

## Selective Catalytic Reduction-An Effective Emission Controller in Ci Engines

*D. Ravi*

Mechanical Engineering Department,  
Bharath University, Chennai, India

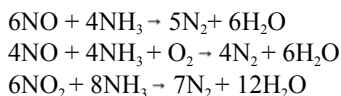
**Abstract:** Control of emission in internal combustion engines can be achieved either by controlling combustion or by treating the exhaust gas. The latter is comparatively easier since there is less or no need to modify the engine itself. One such after treatment method is the use of catalytic converter. But, the 3-way converter is expensive due to use of both platinum and palladium/rhodium catalysts. One of the alternative is the use of selective catalytic reduction, i.e., reduction of a particular emission based on the type of the engine used. For example, the diesel engine being the most efficient engine also gives lower quantities of pollutants like CO and unburnt hydrocarbons. However, the major concern of the diesel engine is its comparatively higher NO<sub>x</sub> which needs development and up gradation of the engine to reduce NO<sub>x</sub> besides CO and HC emissions. This project aims at reduction of NO<sub>x</sub> in CI engines using Selective Catalytic Reduction and its optimization. Various catalysts used in SCR system are studied and also pre-oxidation of the exhaust gases to increase the rate of reaction at the SCR catalyst along with their effects on the performance and emission characteristics of the engine is also discussed.

**Key words:** Pre-oxidation • Catalyst • SCR

### INTRODUCTION

The requirement for energy has grown exponentially over the past decades owing to industrialization and subsequent lifestyle changes. Much of this energy is generated by combusting fossil fuels such as coal, natural gas, gasoline and diesel. The combustion process releases the chemical energy contained in the fuels as thermal energy, which is used to run different power cycles depending upon the application. The combustion process involves complex chemical reactions; the reactants are fuel and air and the products include various species such as water, oxides of carbon, nitrogen and sulfur, unburned fuel, organic compounds and particulate matter [1]. Some of these species have a harmful effect on the living beings and environment and hence are termed as pollutants.

**Selective Catalytic Reduction (SCR):** In selective catalytic reduction ammonia reacts with nitric oxide and nitrogen dioxide [2]. The reactions involved are,



Vanadium pentaoxide, platinum, iron/chromium oxides and zeolites are among the catalysts that can be used. The operating temperature is generally above 200°C and operating pressure has only a minor effect on overall efficiency.

The exhaust gas is pre-heated (if required) to a minimum temperature for good operation of the SCR catalyst. The reactant gas is mixed with the pre-heated exhaust gas and the mixture passed into a reactor containing the catalyst bed [3].

#### The Advantages of the Scr System Are:

- A low NO<sub>x</sub> content can be achieved
- Operating temperatures are lower

#### The Disadvantages of the Scr System Are:

- High capital cost
- Catalyst aging and poisoning

**SCR Process:** The catalysts used are non-noble metal catalyst. SCR processes use ammonia as selective reducing agent, in that, the main sub reactions are of nitrogen oxide reactions. In zeolite catalysts, the NO<sub>x</sub>

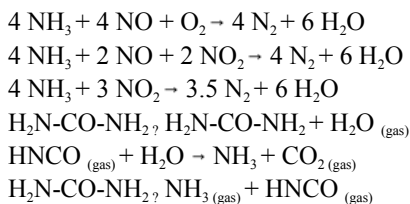
conversion using  $\text{NH}_3$  is independent of the oxygen concentration over a wide range [4]. The consequence in this reaction is a delayed reaction to changes in  $\text{NH}_3$  input concentration with  $\text{NH}_3$  45% to 55%  $\text{NO}_x$  conversion was attained using SCR. In contrast the presence of urea, nearly 98%  $\text{NO}_x$  conversion was attained in the range of 300°C through 350°C.

Prior to modelling the SCR process, it must first be understood in its entirety. Unlike an elementary single step of a gas phase chemical reaction, a catalytic reduction process involves several reaction steps that represent different physical and chemical processes [5-6]. These processes can be independent, i.e. taking place in parallel, regardless of the other processes or dependent, i.e. taking place in series, one using up the product(s) of the process concluding before it. To model such a process requires a thorough understanding of the underlying chemistry and of the chemical and mechanical engineering principles.

The role of a catalyst in the reduction process, the general catalytic reduction mechanism and elementary reaction steps in a catalytic process are discussed in the following subsections [7-10].

