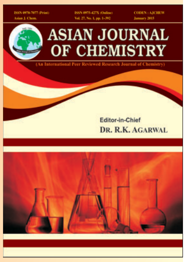
Asian Journal of Chemistry; Vol. 27, No. 6 (2015), 2149-2153

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.17822



Synthesis of Polyoxymethylene Dimethyl Ethers Catalyzed by Rare Earth Compounds

GAO-FENG SHI*, JIAN MIAO, GUO-YING WANG, JIN-MEI SU and HAI-XIAO LIU

School of Petro-chemical Engineering, Lanzhou University of Technology, Lanzhou 730000, Gansu Province, P.R. China

*Corresponding author: E-mail: gaofengshi_lzh@163.com

Received: 15 April 2014; *Accepted*: 30 June 2014; *Published online*: 17 March 2015; AJC-16982

Polyoxymethylene dimethyl ethers ($PODME_n$) have been synthesized in moderate yields by the reaction of methylal ($PODME_1$) and paraformaldehyde catalyzed by rare earth compounds. The activities of catalyst in the reaction were investigated and the results show that La^{3+}/SO_4^{2-} has a high value. The influencing factors of reaction such as catalyst amount, reaction temperature, time, pressure and mole ratio of methylal ($PODME_1$) to paraformaldehyde were also investigated. The appropriate reaction conditions *i.e.*, n(paraformaldehyde)/ n(methylal) = 1.60, catalyst amount of 1 %, 130 °C, 6 h and 0.5 MPa. Under the above conditions, methylal conversion rate and selectivity of $PODME_{2-8}$ is 81.6 and 75.5 %, respectively. In addition to, the combustion and emission characteristics of $PODME_{2-8}$ added diesel was compared with the diesel, polyoxymethylene dimethyl ethers ($PODME_{2-8}$) not only improved the combustion characteristics of diesel, but improved the low temperature fluidity.

Keywords: Rare earth compounds, Polyoxymethylene dimethyl ethers, Methylal, Paraformaldehyde.

INTRODUCTION

Polyoxymethylene dimethyl ethers ($PODME_n$) are important industrial products with the formula $CH_3O\ (CH_2O)_n\ CH_3$, where n ≥ 1. The features of $PODME_n$ are high oxygen content (42-51 %) and high cetane number, which can improve the combustibility of diesel oil, enhance the efficiency of combustion and reduce pollutants. Thus, it is believed to have wide application prospect as a diesel additive[1,2]. Especially, $PODME_{3-8}$ exhibits high oxygen content, moderate boiling points, excellent miscibility with diesel oil and average cetane number of above 76. It was reported that by adding 20 % $PODME_{3-8}$ in the diesel oil, the amounts of powders pollutants and NO_x released upon combustion can be reduced by 80-90 and 50 %, respectively[3,4]. As a result, the conversion of methanol to $PODME_n$ as an additive of diesel oil may not only extend the methanol industry chain and digest the large surplus production capacity of methanol, but also bring enormous benefits with respect to economics and environmental protection[2,5].

The preparation methods for $PODME_n$ (n ≥ 1) have rarely been reported in the literature. At early stage, $PODME_n$ was obtained from methanol, formaldehyde and polyformaldehyde or dioxacyclopentane, using sulfuric acid or hydrochloric acid as catalyst. BASF group used H_2SO_4 or CF_3SO_3H as catalyst to get $PODME_{1-10}$, with methanol, methylal, trioxymethylene and polyformaldehyde as raw materials[6-9]. With zeolites or acidic ion exchange resins as catalyst, BP produced $PODME_{3-8}$ by conversion of dimethyl ether with formaldehyde through a complicated process[10,12]. But the main drawbacks of these method are the catalyst is corrosive and the conversion and selectivity to $PODME_{3-8}$ is low, a complex procedure and a long process. Recently, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences has made progress to synthesize $PODME_{3-8}$ by using ionic liquid as catalyst in a homogeneous reaction system with methanol and trioxymethylene as feed; single-pass yield of $PODME_{3-8}$ reached 50 % with the selectivity to $PODME_{3-8}$ being 70-80 %[13,14]. However, the expensive and corrosive catalyst and the complex purification of product has limited its wide application. Therefore, a catalyst that is inexpensive, high conversion and selectivity, the development of an efficient and environmentally benign process for preparation of $PODME_n$ is still in demand. The study of $PODME_n$ has attracted major attention and many researchers are studying the techniques of preparing $PODME_n$ for industrial production[15,16].

