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Improvement of Sulphur Resistance of a Nickel-modified Catalytic Filter for Tar Removal from Biomass Gasification Gas

Keywords: tar, nickel, calcium oxide, biomass gasification

Introduction

Biomass is a renewable and potential energy on a world-wide scale. The potential offered by biomass for solving some of the world's energy problems has been widely recognised, since it is implying a possibility to decrease the use of fossil fuels. The energy in biomass may be realised either by direct use as in combustion, or by upgrading into a more valuable and usable fuel such as fuel gas, fuel oil, transport fuel or higher value products for the chemical industry (Bridgwater, 1994). Of the available alternatives for producing energy from biomass, gasification is an interesting and promising way because it is very efficient for energy production on a large scale (up to 150 MW$_e$) through the integration gasification combined-cycle (IGCC) process (Simell, 1997). Within the gasifier, the biomass is gasified at 700~1000 °C and converted to gases including hydrogen, carbon monoxide, carbon dioxide, nitrogen (if air is used), methane and small amount of light hydrocarbons. The product gas also contains several harmful impurities such as ammonia, sulphur compounds (mainly H_2S), ash particles, volatile alkali metals and tar, which is a complex mixture of aromatic compounds ranging from light compounds like benzene to heavy polyaromatic hydrocarbons. The concentration of impurities ranges from 5 to 30 g/Nm^3 for particles (Bridgwater, 1995) and 0.5 to 30 g/Nm^3 for alkali metals (Mojtahedi et al. 1989). The tar content in biomass gasification gas varies from 5 to 75 g/Nm^3, depending on the type of gasifier and the characteristics of the feedstock (Coll et al., 2001). The tars always present in gasification gas as a side product and can easily plug the following downstream process equipment. To avoid fouling, plugging, corrosion or abrasion of the down stream equipment, some impurities have to be removed from the gasification gas before feeding to the downstream process. The best way to clean the gasification gas at high temperature is using a catalyst to decompose tar and ceramic candle filter to remove ash particles and volatile metals. If the catalyst for tar decomposition is placed on the pore walls of the candle filter through optimised deposition techniques, a combined process for simultaneous removal of solid particles and tar from biomass gasification can be achieved. This concept can simplify the entire gas cleaning process with a

potential reduction in investment cost, which is really important to make biomass gasification as a viable alternative. Furthermore, the internal mass transfer resistance as in a conventional packed or fluidised bed can be eliminated when the gas flows through the catalytically active pores.

It is well known that supported nickel catalysts are used extensively for high-temperature steam reforming of hydrocarbons. It has been demonstrated that the nickel-based catalysts are very efficient in decomposing both tars and ammonia in biomass gasification gas at 900 °C (Baker et al., 1987; Bridgwater, 1994; Aznar et al., 1993; Simell et al., 1996; Arauzo et al., 1997; Bangala et al, 1997 and 1998; Corella et al., 1999). In our previous work, a complete conversion of benzene (or naphthalene) as tar model compound was given in a sulphur-free and dust-free simulated biomass gasification gas at 900 °C over nickel-modified catalytic filters prepared by urea method (Draelants et al. 2000a; Zhao et al. 2000a). However, the real biomass gasification gas normally contains 20-200 ppm H_2S. Unfortunately, the nickel catalysts are sensitive to sulphur poisoning (Bartholomew et al., 1982; Koningen et al., 1988; Hepola et al. 1997a and 1997b). The catalytic activity of the nickel-based catalyst is decreased in the presence of H_2S due to sulphur adsorption on the nickel surface. Resistance to sulphur poisoning has been investigated over nickel-alumina catalysts with promoters such as Mo, W, Li, K, Mg, Ca and La, and it was found that promoters such as Li, K, Ca and Mg can enhance the resistance to sulphur poisoning of nickel catalysts (Chen et al., 1988). Therefore, calcium oxide is selected as a promoter to enhance the sulphur resistance in this work.

Objectives

This work focuses on the development of catalytic candle filters for the simultaneous removal of tars and particles from the biomass gasification gas at high temperature. An improvement of sulphur resistance of the nickel-activated catalytic filter was developed by the addition of CaO. The influences of preparation procedure of catalytic filter, the ratio of Ni/CaO and the loading of Ni and CaO on the performance of the catalytic filter were investigated.