**SCR Chemistry:** The standard SCR follows a 1:1 stoichiometry for ammonia and NO (> 90% of  $\text{NO}_x$  of an exhaust gas is formed by NO) is maintained along with consumption of oxygen. When equimolar amounts of (50 %) NO and  $\text{NO}_2$  are present in the feed, SCR process is accelerated and is termed as “fast SCR” reaction [11]. When pure (100 %)  $\text{NO}_2$  is present in the feed, the reduction process is termed as “ $\text{NO}_2$ -SCR”. Urea is usually atomized as 32.5 % aqueous solution into the hot exhaust gas (250-450°C). The first steps are the evaporation of water from the droplets and the melting of the urea, which cannot be clearly separated [12]. Subsequently, urea is thermally decomposed (thermolized) into equimolar amounts of ammonia and isocyanic acid.

#### This Easily Hydrolyzes According to Reaction:



**Design of Catalytic Converter:** This project is requires two catalytic converters.

- Pre-Oxidation
- SCR

$\text{NO}_x$  reduction done by the combined effect of pre-oxidation and SCR-catalyst.

**Pre-Oxidation:** The pre-oxidation catalyst is developed based on conventional diesel oxidation catalyst. The selectivity for high  $\text{NO}_2$  formation at lower temperature is the main target in this design; the high  $\text{NO}_2$  formation is a compromise between the higher point loading and catalyst volume [13-15].

- The primary effect of the pre-oxidation catalyst is to increase the  $\text{NO}_2$  fraction of the exhaust this permitting the fast SCR reaction.
- The second effect is a considerable oxidation of hydrocarbon which inhibits the SCR reaction at low temperature; this will be also help increase the  $\text{NO}_x$  conversion at low temperature.

This project is taken ceramic catalyst support is coated with cerium oxide. Dip coating is used for this type of catalyst. It placed before the urea injection system and immediately after the exhaust pipe.

**Cerium Oxide:** Cerium Oxide has been used in catalytic converters in automotive applications. Since ceria can become non- stoichiometric in oxygen content (i.e. it can give up oxygen without decomposing) depending on its ambient partial pressure of oxygen, it can release or take in oxygen in the exhaust stream of an engine. In association with other catalysts, ceria can effectively reduce  $\text{NO}_x$  emissions as well as convert harmful carbon monoxide to the less harmful carbon dioxide. Ceria is particularly interesting for catalytic conversion economically. Because, it has been shown that adding comparatively inexpensive ceria can allow for substantial reductions in the amount of platinum needed for complete oxidation of  $\text{NO}_x$  and other harmful products of incomplete combustion [16-18].

**SCR:** In this project is taken ceramic catalyst support is coated with cerium. Because of durability and activity is more than pellet form. The coating composition is optimizing in addition to performance in respect of adhesion on ceramic substrate. This catalyst is fitted after that pre-oxidation catalyst and urea injection system.

The distance between the urea injection and SCR should be optimized. Catalyst accelerate the chemical reactions by lowering the energy they need to proceed they promote the chemical reaction but should not be consumed in reactions catalyst are either homogeneous or heterogeneous type.

Homogeneous catalyst are in the same phase as the reactant e.g. liquid catalyst in a system however heterogeneous catalyst are used as powder, spheres, tables, wires and in other solid form as well as in a coating.

**Zeolite:** Zeolites are one of the most well known inorganic molecular sieves. The word 'zeolite' comes from the roots *zeo* (for boil) and *lithos* (for stone) in Greek. Water molecules in the zeolite pores are readily lost when the zeolites are heated. The word was coined by Cronstedt, a Swedish mineralogist, who observed a mineral that gave off steam and appeared to boil when heated [19-20].

Zeolites are a well-defined class of naturally occurring crystalline aluminosilicate minerals. They have a three-dimensional structure arising from a framework of  $[\text{SiO}_4]^{4-}$  and  $[\text{AlO}_4]^{5-}$  coordination polyhedral linked by all their corners. The frameworks are generally very open and contain channels and cavities in which cations and molecules are located, both of which have enough freedom of movement to permit cation exchange and reversible dehydration. Water molecules are located in these channels and cavities, as are the cations that neutralize the negatively charged framework.

Many different zeolite structures exist, but the one that will be discussed in the present study is ZSM-5. ZSM-5 is a high silica zeolite with Si:Al ratio usually greater than 10.