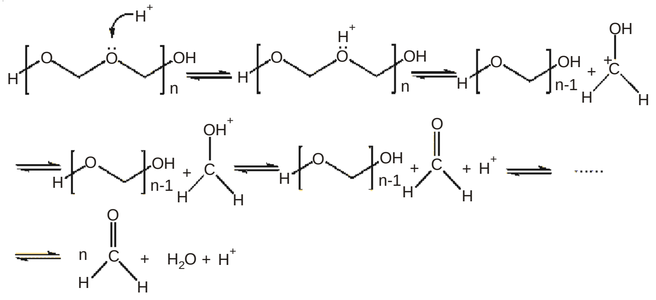
In this work, polyoxymethylene dimethyl ethers ($PODME_n$) was synthesized by the condensation of methylal and paraformaldehyde over the catalysts of several rare earth compounds. The pure components of $PODME_{1-8}$ obtained by rectification were characterized by GC-MS. The influence of the type of rare earth compounds, raw material ratio, amount of catalyst, reaction temperature on reaction conversion and selectivity were investigated.

EXPERIMENTAL

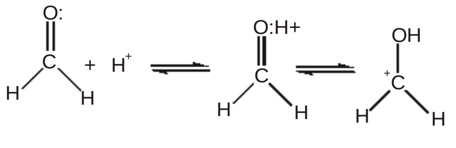
All the materials are commercially available and were used without purification. Paraformaldehyde: AR, Tianjin recovery of fine chemical industry research institute, China. Methylal: Fei Hao Trade Co., Ltd., Zhengzhou, China. Lanthanum chloride: AR, Shanghai mountain pu chemical Co., Ltd, China. Cerium trichloride: AR, Shanghai Zhongtai chemical reagent co., Ltd, China. Neodymium sulfate: AR, Shanghai Zhongtai Chemical Reagent Co., Ltd, China. Praseodymium sulfate: AR, Shanghai Zhongtai Chemical Reagent Co., Ltd, China. Sulfuric acid: AR, Beijing Chemical Plant, China. Hydrochloric acid: AR, Beijing Chemical Plant, China. Nitrogen: commercially available. GSH-0.5 L reaction kettle: Weihai Huanyu Chemical Machinery Co., Ltd, Shandong, China. TRACE DSQ quaternary gas chromatography mass spectrometry instrument, Thermo Company, US.

Synthesis and spectral characterization

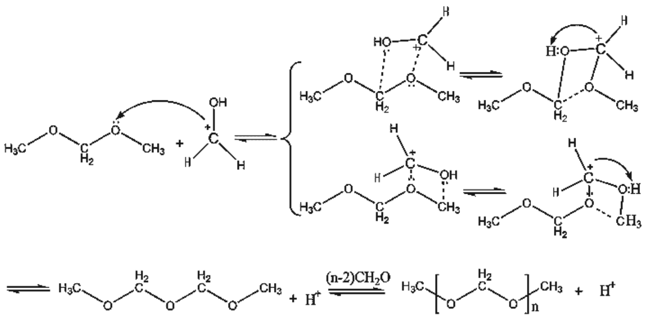
Synthesis: The synthesis of $PODME_n$ from methylal ($PODME_1$) and paraformaldehyde was performed in a 500 mL reaction kettle under the following reaction conditions: the ratio of methylal to paraformaldehyde in the feed was 1 to 3, reaction temperature considered is100 to160 °C, reaction time is 1 to 8 h and the amount of catalyst used is 5 % of the total reactant quantity. Acid catalytic depolymerization of paraformaldehyde, mechanism may see type (1):



The second part, formaldehyde and H^+ form with reactive intermediates, mechanism may see type (2):



The third part, formaldehyde reactive intermediates and methylal reaction, mechanism may see type (3):



