CHAPTER I
INTRODUCTION

With the strong global need in automobile usage, a huge number of used tire rubbers have been increasingly generated. Pyrolysis is an interesting alternative process to decompose waste tires. Polymer chain can be cut in thermal reaction; however, a catalytic reaction is more efficient. Generally, normal zeolite catalysts with a small pore size (< 2 nm) can crack only some substances, which can diffuse into the zeolite pores. In case of cracking bulky molecules, mesoporous catalysts with larger pores (2-50 nm) pay an important role instead. The obtained liquid product from this process is likely to gain more interest nowadays since it can be used as liquid fuel. However, there are some drawbacks from the degradation of waste tire because char remaining from pyrolysis is highly obtained, but it has only a few applications. Additionally, the obtained oil still contains the hetero-atoms such as nitrogen atom. Thus, the N-containing compounds in tire-derived oil (TDO) are also elaborated in this work.

Nowadays, the growth rate of transportations has rapidly increased. The following problem is that the large space of landfill for waste tire is required. Therefore, the recycle of end-of-life tire should be considered. Pyrolysis is one of the effective processes for end-life tire elimination, involving the breaking bond of larger molecules into smaller molecules in the absence of oxygen. Gas, oil, and char are the products obtained from this process. Indeed, the TDO is the attractive product since it can be used as liquid fuel. Nevertheless, the recent research work of Yuwapornpanit and Jitkarnka (2015) stated that the improvement of oil qualities was the important issue because 60-65 % of gas oil and vacuum gas oil, and especially 20-25 % of large-size aromatics (di-, poly-, and polar-aromatics) still remained in TDO in thermal decomposition and catalytic cracking (using normal zeolite, pore size < 8 nm) cases. It is reasonable to use mesoporous materials as a cracking catalyst for increasing the molecular diffusion inside the molecular sieve pore, where has a lot of active sites. The significant issue is that the molecular sieves have ability to break bonds either equivalent to or better than normal zeolites. In general, zeolites have been widely used since they have good performance on cracking. Moreover, zeolites have an excellent thermal stability and mechanical strengths because of their crystallinity, allowing convenient recycling after the removal of organic contaminants through calcination (Na *et al.*, 2013). In order to study conversion of heavy fractions into lighter products, the estimation of molecular sizes of hydrocarbons in TDO is necessary for selecting an oil-upgrading catalyst with an appropriate pore size that can handle all molecules in the feed. However, micro-pore was likely too small to convert large compounds into smaller molecules (Ajaikumar *et al.*, 2013).

Mesoporous silicas have received great interest as catalysts and adsorbents because of their uniform pore structure. It is capable of accommodating relatively large molecules that cannot be accommodated within a zeolite pore (Byambajav and Ohtsuka, 2003). For example, MCM-41 (Mobil Composition of Matter No. 41) and MCM-48 (Mobil Composition of Matter No. 48) with a pore diameter between 1.5 and 10 nm were developed by Mobil group (Chena *et al.*, 2013), and silica nanoparticles named SBA-15 (Santa Babara Amorphous No. 15) with much larger pore of 3.6 to 15 nm were discovered by the University of California, Santa Babara (Wang *et al.*, 2001). MCM-41 and SBA-15 have been reported as well-ordered hexagonal mesoporous silica whereas MCM-48 has a cubic structure.

Char is the attractive solid waste from pyrolysis due to its highly remaining amount. Its structure is similar to graphite but covalent bonding between its graphene sheets shows imperfection structure (On-x Life Technologies, Inc., 2013). If pyrolytic char is upgraded as high quality like activated carbon, it may also provide the valid opportunities such as adsorbents, fuel materials, or catalyst supports.

Nitrogenous compounds can be formed in TDO, resulting from the degradation of accelerators, activators, retarders, and anti-degradants in tire. The nitrogenous compounds in TDO are considered as undesirable products since the formation of NOx can cause the environment problems. Moreover, they pose the effects to refining procedure, particularly leading to fouling, catalyst poisoning, equipment corrosion, and gum formation. In order to identify N-containing in oil, the analysis method is the important factor for better understanding in further treatment.

Therefore, the objectives in this work were to study on the conversion of heavy fraction into lighter products using mesoporous materials as well as the identification of N-containing in TDO using the comprehensive two-dimensional Gas Chromatography with Time of Flight Mass Spectrometer (GC×GC/TOF-MS). There were two main types of the mesoporous catalyst used in this work. The first one was meso-silica materials, including MCM-41, MCM-48, and SBA-15. They were used to take the advantages of their attractive properties such as large pore size and defined pore structure. The results were then used to discuss the relationship between the average molecular sizes of compositions in TDO and the pore size of catalysts. The other type of mesoporous catalyst was pyrolytic carbon, obtained from waste tire pyrolysis. It was used to examine the possibility of using un-treated and acidic-treated pyrolysis char as a catalyst in pyrolysis of waste tire. The molecular compositions in TDO of all experiments were analyzed using GCxGC/TOF-MS whereas the petroleum fractions were analyzed using a SIMDIST GC.