**Cu-ZSM-5 Catalyst:** Cu-exchanged form of the ZSM-5 shows some of the highest known activities for the SCR of NO. Cu-ZSM-5 has the advantage of being able to reduce NO both with and without the addition of a reducing agent [13].

**Fe-ZSM5 Catalyst:** Byrne et al. from Engelhard Corporation developed a commercial SCR catalyst for high temperature applications. This catalyst is based on a Fe promoted zeolite with three dimensional pore structures and a high module. The catalyst was highly selective towards SCR  $\text{NO}_x$  reaction, yielding high  $\text{NO}_x$  removal efficiency over a wide temperature range from 300°C to

600°C. Feng and Hall prepared an over exchanged Fe-ZSM5 catalyst using Fe oxalate precursor salt. They found the catalyst to be highly active at 500°C and stable in the presence of 10 %  $\text{H}_2\text{O}$  and 150 ppm of  $\text{SO}_2$ . Only minimal loss in DeNOx was observed after ageing for 2500  $\text{h}^{-1}$ .

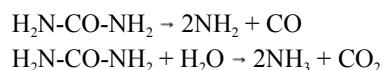
Long and Yang studied the catalytic performance of Fe-ZSM5 catalyst for SCR by  $\text{NH}_3$ . A series of Fe exchanged molecular sieves were studied as catalyst for the SCR reaction. Both Fe-ZSM5 and Fe-mordenite catalysts were highly active for the SCR reaction. Nearly 100 % NO conversion was obtained at 400-500°C at high space velocity. However, Fe-Y and Fe-MCM41 with larger pore sizes showed lower activities for this reaction. For Fe-ZSM5 catalyst, the SCR activity decreased with increasing Si/Al ratio. As the Fe exchange level increased from 58 % to 252 %, NO conversion increased at lower temperatures (e.g. 300°C), but decreased at high temperatures (e.g. 600°C). The catalyst also showed substantially lower activity for  $\text{SO}_2$  oxidation to  $\text{SO}_3$ . Other groups like Ma and Grünert and Chen and Sachtler have reported high activity for Fe-ZSM5 catalysts for  $\text{NH}_3$ -SCR. Krishna et al. have shown that a modified sublimation technique for preparing Fe-ZSM5 results in improved DeNOx activity.

**Reducing Agent:** Urea is produced in large scale worldwide (130 million tons /year) product standard and distribution is orientated to serve the major consumers such as food proceeding and fertilizer industries.

Urea is preferred among the N-containing selective reductants for Nox because of safety and non-toxicity. It is easy to transport in the vehicle in an aqueous solution, which makes it also easy to dosage as required. Aqueous urea is stored in plastic or steel tank, not requiring any special safety equipment. All these advantages make urea solution the preferred reducing agent for nitrogen oxides.

Urea is supplied in a 32.5 wt% aqueous solution (eutectic composition) that is to be injected in front of the SCR. (Also called as Adblue solution).

Urea has high solubility in water (108 g/100ml  $\text{H}_2\text{O}$  at 20°C), enabling higher concentration to be transported in a storage tank. At temperatures above 160°C urea starts to decompose according to the following reaction.



### Dimensions of Catalytic Converter



Fig. 1: Photographic View of Catalytic Converter Cover



Fig. 2: Photographic view of Filter during Zeolite Wash coating



Fig. 3: Photographic view of Filter during Ceria Wash coating

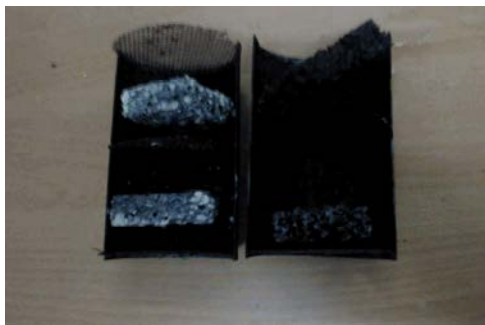


Fig. 4: Photographic view of Catalysts placed with Cover

**Engine Test Procedure:** The engine is started and allowed to warm-up for about 15 minutes. The readings on dynamometer scale (load) time taken for 10cc of fuel consumption. Emission measurement is taken from crypton analyzer smoke measurement in smoke meter has been recorded. This procedure is repeated by changing the loads from No load, 4 kg, 8 kg, 12 kg, 16 kg and 20 kg.

The same procedure is followed after fixing the SCR system and the readings are taken for different load conditions.