Using GC-MS, The reactants and products were analyzed, using peak area normalization method to determine ion flow diagram of the components. GC Status: DB-5MS column elastic silica capillary (30 m × 0.25 mm × 0.25 μm); keep warming conditions: 50 °C for 5 min, followed by 20 °C/min the heating rate of up to 250 °C and keep 5 min; Gasification chamber temperature: 250 °C; carrier gas: helium, the column flow rate of 1 mL/min. Mass Status: ion source temperature: 250 °C; electron bombardment source: 70 eV; emission current: 100 μA; electron multiplier voltage: 1.5 KV; scanning range: 30-650u. Reaction product ion flow diagram of GC-MS as shown in Fig. 1:

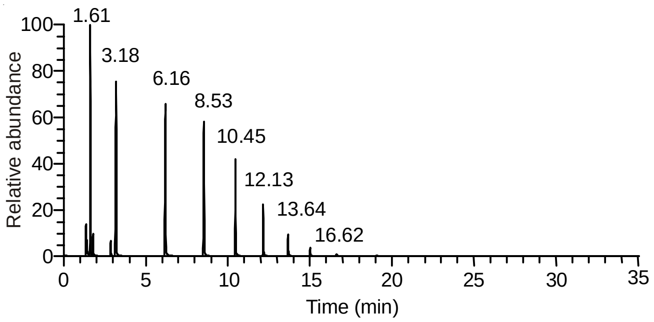


Fig. 1. GC-MS total ion chromatogram of reaction products. Reaction conditions: Wt = 1 %, 125 °C, 6 h, 0.5 MPa, n(Paraformaldehyde): n(methylal) = 1.6

As shown in Table-1, the product $PODME_{1-8}$ can be effectively separated under the above condition, the peak area of $PODME_{1-8}$ with the increased of the degree of polymerization and reduced in turns, used the ion flow diagram of peak area to quantitative components.

RESULTS AND DISCUSSION

Catalytic activity of different rare earth compounds: The catalytic activities for four kinds of rare earth compounds

TABLE-1
POLYOXYMETHYLENE DIMETHYL ETHERS ($PODME_n$) EACH COMPONENT CONTENT

Retention time	m.w.	Degree of polymerization	m.f.	Name	Content (%)
1.61	76	1	$CH_3OCH_2OCH_3$	$PODME_1$	16.70
3.18	106	2	$CH_3O(CH_2O)_2CH_3$	$PODME_2$	25.87
6.16	136	3	$CH_3O(CH_2O)_3CH_3$	$PODME_3$	20.74
8.53	166	4	$CH_3O(CH_2O)_4CH_3$	$PODME_4$	13.77
10.45	196	5	$CH_3O(CH_2O)_5CH_3$	$PODME_5$	8.14
12.13	226	6	$CH_3O(CH_2O)_6CH_3$	$PODME_6$	4.53
13.64	256	7	$CH_3O(CH_2O)_7CH_3$	$PODME_7$	2.37
16.62	286	8	$CH_3O(CH_2O)_8CH_3$	$PODME_8$	1.11

have been showed in Table-2. we can know the comparison value of catalyst activity as follows: $La^{3+}/SO_4^{2-} > Ce^{3+}/ SO_4^{2-} > Pr^{3+} / SO_4^{2-} > Nd^{3+}/SO_4^{2-}$. Therefore, a higher catalytic activity La^{3+}/SO_4^{2-} was selected, factors affecting the reaction were investigated accordingly.

Reaction factors

Mole ratio of reactants: The influences of different ratio of raw materials for production distribution has been shown in Table-3. Table-3 reveals that the ratio of paraformaldehyde to methylal ($PODME_1$) showed a great impact on the reaction. With an increase of mole ratio, the conversion rate of methylal ($PODME_1$) and the selectivity of $PODME_{2-8}$ both increased gradually. When the ratio was higher than 1.60, the conversion rate of methylal ($PODME_1$) and the selectivity of $PODME_{2-8}$ decreased and the product is creamy white colour suspension, even as a white paste. Therefore, it can be most conducive to generate $PODME_{2-8}$ when the ratio is 1.60.

Catalyst amount: Table-4 shows the influence of catalyst amount on the reaction. It was found that with the increase of catalyst amount, methylal conversion rate and selectivity of $PODME_{2-8}$ increased first and then decreased; when the amount of catalyst is greater than 1 %, methylal conversion rate and selectivity of $PODME_{2-8}$ were gradually reduced. The reason is that, as the increasing of the catalyst amount , the acidic of reaction system enhanced , which is not conducive to the presence and stability of $PODME_{2-8}$ and methylal. Considering the above conditions, La^{3+}/SO_4^{2-} catalyst amount was 1 %.

