Synthesis of cyclic acetals by hydroformylation of oct-1-ene in the presence of polyols

*D. N. Gorbunov, S. V. Egazaryants, Yu. S. Kardasheva, A. L. Maksimov, and E. A. Karakhanov**

Department of Chemistry, M. V. Lomonosov Moscow State University,
1 Leninskie gory, 119992 Moscow, Russian Federation.
E-mail: kar@petrol.chem.msu.ru

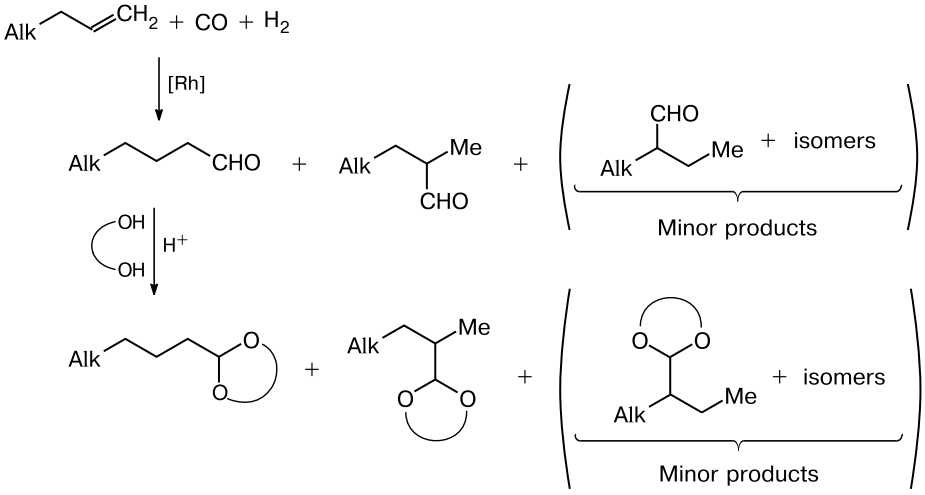
Rhodium-catalyzed hydroformylation of oct-1-ene in acid medium in the presence of polyols gives acetals of the initially formed aldehydes. The use of water-soluble trisodium salt of tris(sulfonatophenyl)phosphine as a ligand favors easy separation of the reaction products and enables repeated use of the catalytic system. A minor additive (2 wt.%) of the obtained acetal mixture improves the lubricating properties of diesel fuel by 30% and markedly reduces gum formation during combustion.

Key words: hydroformylation, homogeneous catalysis, rhodium complexes, acetalization, polyols.

Higher olefins serve as the raw materials for numerous promising syntheses of petrochemicals, for example, for hydroformylation. This reaction is suitable, in particular, for performing tandem one-pot reactions involving two or more chemical transformations within one process flow chart. According to the flow charts that do not require changes in the reaction conditions, the intermediates are not isolated and the starting reactants, materials, and solvents are fed to the reactor in one operation. The products of oxo synthesis, aldehydes, can be used for the synthesis of acetals in the presence of polyols, in particular, those of plant origin. Acetals are of interest as surfactants, components of engine fuels and low-temperature lubricating oils; they can also be used as flavoring agents and disinfectants.[1—3] Despite the broad scope of applicability of acetals based on polyhydric alcohols, methods for their synthesis have not been thoroughly elaborated, especially for acetals of higher aldehydes. Only acetalization taking place between aliphatic aldehydes and alcohols containing two or three hydroxy groups was described in detail.[4,5] Here we attempted to prepare cyclic acetals based on natural polyols and higher olefins by a hydroformylation—acetalization tandem process. Oct-1-ene was taken as the model olefin.

In the general form, tandem process is a sequence of two reactions, where the first stage is olefin hydroformylation, while the second stage is acetalization of the aldehydes formed in the first reaction (Scheme 1).

Scheme 1



Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 0943—0947, April, 2015.

