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# Perspective usage estimation of Volga region combustible shale as a power generating fuel alternative

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**Abstract.** A comprehensive study of combustible shale, common within Tatarstan and Ulyanovsk region, is carried out. The rocks physicochemical parameters are found to meet the power generating fuels requirements. The predictive estimate of ash products properties of combustible shale burning is held.
Minding furnace process technology it is necessary to know mineral and organic components behavior when combustible shale is burnt. Since the first will determine slagging properties of energy raw materials, the second – its calorific value. In consideration of this the main research methods were X-ray, thermal and X-ray fluorescence analyses.
Summing up the obtained results, we can draw to the following conclusions:
1. The combustible shale in Tatarstan and the Ulyanovsk region has predominantly low calorific value ($Q_b^d$ = 5-9 MJ/kg). In order to enhance its efficiency and to reduce cost it is possible to conduct rocks burning together with some other organic or organic mineral power generating fuels.
2. High ash content ($A^d$ = 60-80%) that causes a high external ballast content in shale implies the appropriateness of using this fuel resource next to its exploitation site. The acceptable distance to a consumer will reduce unproductive transportation charges for large ash and moisture masses.
3. The performed fuel ash components characteristics, as well as the yield and volatiles composition allow us to specify the basic parameters for boiler units, designed for the Volga combustible shale burning.
4. The noncombustible residual components composition shows that shale ash can be used in manufacture of materials of construction.

## 1. Introduction

Coal has always been one of the major power resources for thermal power complexes. Despite gasification attempts solid fuels still have an enormous demand in the industry. However, the changed country's economic doctrine requires new approaches to supply regional thermal power stations and heating plants with fuel resources that use local raw materials [1].

In Tatarstan combustible shale of middle upper Jurassic age can be an alternative to imported coal. In the country's territory eight shale bearing strata are known that are separated from each other and located within Tetyushevo, Buinsk and Drozhzhanovsk areas [1]. Similar rocks can be followed to the

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Ulyanovsk region up to the village «Slancevyj rudnik". Estimated reserves by the data type $C_2 + P_1$ are about 900 million tons, in the Ulyanovsk region within Undorsk area – 26.8 million tons. Combustible shale occurs at shallow depth and form aged spreading strata with the power up to 5.0 m (Fig. 1).