Approach
Preparation of Catalytic Filter

A small α-Al_2O_3-based filter disc with diameter of 3 cm and thickness of 1 cm (supplied by Schumacher, Germany) was used in the lab scale, which is representative on a small scale for the real candle filter support body. These filter discs were catalytically modified with nickel or nickel-calcium using a precipitation-deposition method with urea. A series of catalytic filter discs with different Ni/CaO weight ratios and with different loading of Ni/CaO were prepared. A detailed description about the preparation procedure can be found in our previous publications (Draelants et al. 2000a; Zhao et al., 2000b).

The two-dimensional distribution of nickel and calcium in the modified filter disc were examined with SEM/EDX (energy dispersive X-ray) on a polished radial cross section of the disc. The analysis was performed on a JSM 6400 (JEOL) equipped with a NORAN X-ray analysis system. The K_α line of nickel and calcium was used as the X-ray analysis line.

Test of Catalytic Performance

The catalytic filter disc was fixed in the middle of a reactor tube (internal diameter 3 cm and length 50 cm), which was made of dense α-Al_2O_3. The catalytic performance was tested in a

laboratory reaction setup, which has been described in detail in a previous publication (Zhao et al., 2000a).

A simulated biomass gasification gas was used to test the tar removal over the different catalytic filter discs. The gas composition was 50 vol % N_2, 10 vol% H_2, 12 vol % CO, 11 vol% CO_2, 12 vol % H_2O, 5 vol % CH_4 and 0-100 ppm H_2S, which is a typical composition of the product gas from a biomass fluidised bed gasifier operated with air. Benzene was chosen as tar model compound with a concentration of 15 g/Nm^3 (4300 ppmv). The reaction tests were performed under two typical filtration gas velocity of 2.5 or 4 cm/s. All experimental points were monitored for at least 60 min after the reaction reached an apparent steady state at the selected operation condition.

Project Description

This project focuses on improving the cleaning systems in the gasification process, which is one of the most crucial steps in the successful implementation of biomass and waste gasification for powder production. This project was financed by the EU 5th Framework Programme (Contract No. ENK5-2000-00305) and IUAP IV-programme of the Belgian Federal Government (Supramolecular Chemistry and Supramolecular Catalysis).

Results

Preparation of Catalytic Filter Discs

In order to enhance the resistance of the nickel catalyst against sulphur poisoning, CaO as a promoter was added to the catalyst formulation. Mok et al. (Mok et al., 1983) applied the urea method to incorporate a three-component system of nickel-aluminum-lanthanum into ceramic rings and their catalyst has been found a commercial application in steam reforming of naphtha. Therefore, it seemed achievable to prepare a nickel-calcium catalyst by urea method. Fig. 1 shows the X-ray mappings of nickel and calcium of a radial cross-section of the nickel-calcium modified disc with 1 wt% Ni and 0.5 wt% CaO by coprecipitation with urea method. The white dots represent the EDX-mapping for the element nickel (Fig. 1a) or the element calcium (Fig. 1b), the black background is both from the pores and the α-Al_2O_3 particles of the filter disc. As seen in Fig. 1, both nickel and calcium display a fairly uniform spatial distribution on the cross-section. These are positive factors for the catalytic application.

In order to investigate the form in which the nickel and calcium precursors were deposited, further bulk precipitation experiments were performed using the impregnation solution without a disc (Draelants et al. 2000a). The results implied that it is unlikely that the calcium precursor will co-precipitate with the nickel precursor during the urea decomposition reaction. Instead, calcium will mainly precipitate during the drying stage, probably as calcium nitrate, together with the remaining nickel ions. Nevertheless, the macroscopic distribution of calcium in the filter disc seems satisfactory (Fig. 1b). Further study of the coprecipitation of the Ni(II) and Ca(II) system needs to be done.