Results and Discussion

Optimization of the tandem process conditions. The second stage performed under homogeneous conditions is usually catalyzed by mineral acids: *p*-toluenesulfonic acid (*p*-TsOH), H_2SO_4, HCl, or H_3PO_4. Sulfuric acid proved to be the optimal choice for our purpose, as HCl is a catalytic poison, phosphoric acid forms esters with polyols, and the use of *p*-TsOH requires the addition of more water to the system. In a series of experiments, we found that the best results are attained with 1 *M* aqueous H_2SO_4 (the yield of a mixture of acetals was 80%). It was shown that the process can also be performed without an organic solvent (Fig. 1). Thus, the system containing a rhodium catalyst of hydroformylation (soluble in the olefin) and a 1 *M* solution of sulfuric acid taken in a volume equal to the polyol volume proved to be optimal for the synthesis of acetals from olefins. Under these conditions, we carried out the reactions using pinacol, glycerol, pentaerythritol, xylitol, and sorbitol as the polyols (Table 1).

Synthesis and analysis of acetal mixtures. In the first, hydroformylation, stage, oct-1-ene is converted to four isomeric aldehydes. The subsequent reaction with the polyol affords mixtures of acetals, the number of acetal isomers increasing as the polyol structure becomes more complex. In the case of ethylene glycol, isomers **1a**—**d** are formed (see Table 1, run *1*), while pinacol gives rise to isomers **2a**,**b** (run *2*).

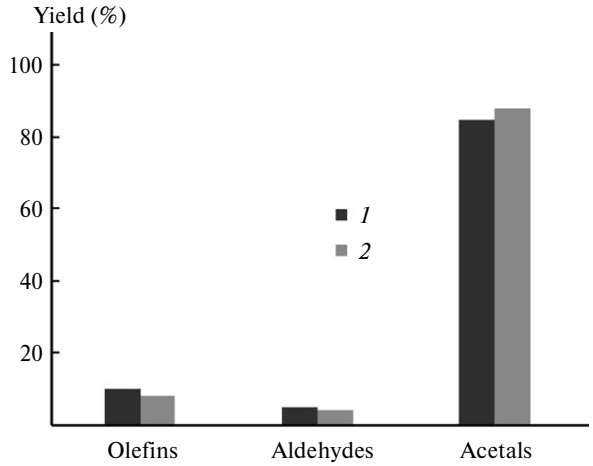
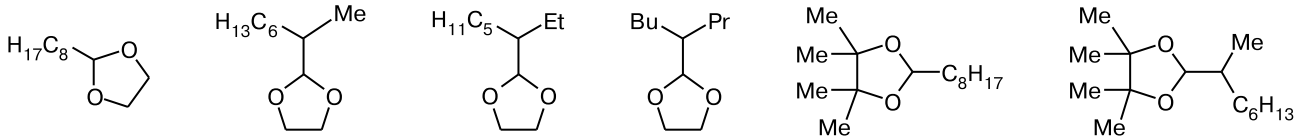


Fig. 1. Composition of the products of oct-1-ene hydroformylation in the presence of ethylene glycol in reaction mixtures containing (*1*) and not containing (*2*) toluene as the solvent. Reaction conditions: synthesis gas ($CO—H_2$ (1 : 1), 4.0 MPa), $Rh(acac)(CO)_2$, 1 *M* H_2SO_4, 70 °C, 5 h.

In order to make the interpretation of the spectra and chromatograms of the obtained mixtures easier, authentic samples of unbranched *n*-nonanal acetals were synthesized. The reaction of *n*-nonanal with ethylene glycol yielded only one product **1a**, whereas the reaction with glycerol furnished four isomers **3a**—**d** in approximately equal amounts (their spectra were reported[6]).



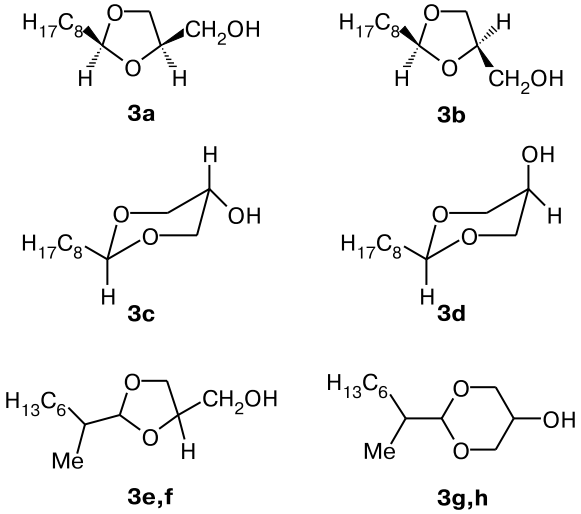
1a **1b** **1c** **1d** **2a** **2b**

Table 1. Synthesis of cyclic acetals by hydroformylation of oct-1-ene in the presence of polyols