Reaction time: The influences of reaction time was also investigated. As shown in Table-5, with the extension of reaction time, the conversion rate of methylal rised; selectivity of $PODME_{2-8}$ during 6 h reached a peak 75.85 % and then declined. It can be attributed to the short reaction time, which resulte in inadequate response; when the reaction reaches equilibrium, extend the reaction time continuously, methylal and PODMEn have undergone different degrees of hydrolysis. The most appropriate choice of reaction time was 6 h.

Reaction temperature: Table-6 shows that results of the temperature on the reaction has obvious effects. When the temperature is low, methylal conversion rate is not high due to

TABLE-2
CATALYTIC ACTIVITIES OF VARIOUS RARE EARTH COMPOUNDS

	La^{3+}/SO_4^{2-}	Ce^{3+}/SO_4^{2-}	Pr^{3+}/SO_4^{2-}	Nd^{3+}/SO_4^{2-}
Conversion of PODME c/%	82.66	80.15	78.87	77.96
Selectivity to $PODME_{2\sim8}$ s/%	75.53	74.91	73.47	72.56

Reaction conditions: n(PF)/n(methylal) = 1.60, 125 °C 6 h, catalyst amount of 1 %

TABLE-3
INFLUENCES OF THE MATERIAL MOLE RATIO ON REACTION

n(PF)/n(m)	$PODME_n$ (%)							Methylal conversion rate (%)	Selectivity (%) $PODE_{2-8}$
	$PODE_1$	$PODME_2$	$PODME_3$	$PODME_4$	$PODME_5$	$PODME_6$	$PODE_{7\sim8}$		
1.00	31.63	25.44	17.55	9.97	5.35	2.12	1.55	66.37	61.98
1.20	29.74	25.79	17.99	10.51	5.37	2.85	1.74	70.26	64.25
1.40	25.66	25.16	19.03	12.18	6.36	2.88	1.88	74.36	67.49
1.60	18.65	25.35	20.65	14.00	7.91	3.91	2.65	81.35	74.47
1.80	21.65	24.65	19.39	13.20	8.09	4.44	3.25	78.35	73.02

Reaction conditions: 125 °C, 6 h, (La^{3+}/SO_4^{2-}) amount of 1 %

TABLE-4
INFLUENCE OF THE AMOUNT OF CATALYST (La^{3+}/SO_4^{2-}) ON REACTION

Catalyst (wt. %)	$PODME_n$ (%)							Methylal conversion rate (%)	Selectivity (%) $PODE_{2-8}$
	$PODE_1$	$PODME_2$	$PODME_3$	$PODME_4$	$PODME_5$	$PODME_6$	$PODE_{7\sim8}$		
0.50	18.35	25.67	20.13	13.54	8.11	4.53	3.40	81.65	75.38
1.00	16.80	25.88	20.75	13.78	8.16	4.56	3.48	83.20	76.61
1.50	17.19	25.06	19.97	13.63	7.33	3.54	2.40	82.81	71.93
2.00	19.98	24.12	18.33	12.56	6.17	2.25	1.11	80.02	64.54
3.00	22.23	24.16	16.88	11.37	5.55	1.79	0.71	77.77	60.46

Reaction conditions: n(PF)/n(m) = 1.60, 125 °C, 6h

TABLE-5
INFLUENCE OF DIFFERENT TIME ON REACTION

Time (min)	$PODME_n$ (%)							Methylal conversion rate (%)	$PODME_{2-8}$ selectivity rate (%)
	$PODME_1$	$PODME_2$	$PODME_3$	$PODME_4$	$PODME_5$	$PODME_6$	$PODME_{7\sim8}$		
60	32.34	22.25	15.42	8.31	1.66	1.18	0.12	67.66	48.94
120	27.55	24.31	16.82	10.18	3.69	2.01	0.78	72.45	57.79
240	18.36	26.26	20.97	13.67	7.57	3.88	2.81	81.64	75.16
360	18.32	26.42	21.11	13.89	7.73	3.89	2.81	81.68	75.85
480	18.55	26.19	20.87	13.71	7.66	3.88	2.82	81.45	75.13
600	19.01	25.88	19.71	13.22	7.32	3.86	2.82	80.99	72.81
720	19.11	25.75	19.66	13.03	7.31	3.85	2.82	80.89	72.42