Influence of Preparation Procedure

Nickel and calcium oxide can be precipitated on the alumina support through co-precipitation or sequential precipitation. To decide which option gives the best catalytic performance, a catalytic disc is prepared by each method containing the same catalyst amount and composition: 1 wt% Ni/0.5 wt% CaO (by co-precipitation) and 0.5 wt% CaO + 1 wt% Ni (by sequential precipitation, first the CaO deposition was performed). For co-precipitation the

impregnation solution contains urea with the Ni-salt and the Ca-salt. From our previous work (Draelants et al. 2000b), the precipitation order is known in that case. First, the majority of the nickel precursor (about 75%) will precipitate during the urea decomposition reaction, while all of Ca-ions remain in the solution. Afterwards, the disc is dried and the calcium precursor will then precipitate at that stage, together with the remaining Ni-species. Consequently, although the nickel and calcium salt are mixed in the impregnation solution, the nickel and calcium catalyst precursor will not always precipitate simultaneously. So, it is not a strict co-precipitation as such, but still there is some degree of mixing and interaction between the Ni and Ca phase occurring during the drying step where both precursors precipitate. For sequential precipitation the impregnation solution contains either urea + Ni-salt or urea + Ca-salt, depending on which component needs to be deposited. For instance the first impregnation cycle is for the deposition of calcium phase and a successive impregnation cycle is for the deposition of nickel phase. Basically, what is obtained then is just one phase on top of the other, with limited mixing and interaction between the two catalyst components as a consequence. In addition, the sequential impregnation is more elaborate for the operation since at least two impregnation and reaction cycles have to be performed.

The results of the deactivation tests with benzene at 900 °C are shown for each disc in Fig. 2. It was found that the co-precipitation method was to be preferred since benzene conversions were systematically 5 to 10 % higher over the disc prepared by co-precipitation than those of the filter disc prepared by sequential precipitation at each gas velocity. A maximum benzene conversion of 93.5 % at 900 °C, 50 ppm H_2S and 2.5 cm/s gas velocity was obtained over the filter disc prepared by coprecipitation. This is possibly due to a better mixing/interaction between the nickel and calcium species in the case of co-precipitation. So it indicates that the better mixing/interaction between nickel and calcium oxide is beneficial to enhance the sulphur resistance. An improvement of the interaction should be improved to further enhance the catalyst performance.

Influence of the Ni/CaO Ratio

Three co-precipitated discs were tested, containing the same Ni-loading (1 wt%) but a different CaO loading (0.1 wt%, 0.5 wt% or 1 wt% CaO), giving a Ni/CaO weight ratio of respectively 10, 2 or 1. As a reference, the deactivation test over the pure nickel activated catalytic filter disc was examined under the same operational condition. Fig. 3 shows an overview of the benzene conversion in the gasification gas containing three levels of H_2S (0, 50 and 100 ppm) at 900 °C over these catalytic filter discs. In our previous work, it was found that both benzene and naphthalene could be completely converted in the H_2S-free and dust-free gasification gas at 800-900 °C over a filter disc with a nickel loading of only 1 wt%. However, an addition of a small amount of H_2S leads to a serious deactivation over it. At 900 °C and 100 ppm H_2S, the benzene conversion is only 28% at 4 cm/s over it. From Fig. 3, it is clear that the addition of CaO significantly improved the sulphur resistance. For example, the benzene conversion at 900 °C over the catalytic filter disc with 1 wt% Ni and 0.1 wt% CaO is 48% at 4 cm/s and 100 ppm H_2S, which is 20% higher than that of the filter disc containing the pure nickel catalyst with the same loading. Increasing the CaO loading till 0.5 wt% further improves performance. The benzene conversion was shown as 67% at 4 cm/s and 100 ppm H_2S. However, when the CaO loading is increased till 1 wt%, performance decreases significantly and becomes even lower compared with using only 0.1 wt% CaO (a ten times lower CaO amount). Comparing these catalysts, the performance of the catalyst with 1 wt% Ni and 0.5 wt% CaO is the best. Consequently, the optimum Ni/CaO weight ratio seems to be around 2.

These results indicate that the CaO phase is necessary to enhance the sulphur resistance of nickel-based catalyst, but if too much CaO is added, the catalytic performance decreases again. The reason for this decrease in performance is related to the co-precipitation method used to deposit the Ni/CaO catalyst in the pores of the filter disc. Our previous work showed that during the urea deposition the nickel and calcium precursors do not really co-precipitate from an impregnation solution containing both metal ions with urea. Part of the first deposited nickel is always covered by a lot of deposited calcium-rich phase, which reduces the potential catalytic surface. On the other hand, the interaction between Ni and CaO is also formed due to the mixing of Ni and CaO, which is helpful to enhance the resistance of sulphur. With the increasing of CaO loading, the mixing phase increases, which causes higher resistance to sulphur. However, the loss in the nickel surface by CaO coverage will be more pronounced with the increase of CaO loading, which starts to dominate the performance of catalyst when the CaO loading is enough high. So a lower activity was observed in that case.