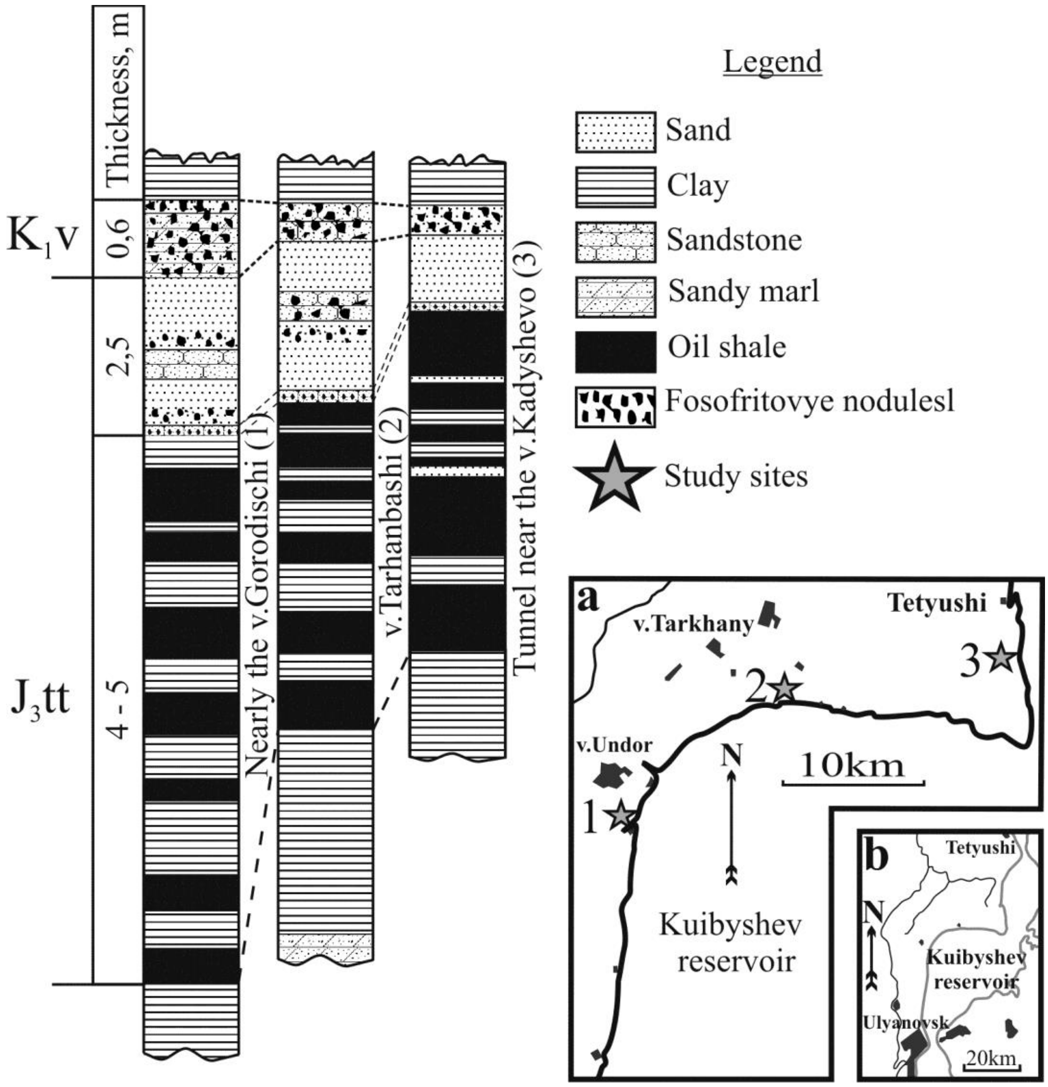


**Figure 1.** Combustible shale deposits schematic diagram in a sectional elevation within the interval of the village B.Tarhany - Undory according to [2].

## 2. Methodology

To assess the given fuel type adequacy for thermal energy production it is necessary to know its thermal characteristics and blend composition. The mentioned combined are to determine the combustible shale effectiveness as a fuel resource. In consideration of this the main research methods were X-ray, thermal and X-ray fluorescence analyses.

The X-ray analysis was carried out on the device SHIMADZU XRD-7000 in order to detail the samples composition. The shooting mode: range 3-60° by 2Θ, step 0.02 deg. / min. with the exposure lasted for 4 sec., copper radiation with the tube voltage 30kV. The standard powder compositions were used.

The thermal analysis was performed on the device STA 449 Jupiter F3 to determine the calorific value and phase transitions of the combustible shale structural components. The burning ranged from 30 to 1000 ° C, the heating step – 10 deg. / min. with constant air blowing.

The X-ray fluorescence analysis was performed with the spectrograph EDX-720P to determine the main rock chemical elements. The measurement accuracy was 0.001%.

## 3. Results and Discussion

Combustible shale in situ is laminated, cryptomerous, dark-grey and black rocks with inclusions of marine animals calcareous shells and pyrite nodules. In massif they are divided by vertical and horizontal cracks into separated blocks of various dimensions. The conducted physical and mechanical studies have shown that the rocks have similar properties to rocky ground species [3]. Most of them are characterized by relatively low porosity, moisture and density with relatively high strength parameters (Table 1).