### Experimental Setup:



Fig. 5: SCR with Pre-Oxidation Chamber

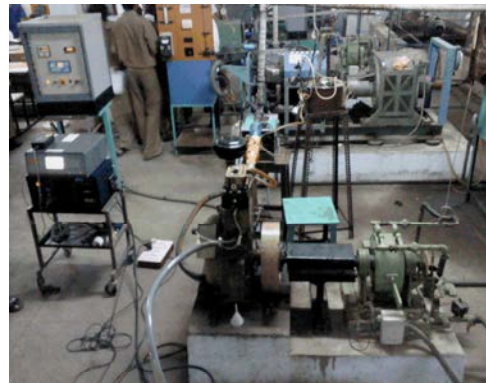


Fig. 6: Engine Setup

## RESULTS and DISCUSSION

**Effect of Engine Brake Power Variation on Various Performance and Emission Characteristics of the Engine Performance Characteristics:** From Figures 7, 8 and 9, we observe that the brake thermal efficiency (BTE) reduces slightly when we implement Selective Catalytic Reduction which increases the total fuel consumption (TFC) and specific fuel consumption (SFC).

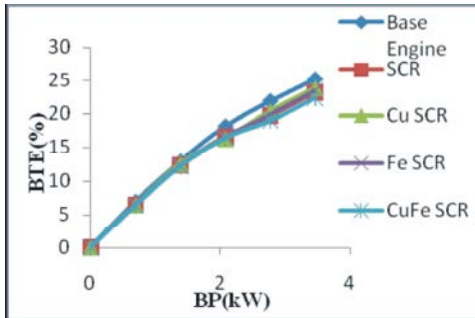


Fig. 7: Effect of Engine Brake Power on Brake Thermal Efficiency

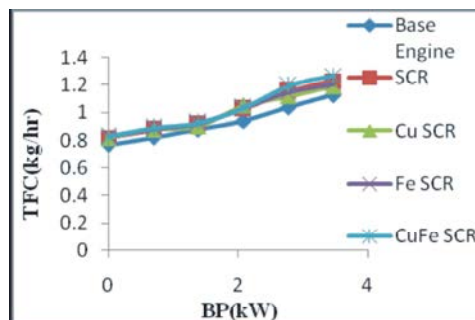


Fig. 8: Effect of Engine Brake Power on Total Fuel Consumption

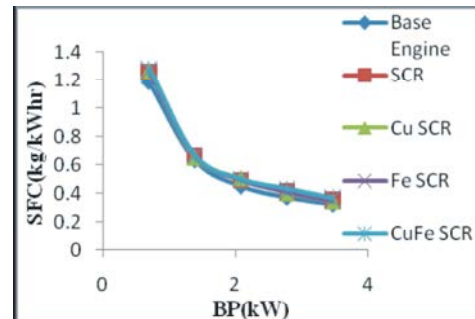


Fig. 9: Effect of Engine Brake Power on Specific Fuel Consumption

This is due to alumina ceramic filter placed in the path of the exhaust gases which increases the back pressure which in turn reduces the combustion efficiency of the engine.

But, the difference between the brake thermal efficiencies of SCR, Cu SCR, Fe SCR and CuFe SCR are negligible. This is because of the fact that during the ion exchange process, only the molecular properties of the zeolite changes. The physical structure of the zeolite and the alumina surface remains the same and thus the back pressure produced is almost same for SCR, Cu SCR, Fe SCR and CuFe SCR.

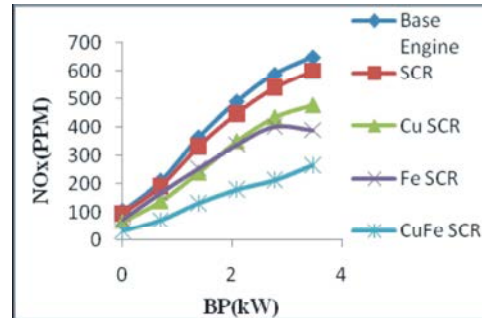


Fig. 10: Effect of Engine Brake Power on NOx Emissions

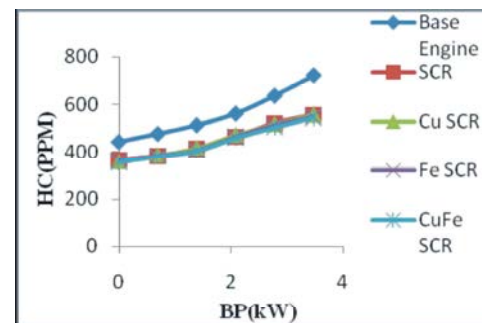


Fig. 11: Effect of Engine Brake Power on HC Emissions

**Emission Characteristics:** From figure 10, it can be noted that as the brake power increases, the peak temperature inside the cylinder increases as more fuel is consumed and thus the oxides of nitrogen in the exhaust increases.