Influence of Nickel Loading

From previous work (Draelants, 2001b) it occurred that increasing the nickel loading from 1 wt% to for instance 1.3 wt% (without CaO) was another way to improve the benzene removal performance of the filter discs in presence of H_2S. Therefore, the usual nickel loading on a disc (1 wt%) was increased to about 2 wt% Ni and 3 wt% Ni. And then the addition of CaO was combined with the loading of nickel, where the Ni/CaO weight ration was kept fixed at 2/1.

The results of the deactivation test with benzene at 900°C are displayed for the two discs with higher nickel loading in Fig. 4, together with the results of the previously tested 1 wt% Ni and the 1 wt% Ni + 0.5 wt% CaO filter disc from Fig. 3. It appeared that increasing the nickel loading caused a slight improvement of the sulphur resistance of the catalytic filter discs. The benzene conversions in the presence of H_2S at 4 cm/s using the 2 wt% Ni + 1 wt% CaO filter disc were only a few percents higher compared with the results obtained with a filter disc containing only half of this catalyst amount (1 wt% Ni + 0.5 wt% CaO). When increasing the nickel loading further to 3 wt%, the benzene conversions were improved only several percents compared with the results over the filter disc with 2 wt% Ni + 1 wt% CaO.

It is clear from these tests that increasing the nickel loading is not worthwhile to improve the catalytic performance of filter disc at the moment. Apparently, it does not increase the available catalytic surface, which is related to the very low surface area available for catalyst deposition in the bulk of the blank filter discs (about 0.3 m^2/g). Currently, we are working on techniques to deposit a secondary highly dispersed alumina support in the blank filter discs to increase their available surface area for catalyst deposition. This could be a way to enhance the dispersion of the Ni/CaO catalyst and hence the activity of the catalytic filter discs.

Application

The catalytic filter as a multifunctional reactor will be applied in the cleaning of the biomass gasification gas by simultaneous removal tar and particles in a single unit, which makes biomass gasification much more attractive for local energy generation to a large number of users. Tests and long-term stability will be performed with the real biomass gasification gas. The preparation procedure of a catalytic candle filter will be developed to realize the application of catalytic filter in pilot-scale.

Future Activities

To improve the sulphur resistance of the nickel-activated filter disc, a modification of highly dispersed alumina into the disc is being developed to increase the potential surface for catalyst deposition. In addition, several other additives such as MgO, K_2O and La_2O_3 will be added into the catalyst formulation to improve the sulphur resistance.

Conclusions

The filter discs were activated with a Ni/CaO catalyst through the urea method. It was found that the Ni/CaO catalyst preferably should be deposited inside the filter pores through co-precipitation. In addition, the Ni/CaO weight ratio should be around 2 and depositing more than 1 wt% Ni does not seem to give enough extra activity at the moment. From this work it can be concluded that a first draft for the optimal catalyst formulation is a co-precipitated 1 wt% Ni + 0.5 wt% CaO catalyst. At 900 °C, this catalyst formulation showed a benzene conversion of 93 % (50 ppm H_2S) and 78% (100 ppm H_2S) at a realistic filtration gas velocity such as 2.5 cm/s. This is encouraging towards future tests using real gas and tars on a slipstream of a biomass gasifier.