Reaction conditions: n(PF)/n(m) = 1.60,125 °C, (La^{3+}/SO_4^{2-}) amount of 1 %

TABLE-6
INFLUENCE OF THE REACTION TEMPERATURE ON REACTION

Temp. (°C)	PODME$_n$ (%)							Methylal conversion rate (%)	PODME$_{2-8}$ selectivity rate (%)
	PODME$_1$	PODME$_2$	PODME$_3$	PODME$_4$	PODME$_5$	PODME$_6$	PODME$_{7\sim8}$		
90	45.32	12.11	10.64	5.27	1.88	-	-	54.68	29.90
100	38.96	18.54	14.42	8.94	3.16	1.09	0.01	61.04	46.16
110	29.65	23.13	18.99	11.47	5.16	2.88	1.17	70.35	62.80
120	18.53	26.11	20.87	13.79	7.52	3.85	2.73	81.47	74.87
130	18.43	26.16	20.93	13.82	7.69	3.88	2.80	81.57	75.28
140	18.57	25.98	20.87	13.81	7.44	3.72	2.81	81.43	74.63
150	19.06	25.62	19.76	13.00	6.56	3.14	2.62	80.94	70.70

Reaction conditions: n(PF)/n(m) = 1.60, 6 h, (La^{3+}/SO$_4^{2-}$) amount of 1 %

the low reactivity, as the reaction temperature rised, the reactivity also increased, conversion rate and selectivity of the reaction showed a rising trend. When the temperature reached 130 °C, the conversion rate of methylal reached a maximum of 81.57 %, PODME$_{2-8}$ reached a maximum selectivity of 75.28 %. Raising the temperature continuously, conversion rate and selectivity of reaction showed a downward trend. First reason is that the elevated temperatures may enhance the activity of the reactants and push the reaction conducted along the forward direction, but the reaction is exothermic, reverse reaction can be accelerated and the reaction product generation was inhibited when the temperature is too high; second reason is that when the temperature is too high, the amount of vaporization of methylal increased, the concentration of methylal in the liquid phase reduced relatively, similarly not conducive to the presence and stability of PODME$_n$ in the system. Taken together, the better reaction temperature is 120-130 °C.

Reaction pressure: Table-7 showed that the reaction pressure on methylal conversion rate and selectivity of PODME$_{2-8}$ is not obvious, when the pressure changed between 0 and 2.0 MPa, the conversion rate of methylal and PODME$_{2-8}$ selectivity changed little. Among those pressures, 0.5 MPa was found to be the best choice. The conversion rate reached 81.63 % and selectivity was up to74.42 %.

Combustion emission performance: The results in Table-8 indicate that technical indicators of polyoxymethylene dimethyl ethers (PODME$_{2-8}$) in line with standard 0# diesel and has a high cetane number, flash point and low solidifying point. Then PODME$_{2-8}$ were added to diesel, compared the combustion and emission characteristics with no addition. Oil products which was mixed by 15 % of PODME$_{2-8}$ and diesel are in line with the national standard 0 # diesel. Meanwhile, the solidifying point of diesel dropped from 0 to -15 °C, cetane number increased to 56.8 from 49 and closed flash point

TABLE-7
INFLUENCE OF THE DIFFERENT PRESSURE ON REACTION

Pressure (MPa)	PODME$_n$ (%)							Methylal conversion rate (%)	PODE$_{2-8}$ selectivity rate (%)
	PODE$_1$	PODME$_2$	PODME$_3$	PODME$_4$	PODME$_5$	PODME$_6$	PODE$_{7\sim8}$		
0	18.45	25.77	20.53	13.94	8.21	3.43	2.20	81.55	74.08
0.5	18.37	25.81	20.56	13.97	8.24	3.48	2.36	81.63	74.42
1.0	18.36	25.79	20.55	13.95	8.20	3.44	2.35	81.84	74.28
1.5	18.40	25.93	20.55	13.99	8.09	3.53	2.32	81.60	74.41
2.0	18.42	25.69	20.60	13.86	8.16	3.49	2.28	81.58	74.08