**Table 1.** Combustible shale physical and mechanical properties.

| Parameters | Letter value | Measurement units | Values | | Average meaning |
|---|---|---|---|---|---|
| | | | from | to | |
| Natural humidity | W | % | 1.5 | 6.0 | 3.2 |
| Full possible humidity | Wo | % | 6.0 | 12.0 | 8.6 |
| Dry soil density | ρ | g/sm$^3$ | 1.72 | 1.90 | 1.81 |
| Porosity | n | % | 6.0 | 10.6 | 8.3 |
| Compressive strength | $R_c$ | MPa | 20.75 | 48.00 | 34.36 |
| Tensile strength | $R_t$ | MPa | 0.83 | 1.92 | 1.37 |

According to the held X-ray analysis the combustible shale mineral part is characterized by multi-component composition (Fig. 2). The clay particles prevail – montmorillonite $(Na,Ca)_{0.4}(Al,Mg,Fe)_{2-3}[Al,Si_3O_{10}](OH)_2{*}nH_2O)$, muscovite $(KAl_2[Al,Si_3O_{10}](OH)_2)$, chlorite $((Mg,Fe)_3[Al,Si_3O_{10}](OH)_2)$ and kaolinite $(Al_4[Si_4O_{10}](OH)_8)$. Allogenic quartz grain $(SiO_2)$ and albite $(Na[Al,Si_3O_8])$, and calcite $(CaCO_3)$, represented by marine animals shell fragments, are present in smaller amounts. Out of authigenic substances minerals pyrite $(FeS_2)$ is noted.

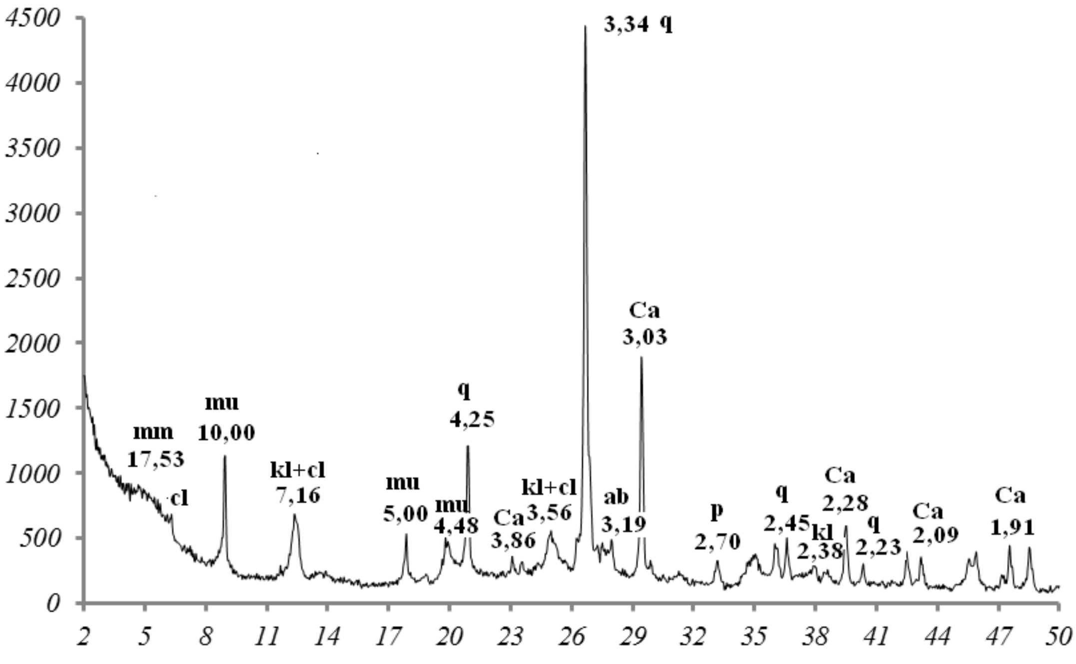

**Figure 2.** Distinctive combustible shale X-ray diffraction pattern: ***ca*** – calcite; ***q*** – quartz; ***mu*** - muscovite; ***cl*** – chlorite; ***kl*** – kaolinite; ***mm*** – illite-montmorillonite; ***p*** – pyrite; ***ab*** – albite.