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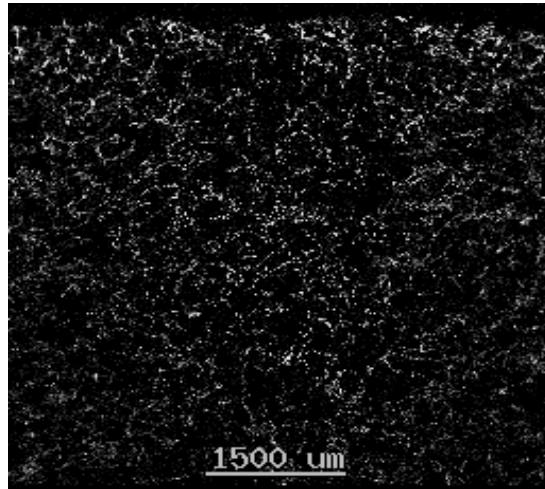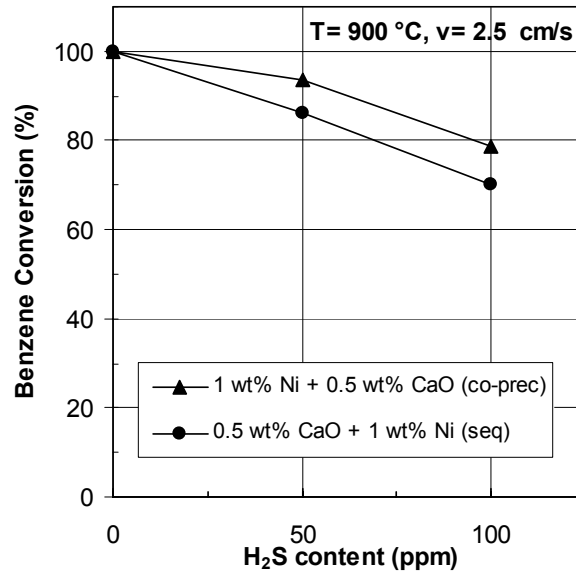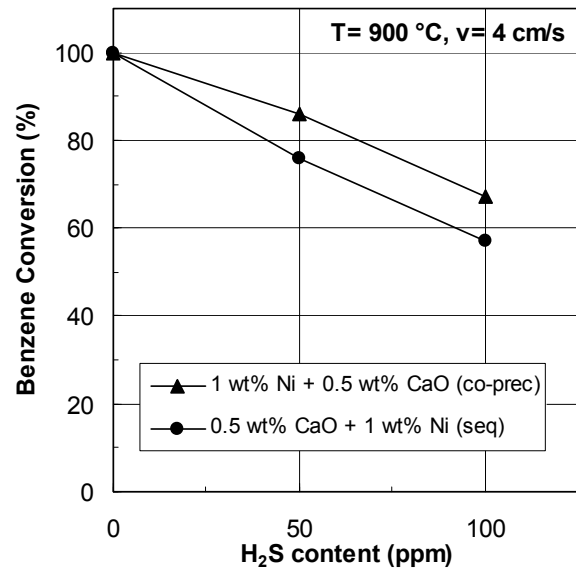
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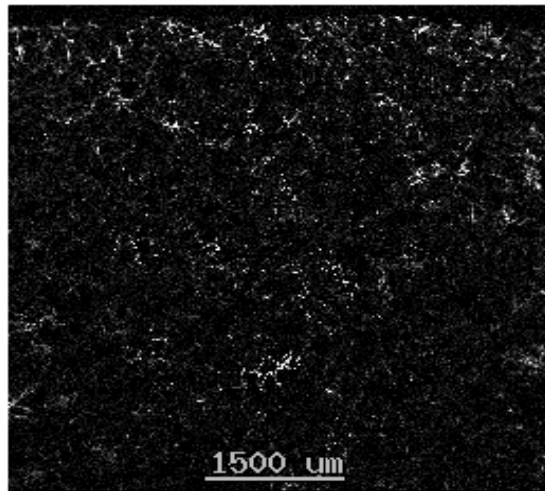
(b)