Reaction conditions: n(PF)/n(m) = 1.60,125 °C, 6h, (La^{3+}/SO$_4^{2-}$) amount of 1 %

TABLE-8
ADD 15 % PODME$_{2-8}$ VEHICLE DIESEL COMBUSTION EMISSIONS PERFORMANCE COMPARISON

Item	0# diesel (GB/T19147-2013)	Blended diesel (0 # diesel + 15 % PODME$_{2-8}$)	PODME$_{2-8}$
Sulfur content (mg/kg)	≤ 350	99.2	20.0
10 % Steamed carbon residue (wt %)	≤ 0.3	0.01	0.20
Ash (wt %)	≤ 0.01	0.002	0.002
Copper corrosion (50 °C, 3 h)/Level	≤ 1	1b	1b
Mechanical impurities	None	None	None
Kinematic viscosity (20 °C) (mm^2 s^{-1})	3.0-8.0	3.564	2.174
Moisture (mg kg^{-1})	Trace	Trace	Trace
Solidifying point (°C)	≤ 0	-15	-27.5
Cetane	≥ 49	56.8	83.2
Flash point (closed) (°C)	≥ 55	56	60
Distillation range:			
50 % (°C)	≤ 300	261.0	185
90 % (°C)	≤ 355	336.0	245
95 % (°C)	≤ 365	350.5	257
Density (20 °C)/(kg m^{-3})	810-860	856	1069

changed from 55 to 56 °C. Thus, polyoxymethylene dimethyl ethers ($PODME_{2-8}$) not only improved the combustion characteristics of diesel, but also improved the low temperature fluidity. Thus, it is suggested that it's a good diesel fuel additives.

Conclusion

Polyoxymethylene dimethyl ethers ($PODME_n$) were synthesized *via* the reaction between methylal ($PODME_1$) and paraformaldehyde, in which the rare earth compounds used as catalyst. Then the activity of catalyst in the reaction was investigated, we can see that La^{3+}/SO_4^{2-} has a high value. Under the optimized conditions of : methylal: paraformaldehyde = 1:1.6, catalyst dosage 1 wt. %, 130 °C, 6 h and 0.5 MPa, the conversion rate of methylal and the selectivity of $PODME_{2-8}$ were obtained as high as 81.6 and 75.5 %, respectively. Next, $PODME_{2-8}$ were added to diesel, compared the combustion and emission characteristics with no addition, the results showed that polyoxymethylene dimethyl ethers ($PODME_{2-8}$) not only improved the combustion characteristics of diesel, but also improved the low temperature fluidity. Therefore, it's a good diesel fuel additives.

REFERENCES

1. Y. H. Lei, *Acta Chim. Sin.*, **67**, 767 (2009).
2. T.H. Fleisch and R.A. Sills, *Stud. Surf. Sci. Catal.*, **147**, 31 (2004).
3. J. Burger, E. Strofer and H. Hasse, *Ind. Eng. Chem. Res.*, **51**, 12751 (2012).
4. J. Burger, M. Siegert, E. Strofer and H. Hasse, *Fuel*, **89**, 3315 (2010).
5. X. Lu, Z. Qin, M. Dong, H. Zhu, G. Wang, Y. Zhao, W. Fan and J. Wang, *Fuel*, **90**, 1335 (2011).
6. H. Schelling, E. Stroefer, R. Pinkos, A. Haunert, G.D. Tebben, H. Hasse and S. Blagov, CN 101048357A (2007).
7. BASF Aktiengesellschaft, WO 2006/045506 (2006).
8. BASF Aktiengesellkschaft, US Patent 2007/0260094 (2007).
9. S.E. Basf, EP 1893667 (2008).
10. G.P. Hagen, W. Chicago and M.J. Spangler, US Patent 005959156A.
11. BP Amoco Corporation, US Patent 6166266 (2000).
12. BP Corporation North America Inc., US Patent 6392102 (2002).
13. J. Chen, Z.H. Tang, C.G. Xia, X.Z. Zhang and Z. Li, CN 101182367A (2008).
14. Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, US 2010/0056830 (2010).
15. F. Li, W. L. Feng, H. X. Gao, H. M. Sun and W. M. Yang, CN 101768057A (2010).
16. F. Li, W. L. Feng, H. X. Gao, H. M. Sun and W. M. Yang, CN 102040491A (2011).