According to the research data organic matter content in combustible shale varies from 8 to 40%. As for chemistry organic matters are represented with so-called kerogen – natural organic polymeric material with a high molecular weight. According to [2] yield of volatile substances when rocks are burnt is 39.2-77.25%. Out of these, $CO_2$ – to 20.7%; $O_3$ - to 3.7%; $N_2$ – to 14.9%; CO – to 0.8%; $H_2$ – to 10.6%; $CH_4$ – 49.6%; heavy hydrocarbons – up to 1.3%.

Minding furnace process technology it is necessary to know mineral and organic components behavior when combustible shale is burnt. Since the first will determine slagging properties of energy raw materials, the second – its calorific value and both of the mentioned will condition the carbon, nitrogen and sulfur with furnace gases release rate. In order to give predictive estimate of these parameters combustible shale thermal analysis was carried out. The obtained thermogram shows that various thermal conversions occur in rocks with sequential temperature increase of burning (Fig. 3). For data interpretation convenience there are two curves in the picture: a thermogravimetric one, showing the change in sample mass when heating, and a differential scanning calorimetry curve, showing the nature of absorption of heat (endo-effect) and liberation of heat (exo-effect).

The first sample mass loss occurs within the temperature interval from 60 to 150°C. Over this range in the differential scanning calorimetry curve two successive endo-effects are clearly manifested resulting from firstly capillary-condensation and then molecular (interlayer) bleeding from clay minerals.

The following changes are observed within the temperature interval from 150 to 500°C. Here in the differential scanning calorimetry curve two distinct exo-effects are observed accompanied by mass loss in the thermogravimetric curve. According to N.D. Topor [4], over this range organic matter thermal-oxidative breakdown occurs: within the interval from 150 to 400°C hydrocarbons light and middle fractions are oxidized, within the interval from 400 to 650°C – heavy fractions and kerogen. The area estimation of exo-effects equal to organic matter burnout, allows us to calculate the calorific value.

Further changes in mass within the temperature interval to 680°C are explained by hydroxyl water ($OH^-$) bleeding from the clay minerals structure. The implicit endo-effects in the differential scanning calorimetry curve is apparently due to imposed exo-effects caused by pyrite oxidation with the formation of hematite ($\alpha$-$Fe_2O_3$). The mass loss within the temperature interval from 680 to 800°C, accompanied by an endo-effect, corresponds to thermal conversion of calcite CaO. The exo-effect in the differential scanning calorimetry curve with its maximum at the point 902°C passing without mass changes corresponds to recrystallization of amorphous clay minerals decomposition products, accompanied by a new mineral phase formation (spinellide, etc.) [5].

Ash combustion products of solid energy fuels have abrasive properties that cause severe wear of convective heating surfaces and other elements of flue gas path. To estimate the ash erosion parameters it is necessary to know the mineral composition of the combustible shale residual components. With this purpose in mind, a radiographic examination of ash residual components from the given rocks burning was conducted. In the obtained diffraction patterns strong diagnostic quartz, wollastonite ($CaSiO_3$), gehlenite ($Ca_2Al_2SiO_7$) and anhydrite ($CaSO_4$), less strong hematite lines are seen (Fig. 3). Taking into consideration a relatively high position of the background line concerning the zero mark, we can assume the amorphous substance presence in the ash constituent. All identified mineral phases are the thermal dissociation product of clay, iron and carbonate combustible shale components.