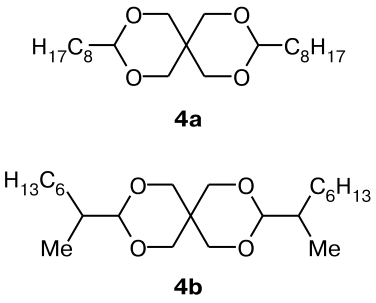
Run	Polyol	Conditions[a]	Products			Total yield[c] (%)
			«linear»	«branched»	ratio[b]	
1	Ethylene glycol	***A***	**1a**	**1b—d**	2 : 1	75
2	Ethylene glycol	***B***	**1a**,**b**	**1c**,**d**	—	92
3	Pinacol	***A***	**2a**	**2b**	2 : 1	75
4	Glycerol	***A***	**3a—d**	**3e—h**	2 : 1	70
5	Glycerol	***B***	**3a—d**	**3e—h**	—	50
6	Pentaerythritol	***A***	**4a**	**4b**	2.5 : 1	55
7	Xylitol	***A***	**5a**,**b**	**5c**,**d**	3 : 1	50
8	Xylitol	***B***	**5a**,**b**	**5c**,**d**	—	45
9	Sorbitol	***A***	**6a—c**	**6d**	3 : 1	50

[a] Conditions ***A***: synthesis gas ($CO—H_2$ (1 : 1), 4.0 MPa), $Rh(acac)(CO)_2$, 1 *M* H_2SO_4, 70 °C, 5 h. Conditions ***B***: synthesis gas ($CO—H_2$ (1 : 1), 4.0 MPa), $Rh(acac)(CO)_2$, TPPTS, 1 *M* H_2SO_4, 70 °C, 5 h.
[b] Ratio of the linear and branched products.
[c] Isolated product yield.

The hydroformylation of oct-1-ene in the presence of glycerol under optimal conditions results in the formation of not only isomers **3a**—**d** but also products **3e**—**h** with a branched alkyl substituent (Fig. 2, Table 1, run *4*).

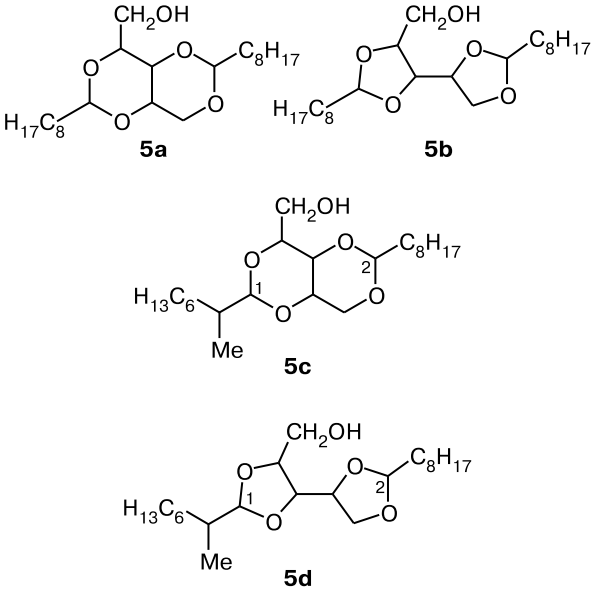


The use of pentaerythritol gives rise to two isomers **4a** and **4b** (see Table 1, run *6*).



The reaction of xylitol with acetaldehyde is known to give acetals with five- and six-membered rings.[7] In the case of *n*-nonanal, one may expect similar products **5a** and **5b**. The structure of products was confirmed by comparison with published data[8] and with the ^{13}C NMR spectra of acetals **1a** and **3a**—**d**.

Apart from products **5a**,**b**, the hydroformylation of oct-1-ene in the presence of xylitol and the acid catalyst yields isomers **5c**,**d** (50% overall yield, see Table 1, run *7*). The ^{13}C NMR spectrum of the acetal mixture (Fig. 3) has a signal at δ 107.8, characteristic of the acetal carbon atoms of compounds **5c** and **5d** and signals at δ 101.5 and 104.9 characteristic of acetals **5a** and **5b** with linear substituents.