Usage of SCR reduces NOx by 7.84% (from 650 PPM to 599 PPM) at maximum load.

Cu SCR reduces NOx by 26.76% (from 650 PPM to 476 PPM) at maximum load. It is also noted that the conversion efficiency of Cu SCR is high at low loads but reduces at high loads.

Fe SCR reduces NOx by 40.15% (from 650 PPM to 389 PPM) at maximum load. It is also noted that the conversion efficiency of Fe SCR is low at low loads but increases at high loads. This is because the conversion efficiency of Fe SCR increases with increase in exhaust gas temperature.

CuFe SCR reduces NOx by 59.23% (from 650 PPM to 265 PPM) at maximum load. This is due to the combined effect of Copper and Iron ions which increases the conversion efficiency.

From figure 11, it can be noted that as the brake power increases, the total fuel required increases but the time required for combustion of fuel decreases which increases the unburnt hydrocarbons.

Pre-Oxidation chamber used in SCR reduces HC from 723 PPM to 556 PPM at maximum load. But, the HC emissions in Cu SCR, Fe SCR and CuFe SCR are almost

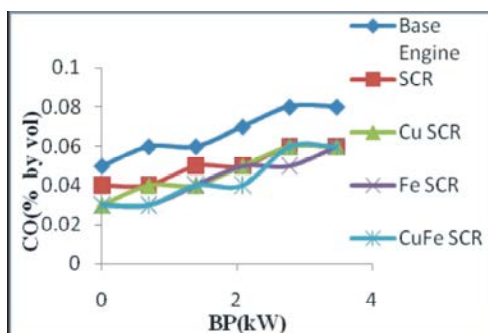
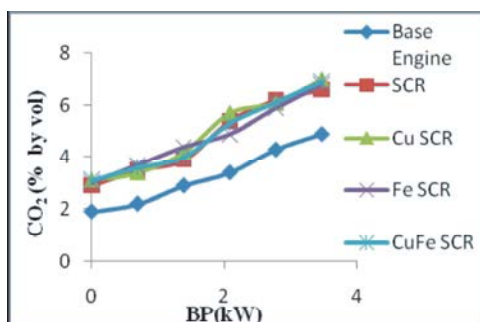


Fig. 12: Effect of Engine Brake Power on CO Emissions

Fig. 13: Effect of Engine Brake Power on CO<sub>2</sub> Emissions

same. This is because ion exchange process is carried out only for the zeolite which is placed in the oxidation which does not affect the preoxidation chamber.

From figure 12, it can be noted that as the brake power increases, the specific fuel consumption decreases which decreases the CO emissions. The CO reduces slightly in all types of SCR compared to base engine due to the pre-oxidation chamber.

From figure 13, it can be noted that As CO molecules are oxidised to CO<sub>2</sub> molecules and as the decomposition of urea results in CO<sub>2</sub>, CO<sub>2</sub> emissions increase with the use of SCR. The CO<sub>2</sub> produced by using the different SCR systems are almost same. This is because the amount of urea utilized in all the SCR systems is same.

The total amount of CO<sub>2</sub> is reduced in electronic urea injection compared to that of the ordinary SCR because the amount of urea injected can be optimised which is not possible in case of ordinary SCR.

### CONCLUSION

Due to the global environmental pollution level and their rapid increase has forced environmental agencies of various countries to enforce very stringent emission norms. The after treatment device like EGR, SNR, NCR, SCR and particulate trap are required to achieve these

emission norms. In this project the improved SCR technology ( Pre-oxidation and Urea-SCR ) is used to carry out the experimentation. The conclusions are summarized as follows.