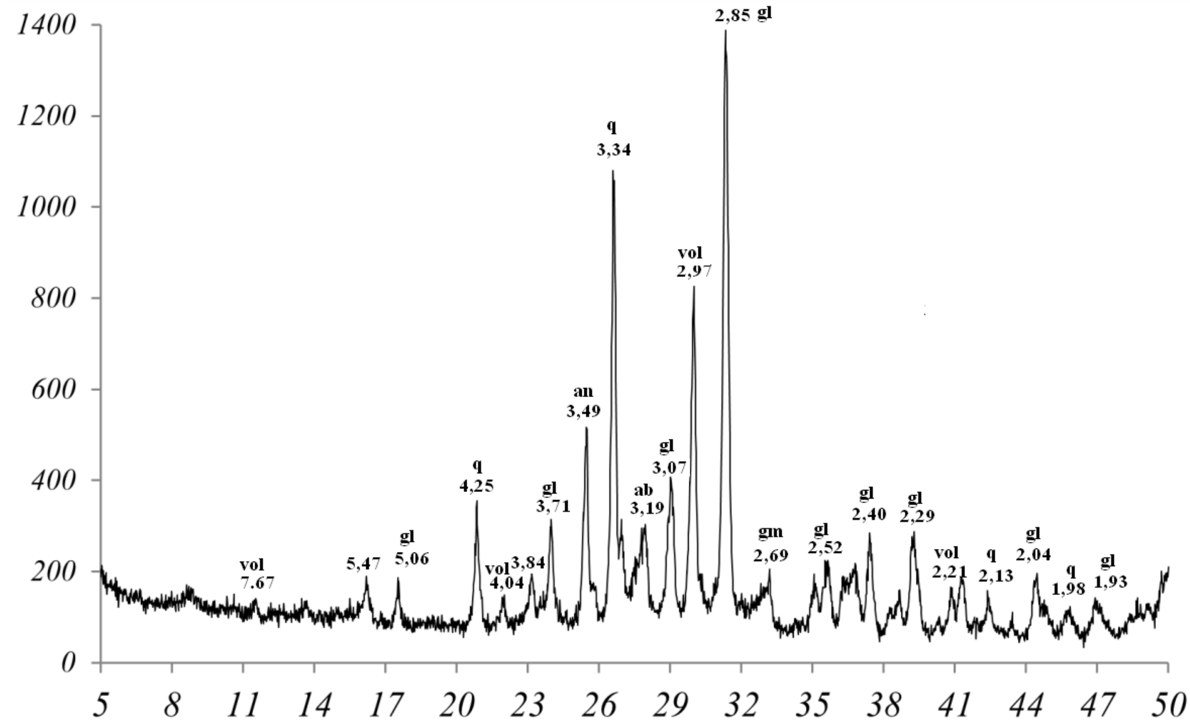


**Figure 3.** The X-ray diffraction pattern of the ash products of combustible shale: ***q*** – quartz; ***wol*** – wollastonite; ***gl*** – gehlenite; ***gm*** – hematite; ***an*** – anhydrite; ***ab*** – albite.

Considering that the properties of the ash combustion products of solid energy fuels are determined by the chemical composition, the X-ray fluorescence analysis of original combustible shale and its ash constituents, obtained after the rock burning at the temperature 1000°C, was held. The results, shown in Table 2, indicate that the noncombustible residual components are represented mainly by silica, calcium, alumina and iron oxides. The high sulfur dioxide content ($SO_3$) is noticeable.

These experiments allow us to give a predictive estimate of combustible shale engineering data as a power generation fuel. The physical-mechanical rocks properties analysis shows that their exploitation can be carried out both by digging and mining. At the same time the high strength properties of shale allow lump sampling technology to be used. This will enable tunnel kilns and box furnace to be used. If it is necessary to use pulverized pieces combustion the lumps can be powered at industry sites. The shale density and its low water saturation allow rocks to be powered at plant crushers without preliminary drying.

**Table 2.** The combustible shale and its ash combustion products according to the X-ray fluorescence analysis.

| Sample | Main elements content in the oxide form, % | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $TiO_2$ | CaO | MgO | $Na_2O$ | $K_2O$ | $SO_3$ |
| Combustible shale | 54.97 | 11.72 | 4.74 | 0.93 | 18.57 | 2.33 | 0.72 | 2.61 | 2.44 |
| Ash constituent | 55.28 | 10.51 | 5.12 | 0.98 | 17.44 | 2.33 | 0.81 | 2.75 | 3.82 |

Since the main solid fuels quality indexes are calorific value, moisture, ash and sulfur contents, we will consider the mentioned further.