The ^{1}H NMR spectrum of a mixture of acetals **5a**—**d** exhibits a triplet at δ 0.88 for protons of the terminal methyl groups and proton signals for the α-acetal methyl group shifted downfield by several ppm. The quantitative ratio of the products was determined from the ratio of the integrated intensities of these signals.

The acetalization of *n*-nonanal in the presence of sorbitol yields a mixture of cyclic dialkyl acetals **6a**—**c**.

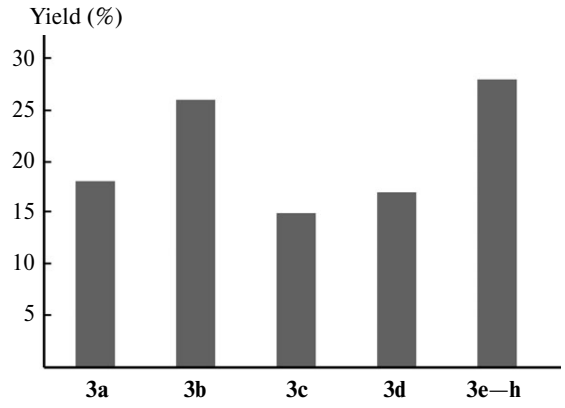


Fig. 2. Quantitative distribution of products **3a**—**h** obtained by oct-1-ene hydroformylation in the presence of glycerol. Reaction conditions: synthesis gas ($CO—H_2$ (1 : 1), 4.0 MPa), $Rh(acac)(CO)_2$, 1 *M* H_2SO_4, 70 °C, 5 h.

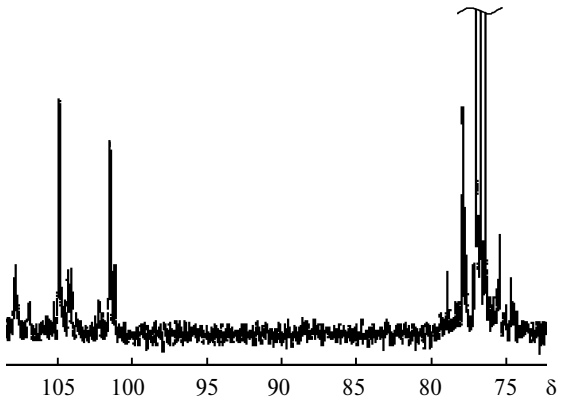
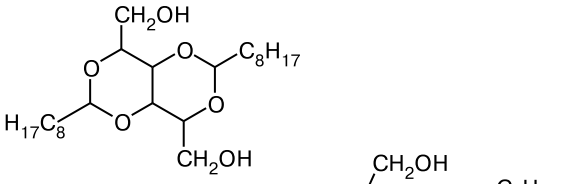
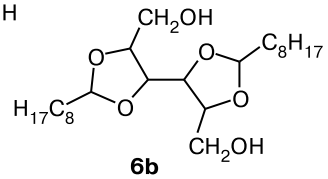


Fig. 3. ^{13}C NMR spectrum of the mixture of acetals **5a**—**d**.

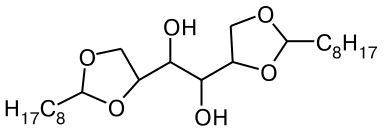
Apart from **6a—c**, tandem process affords products with branched substituent, the predominant compound among them being 2,4:3,5-bis-*O*-(2-methyloctylidene)-D,L-sorbitol (**6d**). The ^{13}C NMR spectrum of this product exhibits a characteristic signal at δ 107.8.



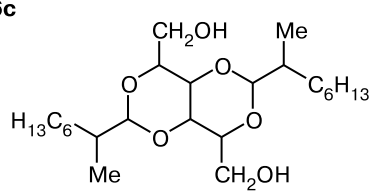
6a



6b



6c



6d

Separation of the catalyst from the reaction products. In all of the above-described cases, the obtained acetal mixture is easily separated from the unreacted polyol; however, it is impossible to separate it from the catalyst. This problem could be solved by using a water-soluble ligand, for example, trisodium salt of tris(sulfonatophenyl)phosphine (TPPTS), which can transfer the catalytic complex into the aqueous phase. In this case, the reaction would proceed in a two-phase system water—organic solvent, the reaction products (acetals) would occur in the organic layer (toluene), while the catalyst and the remaining polyol would be in the aqueous phase. In relation to the reaction of oct-1-ene with ethylene glycol (Table 1, run *2*), we demonstrated that the aqueous phase containing the dissolved catalytic complex can be reused, the catalyst activity remaining at the same level for five cycles (Table 2). The yield of acetal mixture **1a—d** is, on average, 90%. This method also proved useful for the synthesis of other acetals (see Table 1, runs *5*, *8*).