From the Experimental Investigation processes of during Pre-oxidation with Urea-SCR setup diesel engine the following points are concluded,

- It is concluded that the conversion efficiency of electronically controlled CuFe SCR system is maximum which reduces NO<sub>x</sub> emission by 59.23%.
- The reduction in the HC percentage, when the diesel engine with Pre-oxidation Urea-CuFe SCR setup is used is nearly 24.75%.
- There is also a reduction in the CO emission of Pre-oxidized Urea-CuFe SCR setup diesel engine is used the CO emission is decreased by 25%.
- Because of the complete oxidation when the exhaust is oxidized, the CO<sub>2</sub> emission in diesel engine with pre-oxidation Urea-CuFe SCR setup is increased by 40.81%

### REFERENCES

1. Ganesan, V., 0000. Internal Combustion Engines Third Edition.
2. Gieshoff, J. and M. Pfeifer, 2001. A. Schafer-Sindlinger and P.C. Spurk Advanced Urea SCR Catalysts for Automotive Applications SAE-Paper, pp: 01-0514.
3. Ioannis Gekas, Pars Gabriellsson and Keld Johansen, 2002. Urea-SCR Catalyst System Selection for Fuel and PM Optimized Engines and a Demonstration of a Novel Urea Injection System SAE-Paper, pp: 01-0289.
4. Manfred Koebel, 2001. Martin Elsener and Giuseppe madia Recent Advances in the Development of Urea-SCR for Automotive Application SAE-Paper, pp: 01-3625.
5. Maunula, T.R., A. Lylykangas, Lievonen and M. Harkonen, 2003. NO<sub>x</sub> Reduction by Urea in the Presence of NO<sub>2</sub> on Metal Substrate SCR Catalysts for Heavy-Duty Vehicles, SAE, pp: 01-1863.
6. Schar, C.M., C.H. Onder and H.P. Geering, 2003. Control of a Urea SCR Catalytic Converter System for a Mobile Heavy Duty Diesel Engine SAE-Paper, pp: 01-0776.
7. Timothy, V. Johnson, 2001. Diesel Emission Control: in Review, SAE-Paper, pp: 01-0285.

8. James P. Warren, 2001. Diesel Aftertreatment Systems: 2004-2007, A Cost Assessment SAE-Paper, pp: 01-1948.
9. Sawata, A., Y. Murakami, Y. Tsuru and M. Tanoura, 2001. Application of  $V_2O_5$  Catalysts to Diesel NOx Emission Control SAE-Paper, pp: 01-3238.
10. Ken Nagashima, Makoto Nagata and Katsuaki Katou, 2002. Development of deNOx Catalyst Based on Ag/Al<sub>2</sub>O<sub>3</sub> Catalyst for Diesel Applications SAE-Paper, pp: 01-1724.
11. Mitsuru Konno, Takemi Chikahisa, Tadashi Murayama and Masakazu Iwamoto Catalytic Reduction of NO<sub>x</sub> in Actual Diesel Engine Exhaust SAE-Paper, pp: 920091.
12. David R. Monroe, Craig L. DiMaggio and Frederic, 0000. Matekunas Evaluation of a Cu/Zeolite catalyst to remove No<sub>x</sub> from lean exhaust SAE-Paper, pp: 930737.
13. Nunan, J.G., W.B. Williamson and H.J. Robota, 0000. Advanced TWC Technologies Using CeO<sub>2</sub>/XrO<sub>2</sub> Solid Solutions SAE-Paper, pp: 960798.
14. Wolfgang held, Axel konig and Thomas Richter Catalytic NOx reduction in net oxidizing exhausts gas SAE-Paper, pp: 900496.
15. Jim Nebergall, Eric Hagen and Justin Owen, 0000. Selective Catalytic Reduction On-Board Diagnostics: Past and Future Challenges SAE-Paper, pp: 900496.
16. Tatyana Aleksandrovna Skalozubova and Valentina Olegovna Reshetova, 2013. Leaves of Common Nettle (*Urtica dioica* L.) As a Source of Ascorbic Acid (Vitamin C), World Applied Sciences Journal, 28(2): 250-253.
17. Rassoulinejad-Mousavi, S.M., M. Jamil and M. Layeghi, 2013. Experimental Study of a Combined Three Bucket H-Rotor with Savonius Wind Turbine, World Applied Sciences Journal, 28(2): 205-211.
18. Vladimir G. Andronov, 2013. Approximation of Physical Models of Space Scanner Systems World Applied Sciences Journal, 28(4): 528-531.
19. Naseer Ahmed, 2013. Ultrasonically Assisted Turning: Effects on Surface Roughness World Applied Sciences Journal, 27(2): 201-206.
20. Tatyana Nikolayevna Vitsenets, 2014. Concept and Forming Factors of Migration Processes Middle-East Journal of Scientific Research, 19(5): 620-624.