The combustible shale calorific value ranges widely from 2.4 to 9.0 MJ/kg. In Tatarstan low-calorie differences with heating value 650-2134 cal. dominate, in the Ulyanovsk region rocks power-intensity increases and has 1400-3200 cal., and some samples have 5450 cal. The main rock combustible constituents are carbon and hydrogen. Oxygen and nitrogen are organic ballast.

The combustible constituent content per working fuel mass unit is determined by rock moisture and noncombustible mineral constituent amount. Additional moisture will take a certain amount of heat for its evaporation, reducing the combustible shale calorific value, which in fact determines the necessity of its accounting. Near surface rock positions will contribute to water saturation. However, the available porosity will cause a relatively small total water-absorbing capacity of rocks ($W^p$ = 6.0-12.0%). Air-dried fuel, that is, with steady borrow-pit moisture content will contain 1.5-6.0% of gravity-capillary water.

The solid noncombustible residual component, formed after burning of the fuel, is an ash part of rock. According to the calculations the combustible shale ash content ($A^d$) varies from 60 to 80%, which agrees well with the datum given in the research [2]. By its composition shale ash is basic (CaO content exceeds 10%). The foundation modulus (hydrosilicate module) is $M_o$ = 0.35, silicate (siliceous) module – $M_c$ = 3.54, the quality factor – K = 0.54 . According to the set of indexes the Volga combustible shale ash is an active group, which means that it has the property to become solid spontaneously in the open air.

One of the negative aspects of solid noncombustible residual components is thermal effectiveness and performance degradation of boiler units, which is caused by slag deposits and abrasive ability of ash volatility.

The operating experience of the boiler units shows that the rate of deposits formation, in addition to furnace process variable, depends on the ash components chemical activity. Consequently the ash coking properties can be pre-assessed in terms of slagging (R), estimated on the basis of the noncombustible residual component chemical composition:

$$R = \frac{CaO+Mg+Fe_2O_3+Na_2O+K_2O}{SiO_2+Al_2O_3+TiO_2} \times Na_2O = 0.34 \quad (1)$$

In the case of the Volga combustible shale burning, ash with low softening point due to the high alkali metals content in the rocks is expected to be obtained. Even at temperatures of 900 – 1000°C the slagging process will have an avalanche-like character. With the given X-ray analysis results it is possible to suggest that, in addition to an amorphous vitreous phase, the slag content will have a lot of spinel.

The ash abrasive properties include solid particles ability when colliding with pipe wall to cut off them microscopic metal layers. Due to this the pipe thickness gradually decreases, that can lead to breakthrough in the waste gas flue system. The ash wearing is primarily determined by the composition content of noncombustible residual constituents $SiO_2$ and $Al_2O_3$. Therefore, knowing the solid products chemical composition of combustible shale thermal conversion we can calculate the approximate ash abrasive coefficient [6]:

$$a = 0.045 \cdot (SiO_2 + Al_2O_3 - 44) \times 10^{-11} = 9.8 \times 10^{-10} m^2/N \quad (2)$$

According to the obtained results ash got during the Volga combustible shale burning, will have relatively mild abrasive abilities.

The combustion technology for all fuels implies a high yield of gaseous components, some of which represent production problems. One of such components is sulfur. Therefore a special attention is given to the sulphur content of solid mineral fuel. According to the X-ray fluorescence analysis combustible shale contains up to 3.0% of total sulfur, most of which occur in pyrite. The considerable size of the pyrite nodules (1-6 cm) allows admitting that sulfur content is due to the presence of extracted sulfur pyrites from the rocks. During shale exploitation it is quite possible to use manual selection of bur units.

## 4. Conclusions

Summing up the obtained results, we can draw to the following conclusions:

1. The combustible shale in Tatarstan and the Ulyanovsk region has predominantly low calorific value ($Q_b^d$ = 5-9 MJ/kg). In order to enhance its efficiency and to reduce cost it is possible to conduct rocks burning together with some other organic or organic mineral power generating fuels.
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