Table 2. Total yields of acetals **1a—d** in five catalytic cycles of oct-1-ene hydroformylation in the presence of ethylene glycol*

Catalytic cycle	Yield of **1a—d** (%)	Catalytic cycle	Yield of **1a—d** (%)
1	88	4	88
2	92	5	79
3	88		

* Reaction conditions: synthesis gas ($CO—H_2$ (1 : 1), 4.0 MPa), $Rh(acac)(CO)_2$, TPPTS, 1 *M* H_2SO_4, 70 °C, 5 h.

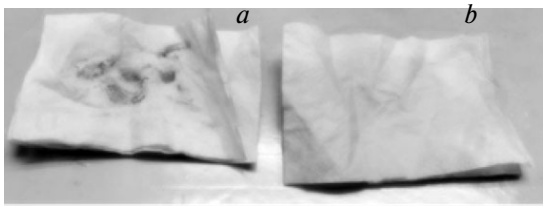


Fig. 4. Gumming products in the diesel fuel (*a*) and absence of such products after the addition of 2 wt.% xylitol acetals (*b*).

To conclude, we demonstrated good prospects of using the hydroformylation—acetalization tandem process for the preparation of cyclic acetals. The obtained mixture of xylitol acetals was tested as a possible diesel fuel additive according to GOST 9490-75 "Liquid Lubricating and Plastic Materials. Method of Testing for Lubricating Properties on a Four-Ball Machine". Using this method, it was shown that the addition of 2 wt.% xylitol acetal mixture to the diesel fuel reduces the relative friction by 30% and markedly reduces the gum formation (Fig. 4).

Experimental

Commercial oct-1-ene, *n*-nonanal, ethylene glycol, glycerol, pinacol, sorbitol, xylitol, and pentaerythritol (Aldrich) were used. The trisodium salt of tris(sulfonatophenyl)phosphine[9] and $Rh(acac)(CO)_2$[10] were prepared as described. ^1H and ^{13}C NMR spectra were recorded on a Varian XL-400 instrument operating at 400 MHz. GC analysis of the mixtures obtained upon the reaction of ethylene glycol with *n*-nonanal and oct-1-ene was carried out on a Hewlett-Packard chromatograph with a flame ionization detector and a 30 m capillary column containing the SE-30 phase, with temperature programming from 60 to 230 °C, using helium as the carrier gas. *n*-Nonane served as the internal standard.

Preparation of cyclic acetals under hydroformylation conditions. The reaction was conducted in a 50 mL steel autoclave equipped with a magnetic stirrer and a temperature control facility at temperatures of up to 110 °C. The autoclave was charged with $Rh(acac)(CO)_2$ (3 mg, 0.01 mmol), oct-1-ene (0.6 mL, 3.8 mmol), polyol (9 mmol), and 1*M* H_2SO_4 (0.5 mL). The autoclave was filled with synthesis gas ($CO : H_2 = 1 : 1$) up to a pressure of 4.0 MPa and heated for 5 h at 70 °C with continuous stirring. The products were analyzed by ^1H and ^{13}C NMR spectroscopy.

Preparation of cyclic acetals under hydroformylation conditions in the presence of TPPTS. The reaction was conducted in a 50 mL steel autoclave equipped with a magnetic stirrer and a temperature control facility at temperatures of up to 110 °C. The autoclave was charged with $Rh(acac)(CO)_2$ (3 mg, 0.01 mmol), TPPTS (34.8 mg, 6 mmol), oct-1-ene (0.6 mL, 3.8 mmol), poly-

ol (10 mmol), 1*M* H_2SO_4 (0.6 mL), and toluene (1 mL). The autoclave was filled with synthesis gas ($CO : H_2 = 1 : 1$) up to a pressure of 4.0 MPa, heated for 5 h at 70 °C with continuous stirring, and cooled to room temperature. The products were analyzed by GC and ^1H and ^{13}C NMR spectroscopy. For GC analysis of the products formed from oct-1-ene and ethylene glycol, *n*-nonane (internal standard, 0.6 mL, 3.8 mmol) was added to the cooled reaction mixture.