Fig. 1. SEM/EDX mapping for the element nickel on a radial cross-section of a nickel/calcium-modified filter disc (1 wt% Ni + 0.5 wt% CaO): nickel mapping (a) and calcium mapping (b).
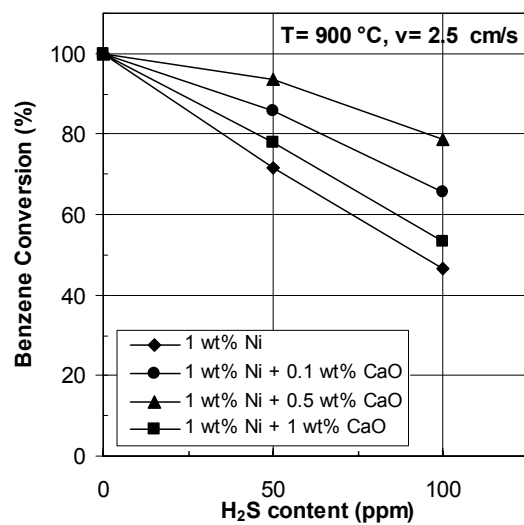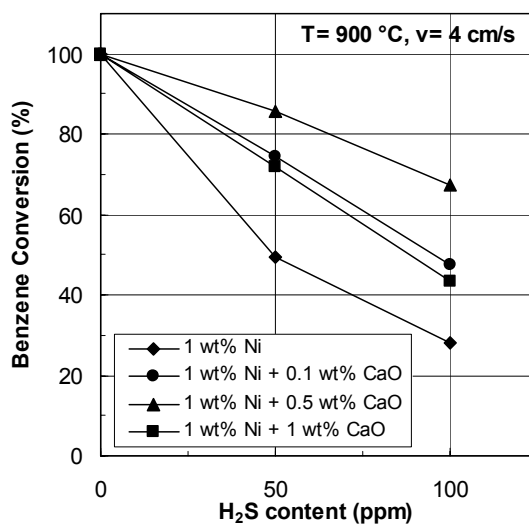
(a)

(b)

Fig. 2. Benzene conversion at 900 °C versus H_2S content of the synthetic gasification gas for a co-precipitated and sequential precipitated filter disc containing the same amount of catalyst at a gas velocity of 2.5 cm/s (a) and 4 cm/s (b).
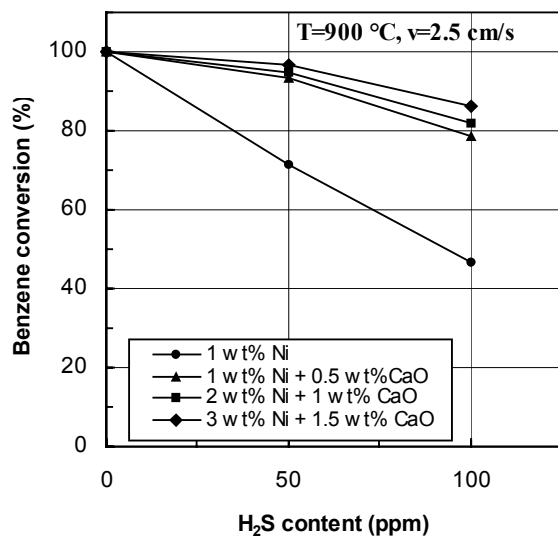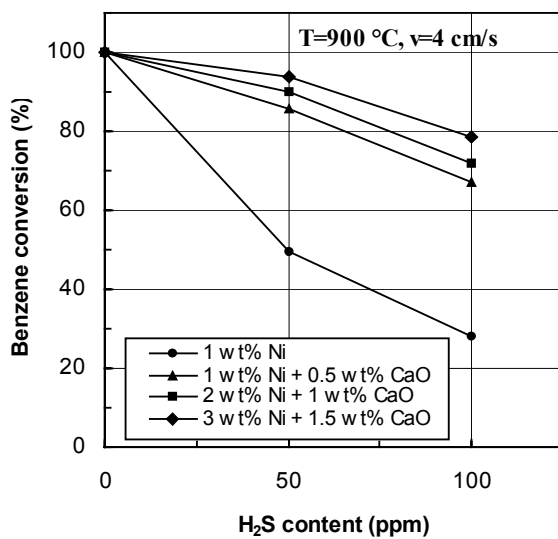
(a)

(b)

Fig. 3. Benzene conversion at 900 °C versus H_2S content of the synthetic gasification gas over the co-precipitated catalytic filter discs with different Ni/CaO weight ratio and a fixed nickel-loading (1 wt%) at a gas velocity of 2.5 cm/s (a) and 4 cm/s (b).

(a)

(b)

Fig. 4. Benzene conversion at 900 °C versus H_2S content of the simulated gasification gas over the co-precipitated Ni/CaO catalytic filter discs with different Ni/CaO loadings and a fixed Ni/CaO weight ratio (Ni/CaO wt%/wt%=2) at a gas velocity of 2.5 cm/s (a) and 4 cm/s (b).