catalyst (bottom). The peak numbers are detailed in table 2. D = dimer (limonene), Tri = trimers, Te = tetramers, P = pentamers, H = hexamers.
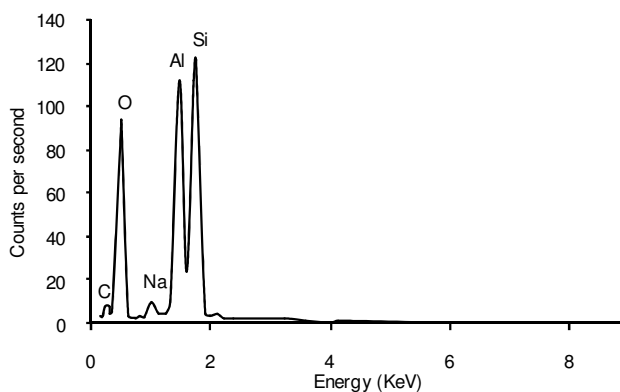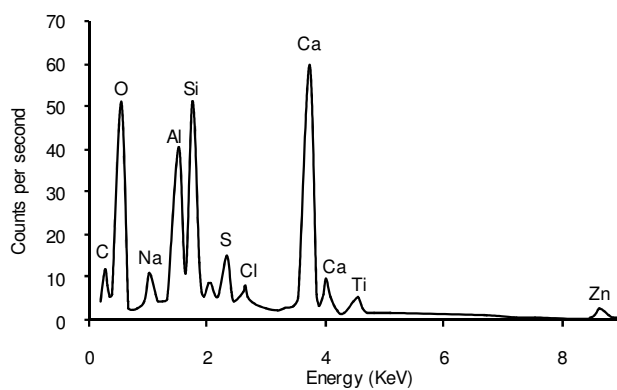

Figure 5 EDX spectra of the black coloured spent catalyst

Figure 6 EDX spectra of the white coloured spent catalyst