2,4:3,5-Di-*O*-octylidene-D-xylitol (5a) and 2,3:4,5-di-*O*-octylidene-D-xylitol (5b) (mixture). ^1H NMR ($CDCl_3$), δ: 0.88 (t, 12H, $C\underline{H}_3$), 1.15—1.75 (m, 40 H, $CH_3(C\underline{H}_2)_5CH_2$); 1.53—1.77 (m, 8 H, $CH_3(CH_2)_5C\underline{H}_2$); 3.30—4.30 (m, $C\underline{H}_2OH$, C(2)H, C(3)H, C(4)H, $C(5)H_2$); 4.3—5.0 (m, 2 H, $C\underline{H}C_8H_{17}$). ^{13}C NMR ($CDCl_3$), δ: 13.7 ($CH_2\underline{C}H_3$), 22.2 ($\underline{C}H_2CH_3$); 24.2 ($\underline{C}H_2(CH_2)_5CH_3$); 28.8 ($\underline{C}H_2(CH_2)_2CH_3$); 29.1 ($\underline{C}H_2(CH_2)_3CH_3$); 31.4 ($\underline{C}H_2(CH_2)_4CH_3$); 33.4 ($\underline{C}H_2(CH_2)_6CH_3$); 61.1 (C(1) (**5a**)), 62.1 (C(1) (**5b**)), 65.4—69.5 (C(2), C(3), C(4), C(5) (**5a**)); 75.4—77.9 (C(2), C(3), C(4), C(5) (**5b**)); 101.4 (C(6), C(7) (**5a**)); 104.9 (C(6), C(7) (**5b**)).

Alternative synthesis of cyclic acetals of *n*-nonanal. Nonanal (0.5 mL, 3.0 mmol), polyol (9.0 mmol), and 1 *M* H_2SO_4 (0.5 mL) were loaded into a reactor kept in a thermostat and equipped with a magnetic stirrer and reflux condenser. The mixture was stirred for 5 h at 70 °C. The product was extracted into chloroform (2×5 mL), washed with aqueous solution of K_2CO_3 and water to neutral pH, and dried with calcined calcium chloride. The solvent was removed on a rotary evaporator.

This work was financially supported by the Ministry of Education and Science of the Russian Federation (the Federal Target Program "Research and Development in the Priority Areas of Development of the Science and Technology Complex of Russia for 2014—2020", event 1.3, Funding Agreement No. 14.607.21.0083).

References

1. A. Behr, J. Eilting, K. Irawadi, J. Leschinskia, F. Lindner, *Green Chem.,* 2008, **10**, 13.
2. P. Sari, M. Razzak, I. Tucker, *Pharm. Dev. Technol.,* 2004, **9**, 97.
3. M. Climent, A. Velty, A. Corma, *Green Chem.*, 2002, **4**, 565.
4. P. Silva, V. Gonçalves, C. Mota, *Biores. Technol.*, 2010, **101**, 6225.
5. K. Shimizu, E. Hayashi, T. Hatamachi, T. Kodama, T. Higuchi, A. Satsuma, Y. Kitayama, *J. Catal.,* 2005, **231**, 131.
6. A. Piasecki, B. Burczyk, A. Sokolowski, U. Kotlewska, *Synth. Commun.*, 2006, **26**, 4145.
7. R. Hann, T. Ness, *J. Am. Chem. Soc.,* 1944, **66**, 665.
8. G. Gamalevich, B. Morozov, A. Vlasyuk, E. Serebryakov, *Tetrahedron*, 1999, **55**, 3665.
9. W. Herrmann, C. Kohlpaintner, B. Hanson, X. Kang, in *Inorganic Syntheses*, Vol. **32**, John Wiley and Sons, Hoboken, 1998, p. 8.
10. Yu. Varshavskii, T. Cherkasova, *Neftekhimiya* [*Petrochemistry*], 1967, **1**, 1709 (*in Russian*).

Received February 16, 2015
in revised form March 6, 2015